

Chapter One

SYNTHESES OF SELECTED SUPRAMOLECULES

1. TOWARD MAGNETIC BUILDING BLOCKS: SYNTHESIS OF A PLANAR Co(III)–CATION RADICAL–COBALT(III) COMPLEX OF THE BINUCLEATING LIGAND 1,2,4,5-TETRAKIS(2-HYDROXY-2- METHYLPROPANAMIDO)BENZENE

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The design of supramolecular architectures has focused on the synthesis of small subunits that bind to each other in a predictable fashion to form extended solids. How such molecular building blocks may be constructed has been discussed in detail.^{1–9} In the design of molecular magnetic structures, the key factors necessary to promote magnetic exchange couplings of a particular type between two or more spin carriers have also been stated eloquently.^{10–15} Despite significant advances in the general research area, there remains a dearth of magnetic building blocks suitable for the construction of extended, well-ordered, magnetic solids. Herein is reported the synthesis of a potentially useful magnetic building block, the Co(III) complex¹⁶ of the multinucleating ligand 1,2,4,5-tetrakis(2-hydroxy-2-methylpropanamido)benzene [$\text{H}_8(\kappa^4\text{:}\kappa^4\text{-}t\text{-HMPA-B})$].

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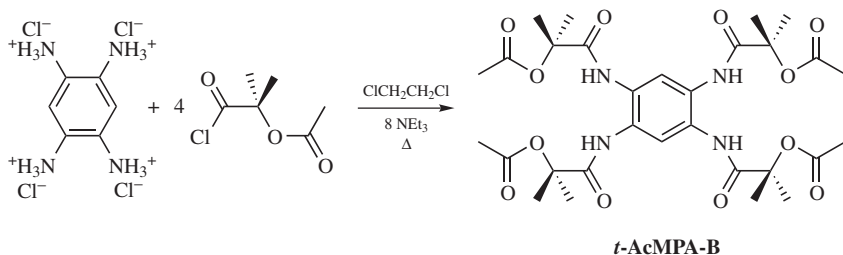
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Five features of the Co_2^{III} ($\kappa^4:\kappa^4$ -*t*-HMPA-B) system considered to be important for the preparation of a supramolecular magnetic solid are as follows:

1. Bimetallic complexes with planar four-coordinate ions in the primary diamido-*N*-dialkoxido sites are capable of achieving planarity across the primary metal, the ligand donor atoms, and the central aromatic ring. This planarity is useful for reducing the complexity of derivative network solids.
2. The ligand strongly coordinates two primary metal ions, each in a strong σ -donor environment, stabilizing the intermediate spin, $S = 1$, Co(III) state.
3. Metallocomplexes such as the bis-Co(III) dianion possess two bidentate coordination sites capable of binding to additional metal ions. Using a similar ligand, with only one primary site and one secondary site, the primary–secondary metal ion exchange interaction has been shown to be ferromagnetic, and it has been postulated that the sign of the exchange interaction is a consequence of the ligand donor interactions at Co(III).¹⁷
4. When coordinated to primary ions such as Co(III), the aryl part of the ligand can be oxidized to form a stable ligand cation radical structure that fosters magnetic communication between the two primary ions via the intermediacy of an organic $S = \frac{1}{2}$ unit.¹⁶
5. Since the ligand is a rigid rectangular unit and the secondary coordination sites are arranged at opposite ends of the rectangular unit, one can calculate the different possible structures (i.e., linear chains, hexagonal sheets, three-dimensional helical structures) that can arise when the ligand in primary metal-coordinated form binds to different secondary ions.¹⁶

Syntheses of the ligand, the di-Co(III) complex, and the one-electron oxidized di-Co(III) complex are relatively straightforward. The overall yields are good [~ 60 – 70% for $\text{H}_8(\kappa^4:\kappa^4$ -*t*-HMPA-B) and $>50\%$ for each metallated complex], and the compounds can be easily prepared on relatively large scales.

A. 1,2,4,5-TETRAKIS(2-ACETATE-2-METHYLPROPANAMIDO) BENZENE (*t*-AcMPA-B)



Procedure

■ **Caution.** *Toxic and highly flammable solvents and reagents are used throughout this procedure and those that follow. All reactions and manipulations described herein should be performed in a well-ventilated fume hood.*

An amount of 1,2,4,5-tetraaminobenzene tetrahydrochloride (15 g, 0.053 mol, Fluka), 300 mL of 1,2-dichloroethane, and a magnetic stir bar are placed in a 500-mL, two-necked, round-bottomed flask. The flask is then fitted with a reflux condenser, which is attached to an N₂ source, a mineral oil bubbler, and a pressure-equalizing addition funnel capped with a rubber septum. The system is purged with N₂ (20 min), and 1-chlorocarbonyl-1-methylethyl acetate (46 mL, 0.32 mol, Aldrich) is cannulated into the addition funnel using positive N₂ pressure and added slowly (20 min) to the stirred solution. After all the 1-chlorocarbonyl-1-methylethyl acetate is added, Et₃N (100 mL, 0.69 mol, Aldrich) is cannulated into the addition funnel using positive N₂ pressure and added dropwise to the stirred solution (1 h). After the Et₃N addition is complete, the funnel is removed and replaced with a greased ground-glass stopper. The system is heated to reflux with a heating mantle and stirred under N₂ for 5 days, during which time a mixture of Et₃N·HCl and the crude product precipitate from the solution.

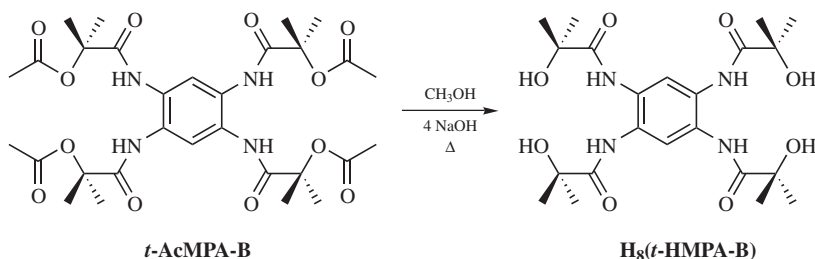
After cooling the solution to room temperature, the solvent is removed under reduced pressure using a rotary evaporator. The remaining yellow solid is dissolved in CH₂Cl₂ (800–1000 mL) and the solution transferred to a separatory funnel without filtering. The solution is first washed with 1.2 M HCl (4 × 400 mL) and then 1 M Na₂CO₃ (3 × 400 mL). The CH₂Cl₂ solution is gravity-filtered through filter paper (Whatman 1) into a 1-L round-bottomed flask and the solvent is removed under reduced pressure using a rotary evaporator. The residue, a tan solid, 1,2,4,5-tetrakis-(2-acetate-2-methylpropanamido)benzene (*t*-AcMPA-B), is scraped from the sides of the flask and slurried with pentane. The *t*-AcMPA-B is separated from the pentane by suction filtration using a medium-porosity glass frit and is air-dried (31 g; checkers obtained 30 g). This material is sufficiently pure to be used for the next step, or it can be recrystallized from acetone as follows. Impure *t*-AcMPA-B (6 g) is added to a 150-mL Erlenmeyer flask containing 110 mL of acetone and a magnetic stirring bar. The slurry is brought to a boil while stirring on a stirrer/hotplate, during which time most of the solid dissolves. The hot solution is rapidly suction-filtered through a coarse-porosity glass frit and the filtrate is placed in a freezer (approximately –20°C for 1–2 h). The white crystalline solid that precipitates is suction-filtered using a medium-porosity glass-fritted funnel, washed with diethyl ether, and air-dried to yield pure *t*-AcMPA-B (5.61 g, after recrystallization, yield 93.5%; checkers obtained 4.45 g, 74.2%).

Anal. Calcd. for $C_{30}H_{42}N_4O_{12}$ [MW (molecular weight) 650.68]: C, 55.38; H, 6.51; N, 8.61. Found: C, 55.48; H, 6.49; N, 8.57.

Properties

The pure material is a white solid. ^1H NMR (CD_3CN) δ ppm) = 8.45 (s, 4H, NH), 7.77 (s, 2H, C_6H_2), 2.08 [s, 12H, $C(O)CH_3$], 1.61 (s, 24H, CCH_3). $^{13}C\{^1H\}$ NMR (CD_3CN) δ pm = 173.4 (amide CO), 171.2 (acetyl CO), 129.3 (Ar CNHR), 121.8 (Ar CH), 81.5 (alkyl quaternary C) 25.2 (alkyl CH_3), 22.1 (acetyl CH_3). IR (Nujol) ν cm^{-1}) = 3275 (s, str, br, amide NH) 1740 (s, str, acetyl CO), 1667 (s, str, amide), 1610 (sh, w, aryl ring/amide). The checkers obtained ^1H NMR (CD_3CN) δ ppm) = 8.45 (s 3.7H), 7.77 (s 1.4H), 2.08 (s, 12.4H), 1.61 (s, 24.4H). $^{13}C\{^1H\}$ NMR (CD_3CN) δ ppm) = 173.2, 171.1, 128.9, 121.4, 81.2, 24.9, 22.0. IR (KBr disk) ν (cm^{-1}) = 3308, 1738, 1670, 1616.

B. 1,2,4,5-TETRAKIS(2-HYDROXY-2-METHYLPROPANAMIDO) BENZENE, [$H_8(t\text{-HMPA-B})$]



Procedure

Solid *t*-AcMPA-B (31.0 g) is added to a 2-L, single-necked round-bottomed flask containing CH_3OH (1000 mL), NaOH (10.3 g, 0.25 mol, ≈ 4.4 equiv assuming pure *t*-AcMPA-B), and a magnetic stirring bar. The flask is fitted with a reflux condenser that is attached to an N_2 source and a mineral oil bubbler. The system is flushed with N_2 (10 min) and then the mixture is stirred and brought to reflux using a heating mantle under static N_2 (24 h). After cooling to room temperature, the CH_3OH is removed under reduced pressure using a rotary evaporator, yielding a tan solid, a mixture of 1,2,4,5-tetrakis(2-hydroxy-2-methylpropanamido) benzene [$H_8(t\text{-HMPA-B})$] and sodium acetate. The solid is placed in a 600-mL beaker containing a 2 : 1 CH_3OH/H_2O mixture (the checkers used 300 mL of the solvent mixture) and a magnetic stir bar. The slurry is stirred and heated to

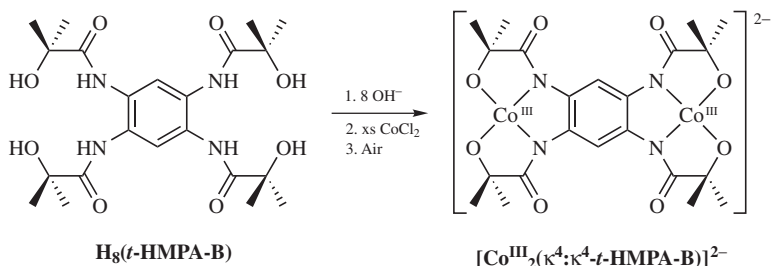
boiling using a stirrer/hotplate. It is then cooled to 10–15°C in a refrigerator. Most of the $H_8(t\text{-HMPA-B})$ is not soluble in the CH_3OH/H_2O mixture, but sodium acetate is soluble. The white CH_3OH/H_2O slurry is suction-filtered while still at $\sim 15^\circ C$ using a medium-porosity glass-fritted funnel, and the white solid product is allowed to air-dry (17.8 g, 0.037 mol; checkers obtained 12.7 g). Overall yields from 1,2,4,5-tetraaminobenzene-tetrahydrochloride are typically 60–70%.

Anal. Calcd. for $C_{22}H_{34}N_4O_8$ (MW 482.53): C, 54.76; H, 7.10; N, 11.6%; Found: C, 54.64; H, 7.05; N, 11.55%.

Properties

$H_8(t\text{-HMPA-B})$ is a white powder that is very insoluble in most solvents except hot CH_3OH , likely attributable to the presence of an extensive hydrogen bonding network. It is slightly soluble in DMSO. ^1H NMR ($DMSO-d_6$) δ (ppm) = 9.5 (s, 4H, NH), 7.7 (s, 2H, C_6H_2), 5.8 (s, 4H, COH), 1.2 (s, 24H, CCH_3). IR (Nujol) ν (cm^{-1}) = 3449, 3305, 3219 (OH alcohol, NH amide), 1656, 1630 (amide). The checkers obtained ^1H NMR ($DMSO-d_6$) δ (ppm) = 9.5 (s, 4.8H), 7.7 (s, 1.7H), 5.7 (s, 3.3H), 1.3 (s, 24H). IR (KBr disk) ν (cm^{-1}) = 3447, 3307, 3223, 1655, 1629.

C. BISTETRAPHENYLPHOSPHONIUM-DI-COBALT(III)- $\kappa^4:\kappa^4$ -[1,2,4,5-TETRAKIS(2-OXY-2-METHYLPROPANAMIDO) BENZENE] {[PPh_4] $_2$ [$Co_2^{III}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})$]}



Procedure

$H_8(t\text{-HMPA-B})$ (2.01 g, 4.11 mmol), 400 mL CH_3OH , anhydrous $CoCl_2$ (1.3 g, 10.0 mmol, Aldrich), $NaOH$ [1.18 g, 29.5 mmol (although 8 equiv of $NaOH$ are

stoichiometrically correct, better yields were obtained using ~ 7.2 equiv under aerobic conditions)], and a magnetic stirring bar are combined in a 500-mL Erlenmeyer flask. The resulting slurry is stirred at room temperature, *in air*, for 2 days. During this time, the $\text{H}_8(t\text{-HMPA-B})$ dissolves and a homogeneous green-brown solution of the sodium salt of the Co(III) complex forms. Tetraphenylphosphonium chloride, $[\text{PPh}_4]\text{Cl}$, (4.61 g, 12.3 mmol, Aldrich) is then added to the solution, which is stirred for an additional 2 h [3 equiv of $(\text{PPh}_4)\text{Cl}$ are used here; ≤ 5.5 equiv of $(\text{PPh}_4)\text{Cl}$ have been used, with an improved product yield of $>70\%$, but multiple washings and recrystallizations, described below, are required to purify this higher-yield product]. The reaction mixture is then transferred to a 1-L round-bottomed flask and the CH_3OH is removed under reduced pressure using a rotary evaporator leaving a dark green-brown solid. CH_2Cl_2 (800 ml) and a magnetic stir bar are added to the dark green solid, the flask is capped, and the slurry is stirred (24 h). During this time, most of the solid dissolves, giving a dark green solution. The solution is gravity-filtered through filter paper (Whatman 1) and the CH_2Cl_2 is removed under reduced pressure using a rotary evaporator. The resulting dark green solid is triturated in dry diethyl ether (the checkers used 100 mL of diethyl ether) suction-filtered through a medium-porosity glass-fritted funnel, and air-dried to yield a mixture of $(\text{PPh}_4)_2[\text{Co}(\text{III})_2(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]$ and $(\text{PPh}_4)\text{Cl}$. The crude dark green powder is placed in a 100-mL beaker containing CH_3CN (50 mL) and a magnetic stir bar. The resulting slurry is stirred and heated to a boil on a stirrer/hotplate for 10 min (the checkers reduced the volume to 10 mL, and then cooled to -20°C in a freezer). On cooling, more dark green powder precipitates. The dark green precipitate is suction-filtered through a medium-porosity glass-fritted funnel and air-dried. The solid is washed one more time with CH_3CN to yield a dark green solid, 2.65 g, 2.08 mmol, yield = 50.7% (checkers obtained 3.44 g, 65.8%).

A second crop of material is obtained by combining the CH_3CN washes, reducing the solution volume to 30–40 mL, and then allowing diethyl ether vapor to diffuse into the CH_3CN solution. After $\sim 5\text{--}7$ days, the dark green crystals are isolated from the mother liquor and air-dried to yield the second crop of the compound (0.2 g, 0.15 mmol, total yield = 54.2%). Typical total yields range from 50 to 60%. X-ray diffraction quality crystals are grown by allowing diethyl ether to vapor-diffuse into a concentrated solution of purified $(\text{PPh}_4)_2[\text{Co}_2^{\text{III}}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]$ in CH_3CN .

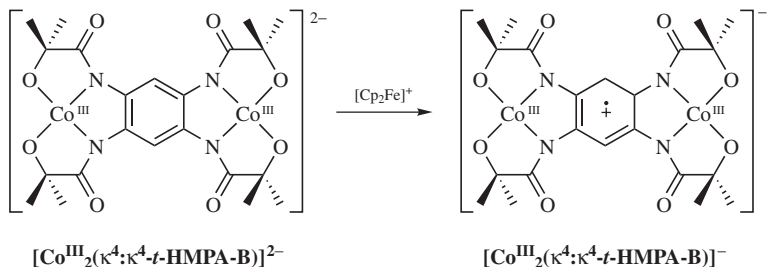
Anal. Calcd. for $\text{C}_{70}\text{H}_{66}\text{N}_4\text{O}_8\text{Co}_2\text{P}_2 \cdot 1.5\text{H}_2\text{O}$ (MW 1298): C, 64.77; H, 5.36; N, 4.32; P, 4.77. Found: C, 64.86; H, 5.35; N, 4.41; P, 4.55. The number of water molecules varies from zero to two depending on recrystallization and storage conditions as shown by elemental analysis and NMR data. The stoichiometry of the analytical sample was established by ^1H NMR. The crystal used for

crystallographic analysis had two water molecules in the lattice for each $(\text{PPh}_4)_2[\text{Co}_2^{\text{III}}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]$.

Properties

Crystals of $(\text{PPh}_4)_2[\text{Co}_2^{\text{III}}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]$ are green-black rectangular parallelepipeds and are comparatively air-stable. They are mildly hygroscopic and thus are best stored in a desiccator over CaSO_4 . ^1H NMR (CD_3CN) δ (ppm) = 9.8 (s, 24H, alkyl CH_3), 7.4, 7.22, 7.18, 7.155 (40H, aryl of phosphonium cation), 3.2 (H_2O), -0.8 (s, 2H, ArH). IR (Nujol) ν (cm^{-1}) = 1632 (amide). UV-vis (95% ethanol) λ_{max} (nm) as in Table I, Syn. 2 (on p. 34) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 238 (68,000), 376 (10,000), 468 (7300), 766 nm (2600). The cyclic voltammogram of the complex shows two well-resolved, reversible one-electron oxidation processes at 290 mV ($\Delta E_p = 60$ mV) and 885 mV ($\Delta E_p = 82$ mV) and two closely spaced, reversible or quasireversible¹⁸ one-electron reductions at -1110 mV ($\Delta E_p = 60$ mV) and -1240 mV ($\Delta E_p = 76$ mV). [Conditions: Pt working electrode, Pt counterelectrode, saturated sodium chloride calomel reference electrode (SSCE) and 0.1 M ($n\text{-Bu}_4\text{N}$)(PF_6)/ CH_3CN , puriss grade ($n\text{-Bu}_4\text{N}$)(PF_6) was purchased from Fluka; CH_3CN was freshly distilled from CaH_2 .] The reversibility of the second oxidation couple is sensitive to solvent purity, becoming totally irreversible if the CH_3CN is wet. The checkers obtained ^1H NMR (CD_3CN) δ (ppm) = 10.0 (s, 23.4H), 7.5, 7.32, 7.30, 7.26 (40H), 2.8 (H_2O), -0.72 (s, 2.6H). IR (KBr disk) ν (cm^{-1}) = 1633. UV-vis (95% ethanol) λ_{max} (nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 228 (87,000), 262 (44,000), 374 (8900), 476 (7200), 780 (3600) with ϵ values based on MW = 1298. $E_{1/2}$ values were measured against a ferrocene/ferrocenium reference (+320 mV vs. SSCE¹⁹) mV (ΔE_p) = 482 (125), -109 (84), -1482 (78), -1599 (98).

D. TETRAPHENYLPHOSPHONIUM-DI-COBALT(III)- $\kappa^4:\kappa^4$ -[1,2,4,5-TETRAKIS(2-OXY-2-METHYLPROPANAMIDO)BENZENE] $\{[\text{PPh}_4][\text{Co}_2^{\text{III}}\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]^{-}\}$



Procedure

The compounds $(\text{PPh}_4)_2[\text{Co}_2^{\text{III}}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B})]$ (243 mg, 0.19 mmol), CH_2Cl_2 (15 mL), and a magnetic stir bar are placed in a 50-mL, two-necked, round-bottomed flask. One neck of the flask is fitted with a gas inlet valve that is attached to a conventional Schlenk vacuum/ N_2 line and the other with a rubber septum. The green solution is stirred and N_2 is bubbled through the solution (≥ 10 min) to remove O_2 . The rubber septum is removed, a sample of freshly prepared, solid ferrocenium hexafluorophosphate, $(\text{Cp}_2\text{Fe})(\text{PF}_6)^*$ (63 mg, 0.19 mmol) is added to the stirred solution under a flow of N_2 , and the rubber septum is replaced. [$*(\text{Cp}_2\text{Fe})(\text{PF}_6)$ was prepared from ferrocene²⁰ by dissolution in conc. H_2SO_4 with aerial oxidation followed by dilution and precipitation with a concentrated aqueous solution of $(\text{NH}_4)(\text{PF}_6)$. Solid $(\text{Cp}_2\text{Fe})(\text{PF}_6)$ is modestly air-stable, and can be stored for weeks to months under an inert atmosphere. Solutions of $(\text{Cp}_2\text{Fe})(\text{PF}_6)$, however, are relatively unstable under aerobic conditions.] After addition of $(\text{Cp}_2\text{Fe})(\text{PF}_6)$, the solution immediately turns deep purple. The mixture is stirred under static N_2 (1 h) and then exposed to air (30 min). A small amount of white solid precipitate in the dark purple solution is removed by suction filtration through a medium-porosity glass-fritted funnel in air and then the CH_2Cl_2 is removed in vacuo. The oxidized product appears to be somewhat water-sensitive, so it is best to filter and remove the CH_2Cl_2 using the Schlenk line rather than using equipment attached to a water aspirator. The remaining purple-black solid product is washed copiously with toluene (500–700 mL) to remove ferrocene and then diethyl ether (~ 200 mL). The purple powder is dissolved in a minimum amount of 1,2-dichloroethane and pentane vapor is diffused into the 1,2-dichloroethane solution. After a few days, the purple-black crystalline product is collected by suction filtration on a medium-porosity glass-fritted funnel, washed with pentane (~ 100 mL), and air-dried, 148 mg, 75% yield (checkers obtained 160 mg, 81%).

Anal. Calcd. for $\text{C}_{46}\text{H}_{46}\text{N}_4\text{O}_8\text{Co}_2\text{P}\cdot\text{C}_2\text{H}_4\text{Cl}_2$ (MW 1030): C, 55.94; H, 4.89; N, 5.44. Found: C; 55.68, H; 4.89, N; 5.42. Presence of 1,2-dichloroethane in the solid is confirmed by a 9.6% weight loss on thermogravimetric analysis.

Properties

In the solid state, the cation radical containing compound $(\text{PPh}_4)(\text{Co}_2^{\text{III}}(\kappa^4:\kappa^4\text{-}t\text{-HMPA-B}))$ is best stored in an inert-atmosphere glovebox under nitrogen or argon. Storage of the purple solid in a desiccator charged with CaSO_4 is also

acceptable for short time periods (days–weeks). Solutions are most stable when prepared using halogenated solvents such as 1,2-dichloroethane. IR (KBr disk) ν (cm^{-1}) = 1687 (s, amide). UV–vis (1,2-dichloroethane) λ_{max} (nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 274 (37,400), 300 (21,000), 327 (20,700), 387 (10,000), 508 (8300), 548 (15,000), 657 (29,800), 816 (2000). EPR and SQUID (superconducting quantum interference device) magnetic susceptibility data reveal relatively strong antiferromagnetic coupling between the two rhombic $S = 1$ Co(III) ions and the $S = \frac{1}{2}$ ligand cation radical, $J \approx 75 \text{ cm}^{-1}$ (using $H = JS_i \cdot S_j$), yielding a ground spin state for the complex of $S_{\text{T}} = \frac{3}{2}$. The checkers obtained IR (KBr disk) ν (cm^{-1}) = 1696. UV–vis (1,2-dichloroethane) λ_{max} (nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) = 276 (27,500), 302 (15,500), 328 (14,800), 388 (7400), 506 (5400), 546 (10,500), 658 (21,900), 816 (1600) with ϵ values based on MW 1030.

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2. A LUMINESCENT DECANUCLEAR RUTHENIUM(II) POLYPYRIDINE COMPLEX: A CONVERGENT APPROACH TO A DENDRITIC STRUCTURE EMPLOYING THE “COMPLEXES AS METALS/COMPLEXES AS LIGANDS” SYNTHETIC STRATEGY

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The “complexes as metals/complexes as ligands” strategy is a general method for the synthesis of polynuclear metal complexes.¹ Such a strategy can also be applied to the convergent synthesis of metal-based dendritic species. Herein the preparation of a dendritic decanuclear Ru(II) complex is reported. In a typical convergent approach to dendritic structures, preformed arms are mounted on a central core.² In the present syntheses, the complex [Ru(2,3-dpp)₃](PF₆)₂ (**1**; 2,3-dpp = 2,3-bis(2-pyridyl)pyrazine) is used as the central core. The presence of three free chelating sites in **1** makes it a “complex ligand.”

The arms that can be mounted on this core are complexes carrying labile ligands (“complex metals”) that can be easily substituted by the free chelating sites of the core. Chlorides have been found to be effective labile ligands in these processes. The use of mononuclear arms such as M(L)₂Cl₂ [M = Ru(II), Os(II); L = 2,2'-bipyridine (bpy) or 2,2'-biquinoline] allows for the syntheses of various

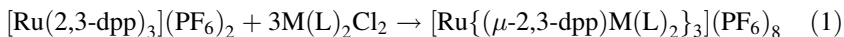
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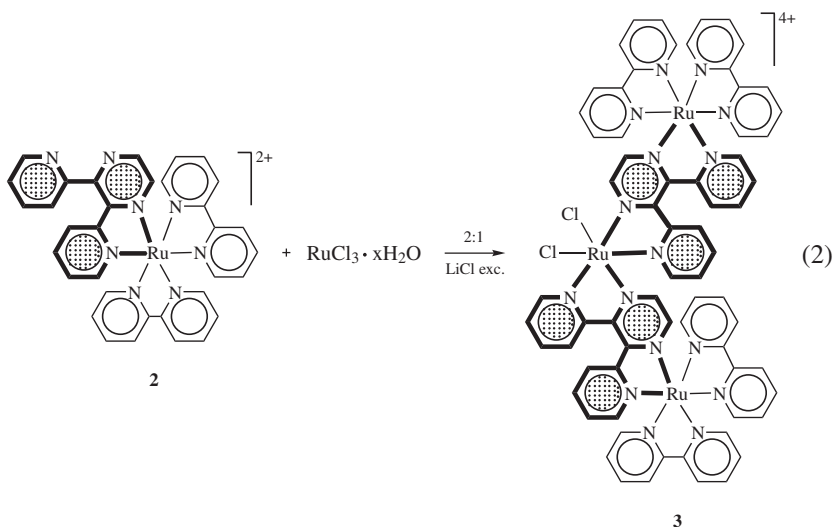
[§]Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, MN 55455-0431.

tetranuclear species:^{3,4}

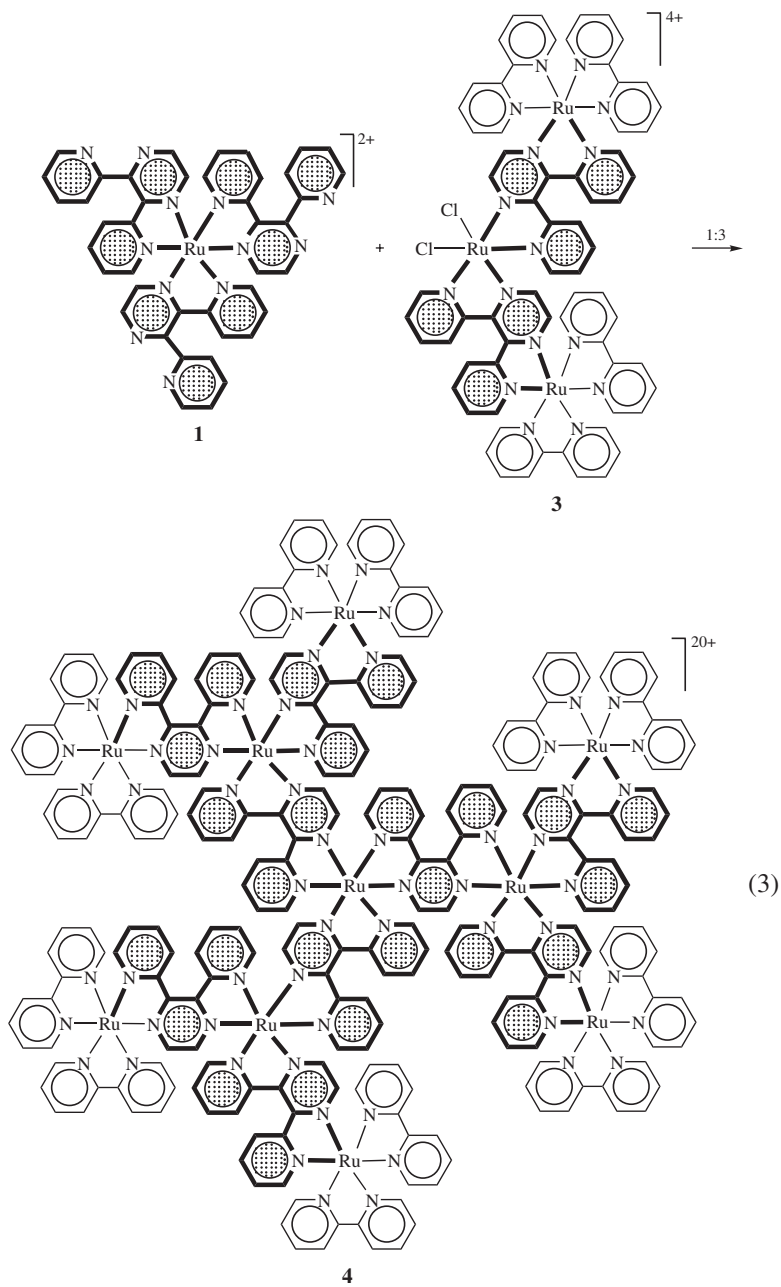


For the synthesis of dendritic complexes of higher nuclearity, polynuclear arms must be used in reaction (1).

The preparation of complex metals like $\text{M}(\text{L})_2\text{Cl}_2$ is based on the reduction of the appropriate metal precursor (e.g., metal chloride) by means of the solvent, with coordination of the L ligand.⁵ In order to inhibit the formation of $[\text{M}(\text{L})_3]^{2+}$ species, the reaction must be carried out in the presence of an excess of chloride ions provided either by the metal precursor itself (e.g., in the case of K_2OsCl_6) or by added LiCl. On the basis of these considerations, the experimental conditions are set for the reaction between the metal precursor $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and the mononuclear complex ligand $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$ (**2**) to obtain the trinuclear system **3**. The latter contains two labile chloride ligands on the central metal. This reaction is represented in Eq. (2), where, for clarity, the bridging ligands are illustrated graphically.



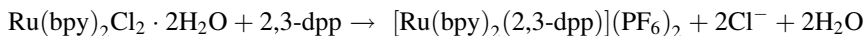
By using the complex metal **3** [Eq. (2)] it is possible to introduce trinuclear subunits in suitable ligand substrates; for example, **3** can be used in the reaction that gives, in good yield, the title compound **4**:



Materials and General Procedures

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ is purchased from Aldrich Chemicals. 2,3-dpp,⁶ $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$,^{5a} and $[\text{Ru}(2,3\text{-dpp})_3](\text{PF}_6)_2$ ³ are synthesized according to literature methods. It is also possible to purchase 2,3-dpp and $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ from Aldrich Chemicals, but sometimes further purification before use is necessary. Although 2,3-dpp can be purified by sublimation (200°C, under vacuum), $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ has to be washed with H_2O until the yellow-orange color, due to $\text{Ru}(\text{bpy})_3^{2+}$, disappears from the washing liquor.

A. BISHEXAFLUOROPHOSPHATE-BISBIPYRIDYL-2,3-BIS (2-PYRIDYLPYRAZINE)RUTHENIUM(II) [$[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$]



Procedure

■ **Caution.** *Because of the toxic nature of acetonitrile, it should be handled under a well-ventilated hood.*

A nitrogen-flushed apparatus is set up (Fig. 1) and used as follows. The 50-mL, two-necked, round-bottomed flask is charged with 67 mg (0.29 mmol) of 2,3-dpp, 5 mL of deaerated 95% ethanol, and a stirring bar. The 50-mL, pressure-equalizing dropping funnel is charged with 100 mg (0.19 mmol) of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and 15 mL of deaerated 95% ethanol. The flask is placed in an oil bath on a stirrer/hotplate, and the stirred ethanolic suspension of 2,3-dpp is heated to reflux. The ethanolic suspension of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, stirred by means of the nitrogen flow, is then dropwise added (in ~ 1 h) to the refluxing solution of the ligand. The sparging needle may also be used to prevent funnel clogging. During this step the N_2 is provided only by the inlet and the N_2 line stopcock is closed. At the end of the addition, the N_2 line stopcock is open and the funnel is substituted with a ground-glass stopper. The reaction mixture is refluxed for 12 h, then cooled to room temperature. The reaction can be followed by TLC: neutral alumina, $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9 : 1 (v/v); under these conditions the R_f values decrease in the following order: (1) the ligand (the spot is visible under a UV lamp), (2) the solvated metallic precursor (bordeaux spot), (3) the product (orange spot), (4) the binuclear complex $[(\text{bpy})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ sideproduct (purple spot). After 12 h, some solvated metallic precursor can still be present, but it is not possible to achieve a higher conversion with a longer reaction time.

From now on, the reaction mixture can be handled under air. It is transferred in one-necked, round-bottomed flask and the solvent evaporated to dryness on a rotary

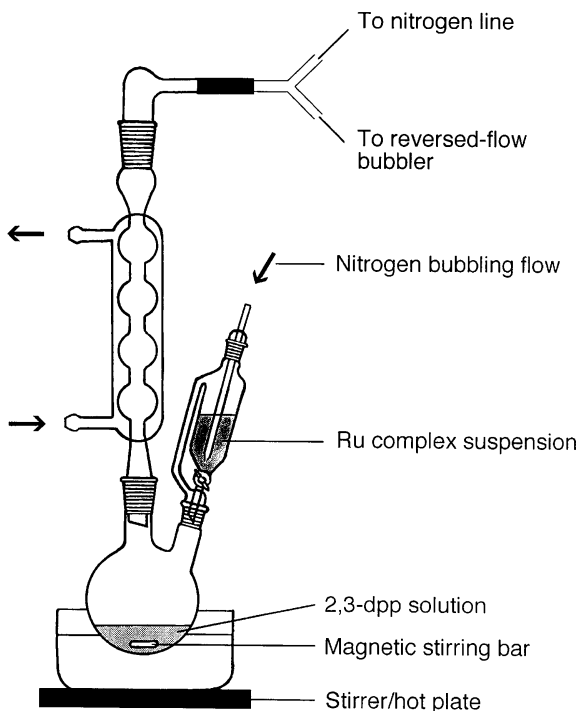


Figure 1. Apparatus for the preparation of $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})]^{2+}$.

evaporator. The crude product so obtained is purified as follows. It is dissolved in the minimum quantity of a mixture $\text{H}_2\text{O}/\text{acetone}$ 5 : 3 (v/v) 0.05 M in NaCl and chromatographed on a Sephadex-CM C-25 (Aldrich Catalog 27,124-1. Column dimensions: 2.5×20 cm) using the same solvent mixture as eluant. The product is contained in the dark orange band. The eluate is rotary-evaporated to remove acetone, then the product is precipitated from the aqueous solution by adding an excess of solid NH_4PF_6 . The dark-orange solid so obtained is collected on a sintered-glass filter by suction and dried overnight under vacuum in a desiccator.

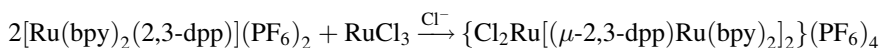
If a spectrofluorimeter is available, it is possible to check the purity of the sample and the effectiveness of the purification by comparing the emission spectra of the crude product to that of the purified product. In the spectrum of the former, the band of the product [$\lambda_{\text{max}} = 670$ nm, in acetonitrile at room temperature (RT)] and the band of the binuclear sideproduct ($\lambda_{\text{max}} = 756$ nm, in acetonitrile at RT) can be observed; after purification, the emission band of the sideproduct is no longer present (excitation wavelength, 450 nm).⁷

In order to remove possible traces of inorganic salts, the product is dissolved in the minimum quantity of acetonitrile and chromatographed on Sephadex G-10 (Aldrich Catalog 27,103-9. Column dimensions: 2.5×5 cm) by using the same solvent. The eluate is rotary-evaporated to the small volume and then Et_2O is added to induce the precipitation of the product that is collected on a sintered-glass filter by suction, washed three times with Et_2O and dried under vacuum. Yield: 140 mg (78%).

(Note: It is necessary to swell the Sephadex-CM C-25 resin in excess eluant mixture, at room temperature without stirring, for about 24 h before use. Attention must be paid to the quantity of Sephadex-CM C-25 resin used, since its volume increases about twice on swelling. It is recommended that the Sephadex G-10 resin be allowed to swell in excess acetonitrile for at least 3 h prior to use.)

Anal. Calcd. for $\text{C}_{34}\text{H}_{26}\text{N}_8\text{F}_{12}\text{P}_2\text{Ru} \cdot \text{H}_2\text{O}$: C, 42.73; H, 2.95; N, 11.73. Found: C, 42.80; H, 2.75; N, 11.28.

B. TETRAKIS-HEXAFLUOROPHOSPHATE-BIS-BISBIPYRIDYL-2,3-BIS(2-PYRIDYLPYRAZINE)RUTHENIUM(II)-DICHLORORUTHENIUM(II) ($\{\text{Cl}_2\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\}(\text{PF}_6)_4$)



This synthesis must be repeated twice in order to get the amount of product necessary for the subsequent synthesis of $(\text{Ru}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\}_3)(\text{PF}_6)_{20}$.

A nitrogen flushed 50-mL, two-necked, round-bottomed flask fitted with a condenser is charged with 11.5 mg (0.04 mmol) of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 80 mg (0.08 mmol) of $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$, 11.9 mg (0.28 mmol) of LiCl, 15 mL of 95% ethanol, and a stirring bar. The flask is placed in an oil bath on a stirrer/hot-plate, and the stirred reaction mixture is heated to reflux. After 7 h the reaction mixture is cooled to room temperature. The reaction can be followed by TLC: neutral alumina, $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9 : 1 (v/v); in these conditions the R_f values decrease in the following order: (1) mononuclear precursor (orange spot), (2) trinuclear product (green spot).

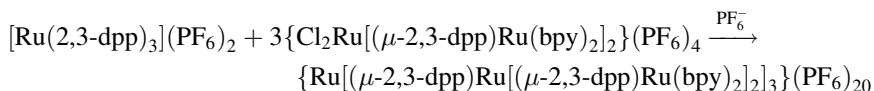
From now on, the reaction mixture can be handled under air. An excess of solid NH_4PF_6 is added causing the formation of a dark green solid that is collected on a sintered-glass filter by suction, washed with Et_2O . The crude product is dissolved in the minimum quantity of a 1 : 1 (v/v) CH_3CN /toluene mixture and purified by column chromatography on neutral aluminum oxide (diameter 2.5 cm, length 20 cm; aluminum oxide activity: 1) by using the same solvent mixture [1 : 1 (v/v) CH_3CN /toluene] as eluant. The elution of the column is performed slowly. In these experimental conditions, the first band eluted (orange) contains the unreacted mononuclear $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$ complex. After the

collection of this first band, the quantity of CH₃CN in the elution mixture is increased progressively [up to 3 : 1 (v/v) CH₃CN/toluene] in order to obtain the green-blue band that contains the trinuclear product. At times, after the elution of the trinuclear complex, a dark byproduct (maybe a tetranuclear complex) stays on the top of the column. The green-blue band is eluted and the solution containing the desired product is rotary-evaporated to dryness. The product is dissolved in a very small amount (~2 mL) of CH₃CN and precipitated by adding diethyl ether. The column yield is 70%. Total yield of the reaction (after purification) 55%.*

If a spectrofluorimeter is available, it is possible to check the purity of the sample and the effectiveness of the purification by comparing the emission spectra of the crude product and the purified product. In the former the band of the mononuclear complex can be present ($\lambda_{\text{max}} = 670$ nm in acetonitrile at RT);⁷ after purification, no emission should be detectable (excitation wavelength 450 nm).

Anal. Calcd. for C₆₈H₅₂N₁₆Cl₂F₂₄P₄Ru₃·3H₂O: C, 38.87; H, 2.78; N, 10.67; P, 5.90; Ru, 14.43. Found: C, 38.89; H, 2.66; N, 10.56; P, 6.38; Ru, 14.21. FAB⁺(*m*-NBA). Calcd. for (MPF₆)⁻: 1903.0. Found: 1903.

C. ICOSAKISHEXAFLUOROPHOSPHATE-TRIS-BIS-BISBIPYRIDYL-2,3-BIS(2-PYRIDYLPYRAZINE)RUTHENIUM(II)-2,3-BIS(2-PYRIDYLPYRAZINE) RUTHENIUM(II) [(Ru(μ-2,3-DPP)Ru(μ-2,3-DPP)Ru(BPY)₂)₂)₃](PF₆)₂₀]



A nitrogen-flushed 50-mL, two-necked, round-bottomed flask fitted with a condenser is charged with 116 mg (0.06 mmol) of {Cl₂Ru[(μ-2,3-dpp)Ru(bpy)₂]₂}(PF₆)₄, 19.2 mg (0.12 mmol) of AgNO₃, 4 mL of a MeOH/H₂O 2 : 1 (v/v) mixture, and a stirring bar. After 2 h stirring at room temperature 20.6 mg (0.02 mmol) of [Ru(2,3-dpp)₃](PF₆)₂ and 4 mL of ethylene glycol are added, and the reaction mixture is refluxed for 48 h. The reaction can be followed by TLC: neutral alumina, CH₂Cl₂/MeOH 9 : 1 (v/v); in these conditions the *R_f* values decrease in the following order: (1) mononuclear core (orange spot), (2) solvated trinuclear precursor (green-blue spot), (3) possible impurities of the tetra- and heptanuclear complexes in which one or two free chelating sites are still present on the core (purple spots), (4) decanuclear complex (purple spot).

* The checkers point out that the activity grade of the alumina can be important; a higher activity grade of alumina (i.e., freshly opened bottle of alumina activity 1) requires a higher CH₃CN/toluene ratio for release all the product. They suggest that the optimal CH₃CN/toluene ratio be determined with a preliminary “disposable pipette column” study.

After cooling to room temperature the reaction mixture can be handled under air. The AgCl formed is removed by repeated centrifugations. The reaction mixture is rotary-evaporated to remove the low-boiling solvents. An excess of solid NH_4PF_6 is added to the remaining solution (mainly ethylene glycol) and the mixture is stirred for 20 min. After addition of an equal volume of Et_2O , a two-phase system is formed. Methanol is added dropwise, under stirring, until a single solvent phase is obtained, and this solution is stirred for 30 min. A purple precipitate forms and is collected on a sintered glass filter by suction. This crude product is dissolved in the minimum volume of acetonitrile and chromatographed on Sephadex G-25 (Aldrich Catalog 27,109-8. Column dimensions: 2.5×5 cm) by using the same solvent. An amount of 95% ethanol (~ 6 mL) is added to the eluate and the solution is rotary-evaporated until the product precipitates. The solid is collected on a sintered-glass filter by suction, washed 3 times with Et_2O and dried under vacuum. Yield: 118 mg (80%).

If a spectrofluorimeter is available, it is possible to check the purity of the sample by looking at the emission spectrum of the product; only the band of the decanuclear complex ($\lambda_{\text{max}} = 785$ nm in acetonitrile at RT)⁷ must be present. The band of the mononuclear core ($\lambda_{\text{max}} = 635$ nm, in acetonitrile at RT)⁷ should be absent (excitation wavelength 450 nm). (Note: For the swelling of Sephadex G-25 resin, see the indications given for the Sephadex G-10.)

Anal. Calcd. for $\text{C}_{246}\text{H}_{186}\text{N}_{60}\text{F}_{120}\text{P}_{20}\text{Ru}_{10} \cdot 10\text{H}_2\text{O}$: C, 36.60; H, 2.57; N, 10.41; P, 7.67; Ru, 12.51. Found: C, 36.19; H, 2.70; N, 10.83; P, 8.30; Ru, 12.01.

Properties

The complexes dealt with in this contribution are soluble in polar solvents (like acetonitrile and acetone). They are air-stable in both the solid state and in

TABLE I. Properties of Complexes 1, 2, 3, and 4^a

Compound	IR Frequencies (KBr Pellets), cm^{-1}	Absorption λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	E_{ox} , V. vs SCE
1	1576(w), 1556(w), 1544(m), 1462(w), 1428(w), 990(w)	455 (13,000) 281 (52,300)	+1.60
2	1590(m), 1555(m), 1578(s), 1436(s), 1402(m), 1386(m), 990(w)	475(sh) (11,500) 285 (72,100)	+1.31
3	1607(m), 1559(w,br), 1470(s), 1450(s), 1423(m), 1393(s)	615 (24,300) 285 (107,000)	+0.72 +1.45
4	1605(m), 1560(w,br), 1470(s), 1450(s), 1420(s), 1399(s)	541 (125,000) 282 (312,000)	+1.53

^aThe numbering of the complexes is identical to that defined in the introduction and also shown in Eqs. (1) and (2).

solution. Their solutions are strongly colored. Relevant spectroscopic and electrochemical data are gathered in Table I. The weak band at 990 cm^{-1} in the IR spectra is diagnostic of the presence of unbridged 2,3-dpp ligand.

Acknowledgments

We thank C. Mingazzini for the elemental analyses and G. Gubellini for technical assistance.

References and Notes

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7. Emission spectra have been obtained with a Perkin-Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R958 phototube. Data are uncorrected for spectral sensitivity of the phototube.

3. DODECATUNGSTOALUMINIC ACID AND ITS MONOLACUNARY AND MIXED-ADDENDUM DERIVATIVES

Submitted by JENNIFER J. COWAN,* CRAIG L. HILL,*
 RICHARD S. REINER,[†] and IRA A. WEINSTOCK[‡]
 Checked by WALT KLEMPERER[‡] and KEITH MAREK

Heteropolyoxometalates of the Keggin structural class, including their transition-metal-substituted derivatives, are effective homogeneous catalysts for selective oxidations of organic and inorganic substrates by a variety of oxidants.^{1,2}

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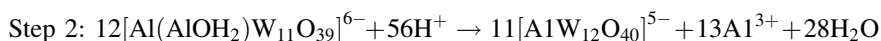
While many polyoxometalates (POMs) of this class are remarkably stable to oxidizing conditions, they are often unstable with respect to hydrolysis, limiting the use of POMs in water to acid pH values.³ In light of the increasing drive toward more environmentally benign chemical systems, it would be advantageous to develop POMs that are stable in water over a wider range of pH values. Compared to the Si-centered and P-centered analogs⁴ of the Keggin anion, an Al-centered Keggin anion possesses a more negative charge, which correlates with greater base stability.^{5,6} The $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ anion is known, but comparatively little has been published about it; this may be attributable to the low yield of the published synthetic method.⁷⁻¹⁰ The shortcoming of this method is that it fails to account for the ability of Al(III) to function as both a heteroatom and an addendum atom, which results in the competitive formation of $[\text{Al}(\text{AlOH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$ during aluminum addition.⁸⁻¹¹

This contribution details a new, high-yield route to $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$. By deliberately adjusting the reaction stoichiometry to 2Al:11W and choosing the proper pH value, $[\text{Al}(\text{AlOH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$ is formed selectively and then is cleanly converted to $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ by refluxing at low pH.^{12,13} As this procedure generates a mixture of the α and β isomers, the separation of the β isomer and the conversion to the α -isomer are described. Also included is the first reported synthesis of its monolacunary derivative $\alpha\text{-}[\text{AlW}_{11}\text{O}_{40}]^{9-}$ which is an obvious precursor to a variety of transition-metal-substituted Keggin anions. The preparation of one of these, $\alpha\text{-}[\text{AlVW}_{11}\text{O}_{40}]^{7-}$, is provided here by way of example. The preparation of the oxidized derivative of the vanadium-substituted anion, $\alpha\text{-}[\text{AlVW}_{11}\text{O}_{40}]^{6-}$, is also presented as an example of the use of ozone as an oxidant that introduces no exogenous elements.

A useful property of the aluminum heteroatom is that the ^{27}Al isotope, present in 100% abundance and possessing a nuclear spin quantum number of $\frac{5}{2}$, is easily and rapidly observed by nuclear magnetic resonance (NMR) spectroscopy. The chemical shift and linewidth of ^{27}Al NMR signals provide readily accessible information regarding both the coordination number of the aluminum atom and the chemical symmetry of its environment.⁸ However, care must be taken in collection of samples to allow a sufficient delay between pulses, as narrow resonances of quadrupolar nuclei relax more slowly (a 5-s delay is usually sufficient). An additional caveat regards the use of dilute samples or those with broad signals; in some cases a broad resonance has been observed (from ~ 105 to 35 ppm) in addition to those expected from the sample (it is also observed in the absence of a glass sample tube in the probe). This broad signal is due to aluminum present in glass in the NMR probe itself (not all NMR instruments possess Al-containing glassy compounds). In either case, the relative intensity of the resonance can be minimized by using concentrated samples. The effectiveness of this technique improves with decreasing peak width. There are other (less satisfactory) methods of dealing with this problem, which are addressed in Ref. 12.

Materials and General Procedures

Reagent-grade chemicals (sodium tungstate dihydrate was Folin reagent grade) were obtained from commercial sources. Deionized water is used throughout. All NMR experiments were carried out in deuterium oxide and referenced externally: ^{27}Al to 0.1 M AlCl_3 in deuterium oxide, ^{183}W to saturated Na_2WO_4 in deuterium oxide, and ^{51}V to neat VOCl_3 .

A. DODECATUNGSTOALUMINIC ACID $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ *Procedure*

■ **Caution.** *Hydrochloric acid is corrosive. Precautions should be taken to avoid coming into direct contact or breathing HCl fumes.*

Step 1. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 100 g, 0.304 mol) is dissolved in 400 mL of H_2O in a 1000-mL, three-necked, round-bottomed flask containing a magnetic stirring bar and fitted with an addition funnel and condenser. Hydrochloric acid (~ 23.0 mL, 0.276 mol) is added to the solution dropwise with vigorous stirring to pH 7.7 (use of a calibrated pH meter in the solution during this procedure is necessary). After every several drops the addition is momentarily stopped to allow the local precipitate of tungstic acid to dissolve. The solution is then heated to reflux, and aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 13.32 g, 0.0552 mol), dissolved in 80 mL deionized water, is added dropwise by means of the addition funnel over ~ 90 min (~ 5 – 6 drops/min) with constant stirring. During the addition, the solution becomes slightly cloudy. However, addition should be kept at a slow enough rate to prevent the mixture from becoming opaque. If this should occur, however, the addition must be stopped and the solution stirred until it becomes clearer. After all the AlCl_3 has been added, the solution is kept at reflux for 1 h, cooled to room temperature, and filtered through a 0.5-in.-thick pad of Celite (diatomaceous earth) on a medium sintered-glass-fritted funnel. The final pH should be approximately 7.

Step 2. The solution, now containing $\text{Na}_6[\text{Al}(\text{AlOH}_2)\text{W}_{11}\text{O}_{39}]$ (^{27}Al NMR: 73 ppm, $\Delta\nu_{1/2} = 89$ Hz; 8 ppm, $\Delta\nu_{1/2} = 256$ Hz), is transferred to a 1000-mL, round-bottomed flask fitted with a reflux condenser. The solution is acidified to

pH 0 by careful dropwise addition of concentrated sulfuric acid (~ 20 mL, 0.376 mol). After the pH has reached 0, an additional 3 mL of conc. sulfuric acid is added and the solution is heated to reflux. The solution becomes cloudy and slightly yellow as the acid is added, but should clear within 16 h of the beginning of reflux. To ensure complete conversion to product, the solution should be kept at reflux for 6 days (monitoring the progress by ^{27}Al NMR is also recommended). Then, after cooling to room temperature, the solution may be filtered (if cloudy) using a medium-porosity glass-fritted funnel {this is seldom necessary if the two steps are performed in quick succession, that is, provided the $[\text{Al}(\text{AlOH}_2)\text{W}_{11}\text{O}_{39}]^{6-}$ is not allowed to stand in solution for more than 24 h}.

Workup. The solution, which now contains $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ and 1.08 (i.e., $\frac{13}{12}$) equiv of soluble Al(III) salts, is transferred to a 1000-mL beaker and cooled to 0°C .

■ **Caution.** *The following acidification and extraction procedure should be performed in a ventilated hood, while wearing appropriate safety clothing including splash goggles. Sulfuric acid is extremely corrosive, and during the ether extraction, due to possible excessive pressure generation, there is a danger of splashing the sulfuric acid. Careful, frequent ventilation of the separatory funnel must be applied.*

Cold (0°C) conc. sulfuric acid (147 mL) is added carefully to avoid excessive heating. The solution is then cooled in an ice-water bath to 0°C and transferred to a 2000-mL separatory funnel. Diethyl ether (500 mL) is added and the mixture shaken very gently with frequent ventilation until rapid evaporation of diethyl ether subsides. Then, the mixture is shaken more vigorously, still with frequent venting, and allowed to settle until three layers separate. The top clear colorless layer is diethyl ether, the middle somewhat cloudy layer is the aqueous phase, and the bottom layer (a dense, pale yellow, viscous liquid) is the etherate of $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$. The bottom (etherate) layer is collected and the shaking and venting procedure is repeated until the etherate layer no longer forms (the aqueous layer appears clearer as the extraction nears completion). The combined etherate layers (~ 20 mL) are concentrated to dryness by rotary evaporation. The crude product (69.2 g, 95%) is reprecipitated by dissolving in 20 mL of hot water, concentrating to a volume of 23 mL by gentle heating, and then cooling to 0°C for 16 h. Yield: 50.46 g, 64%.*

*The product prepared as described is a mixture of α - and β -isomers, with β the dominant isomer (typically 85–90%). However, when $\text{K}_9[\text{AlW}_{11}\text{O}_{39}]$ is prepared from this mixture as described below, the product is 100% α - $\text{K}_9[\text{AlW}_{11}\text{O}_{39}]$.

Separation of the β isomer of $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ from the α isomer may be accomplished by careful fractional crystallization—this procedure is not required for the preparation of the lacunary species, $\alpha\text{-K}_9[\text{AlW}_{11}\text{O}_{39}]$; see footnote below. [Conversion to and collection of the pure α isomer, i.e., $\alpha\text{-Na}_5[\text{AlW}_{12}\text{O}_{40}]$, is described in the following section.] Monitoring of the products by ^{27}Al NMR is necessary to observe whether the separation is complete. The product from the procedure described above is dissolved in minimum warm H_2O in a 250-mL beaker and allowed to stand in a drafty location (the back of a fume hood, for example) until crystals form, 3 days or more.

If the crystallization takes place slowly enough, the first crop (9.56 g) contains a high percentage of $\alpha\text{-H}_5[\text{AlW}_{12}\text{O}_{40}]$ (77% α isomer in one case, determined by ^{27}Al NMR), due to its lower solubility. The subsequent mother liquor is treated in a similar fashion—the product is allowed to crystallize slowly and then is removed by filtration once a few grams of crystals form. The second crop (7.31 g) collected in this manner has a smaller (19%), but still substantial, amount of the α isomer. The mother liquor is then allowed to stand again to give a larger third crop (26.42 g) that contains a small percentage of α isomer (4.4%). Very slow recrystallization of the third crop from a minimum of H_2O (perhaps over one week) gives pure $\beta\text{-H}_5[\text{AlW}_{12}\text{O}_{40}]$ (7.76 g, 9.8%).

Properties

The mixture of α - and β -dodecatungstoaluminic acid prepared as described in step 2 is a water-soluble slightly yellow amorphous solid. The pure β isomer is pale yellow and crystalline, but becomes amorphous on drying. To avoid reduction of the free acid $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$, metal implements should not be used in handling it as a solid, and especially while in solution. The two polyanions are stable in water below pH 6 and characterized by ^{27}Al NMR: β isomer, 71.6 ppm ($\Delta\nu_{1/2} = 4.6$ Hz); α isomer, 72.1 ppm ($\Delta\nu_{1/2} = 1.3$ Hz); ^{183}W NMR β isomer (integration), $-110.8(1)$, $-118.7(2)$, and $-136.8(1)$ ppm; α isomer, -110.1 ppm. IR (2–5 wt% KBr pellet, cm^{-1}): 972(s), 899(s), 795(broad, s), 747(broad, s), 538(m), and 477(m).

Anal. Calcd. (found) for $\text{H}_5[\text{AlW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$: H, 1.12 (1.15); W, 70.07 (70.23); Al, 0.86 (0.89).

B. α -PENTASODIUM DODECATUNGSTOALUMINATE

$\alpha\text{-Na}_5[\text{AlW}_{12}\text{O}_{40}]$

This procedure converts a mixture of α - and $\beta\text{-H}_5[\text{AlW}_{12}\text{O}_{40}]$ to $\sim 95\%$ $\alpha\text{-Na}_5[\text{AlW}_{12}\text{O}_{40}]$. The α isomer, because of its lower solubility, is easily separated from the residual amount of β isomer. A 31.9-g sample of $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$

is dissolved in 65 mL of water and filtered if cloudy. The pH of the solution is adjusted to ~ 6 using a 0.75 M solution of Na_2CO_3 (~ 42.5 mL) and is then heated at reflux for 3 days. At this point, the solution typically contains about 95% α - $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ (with 5% β , determined by ^{27}Al NMR). The solution may be heated longer if the proportion of α isomer is less than 95%. After cooling, the solution is concentrated by rotary evaporation until precipitate begins to form, and is then refrigerated at 5°C . The product is collected on a coarse glass-fritted funnel and air-dried. Yield (2 crops): 20.07 g (60.8%).

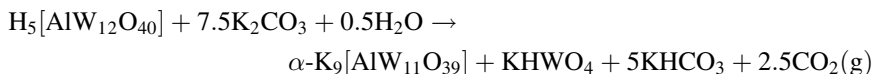
Properties

^{183}W NMR, δ : -112.8 ppm. ^{27}Al NMR, δ : 72.1 ppm ($\Delta\nu_{1/2} = 1.1$ Hz). IR (KBr pellet, cm^{-1}): 955(m), 883(s), 799(s), 758(s), 534(w), 498(w).

Anal. Calcd. (found) for $\text{Na}_5[\text{AlW}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$: H, 0.81 (0.78); W, 68.47 (68.22); Al, 0.84 (0.88); Na, 3.57 (3.39).

C. α -NONAPOTASSIUM UNDECATUNGSTOALUMINATE

α -K₉[AlW₁₁O₃₉]



Procedure

The isomeric composition of the starting $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ does not affect that of the lacunary product; under the conditions described here, the α isomer is always obtained in near-quantitative yield. The typical starting material used in this procedure is the isomeric mixture of $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ prepared and collected as described in procedure A, step 2 (without separation of the β isomer by fractional crystallization). Dodecatungstoaluminic acid $\text{H}_5[\text{AlW}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ (43.76 g, 14.1 mmol) is dissolved in 100 mL of H_2O and heated with stirring to 60°C . Three equivalents of potassium carbonate (1.5 hydrate) ($\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$, 6.97 g, 42.3 mmol) are added gradually as a solid. The pH should rise to about 2. Another 5 equiv of potassium carbonate (1.5 hydrate) (11.62 g, 70.5 mmol, dissolved in 20 mL H_2O) are added dropwise carefully over about 60 min. The pH of the solution should not be allowed to rise above 8 until at least 75% of the potassium carbonate solution has been added, and should at all times be kept below 8.5. A white precipitate begins to form as addition of the potassium carbonate solution proceeds. The final pH of the mixture should be near 8.25. After

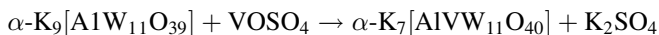
addition of the potassium carbonate solution is complete, the mixture is cooled to 5°C for several hours. The product, a fine white precipitate, is then collected, washed 3 times with H₂O, and dried on a medium-porosity glass frit. Yield 41.8 g, 92%.

Properties

The potassium salt of the lacunary anion is a white amorphous solid, which is slightly soluble in water (2 g/100 mL at 22°C). ²⁷Al NMR (47,000 scans at 30°C): 63.3 ppm ($\Delta\nu_{1/2}$ = 784 Hz). IR (2–5 wt% KBr pellet, cm⁻¹): 937(m), 868(s), 789(s), 756(sh), 704(m), 524(w), 493(w).

Anal. Calcd. (found) for K₉[AlW₁₁O₃₉]·12H₂O: H, 0.75 (0.79); W, 62.39 (62.05); Al, 0.83 (0.92); K, 10.86 (10.80).

D. α -HEPTAPOTASSIUM VANADOUNDECATUNGSTOALUMINATE **α -K₇[AlV^{IV}W₁₁O₄₀]**



Procedure

To a well-stirred slurry of α -K₉[AlW₁₁O₃₉] (5.43 g, 1.80 mmol) in 10 mL of H₂O in a 50-mL beaker, vanadyl sulfate trihydrate (VOSO₄·3H₂O, 0.39 g, 1.80 mmol), dissolved in 5 mL of H₂O, is added dropwise rapidly at room temperature. The color changes immediately to dark purple. The mixture is stirred for 30 min and filtered on a medium-porosity glass frit, then the dark purple filtrate is cooled to 5°C for 2 h. The resulting dark purple crystals are collected on a coarse fritted funnel and recrystallized from a minimum of warm (60°C) H₂O. Recrystallized yield: 3.5 g (61%).

Properties

Dark purple crystalline α -K₇[AlVW₁₁O₄₀]·15H₂O is characterized in the solid state by IR: (2–5 wt% KBr pellet, cm⁻¹): 942(m), 871(m), 793(s), 761(m), 697(w), 537(w), 492(w), 473(w).

Anal. Calcd. (found) for K₇[AlVW₁₁O₄₀]·15H₂O: H, 0.92 (0.84); W, 61.58 (61.66); Al, 0.82 (0.97); V, 1.55 (1.32); K, 8.33 (8.17).

The vanadyl ($\text{V}^{\text{IV}}=\text{O}$) $^{2+}$ containing anion, $[\text{AlVW}_{11}\text{O}_{40}]^{7-}$, is paramagnetic. However, solutions of $[\text{AlVW}_{11}\text{O}_{40}]^{7-}$ are readily oxidized to bright yellow solutions of $[\text{AlVW}_{11}\text{O}_{40}]^{6-}$ by addition of elemental bromine. Diamagnetic $[\text{AlVW}_{11}\text{O}_{40}]^{6-}$, prepared in situ, can be observed by ^{27}Al , ^{51}V , and ^{183}W NMR. ^{27}Al : 72.5 ppm ($\Delta\nu_{1/2} = 175$ Hz); ^{51}V : -535.5 ppm ($\Delta\nu_{1/2} = 220$ Hz); ^{183}W (integration): -79.7(2), -96.0(2), -116.2(2), -119.5(1), -121.4(2), -141.2(2) ppm.

E. α -HEXAPOTASSIUM VANADOUNDECATUNGSTOALUMINATE $\alpha\text{-K}_6[\text{AlV}^{\text{V}}\text{W}_{11}\text{O}_{40}]$

The fully oxidized anion, $[\text{AlV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{6-}$, is conveniently prepared from the reduced species $[\text{AlV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{7-}$, prepared in situ from $\text{K}_9[\text{AlW}_{11}\text{O}_{39}]$ and vanadyl sulfate as described in procedure D, by passing a stream of ozone through its acidic solution (acid must be present during the ozonation to consume the hydroxide generated by the reduction of ozone in water). If ozone is not available, other oxidants, such as Br_2 or sodium hypochlorite, may be used. A 0.5 M solution of vanadyl sulfate trihydrate ($\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, 12.20 mL, 6.1 mmol) is added dropwise to a well-stirred slurry of $\alpha\text{-K}_9[\text{AlW}_{11}\text{O}_{39}]$ (20 g, 6.1 mmol in 50 mL H_2O), resulting in a dark purple solution of $[\text{AlVW}_{11}\text{O}_{40}]^{7-}$. Then 2 equiv of hydrochloric acid (4 mL of a 3 M solution) are added to the polyanion solution and a stream of ozone is bubbled through the solution until the dark purple color is discharged and a bright yellow solution obtained (the extinction coefficient of the reduced species is large enough that even very small amounts can be detected by eye in the presence of the oxidized species). Then oxygen is bubbled through the solution for several minutes to flush out unreacted ozone, and the solution is concentrated by rotary evaporation to approximately half its volume. The solution is refrigerated overnight at 5°C ; yellow crystals of $\text{K}_6[\text{AlV}^{\text{V}}\text{W}_{11}\text{O}_{40}]$ are collected and dried on a medium frit, and recrystallized from a minimum of hot H_2O . Yield: 12.95 g (66%).

Properties

The potassium salt of $\alpha\text{-K}_6[\text{AlV}^{\text{V}}\text{W}_{11}\text{O}_{40}]$ is a water-soluble yellow crystalline solid. ^{27}Al NMR, δ : 72.5 ppm ($\Delta\nu_{1/2} = 175$ Hz); ^{51}V NMR, δ : -535.5 ppm ($\Delta\nu_{1/2} = 220$ Hz); ^{183}W (relative intensities): -83.1(2), -99.1(2), -119.5(2), -123.0(1), -124.0(2), -144.4(2) ppm. IR (2–5 wt% KBr pellet, cm^{-1}): 950(m), 878(s), 794(s), 756(s), 542(w), 487(w).

Anal. Calcd. (found) for $\text{K}_6[\text{AlVW}_{11}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$: H, 0.82 (0.78); W, 63.02 (62.97); Al, 0.84 (0.88); V, 1.59 (1.88); K, 7.31 (7.29).

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4. SUPRAMOLECULAR COMPLEXES OF BIS(2,2'-BIPYRIDINE)OSMIUM(II) AND RUTHENIUM(II)

Submitted by JEFF A. CLARK, MARK M. RICHTER,[†] and KAREN J. BREWER^{*}

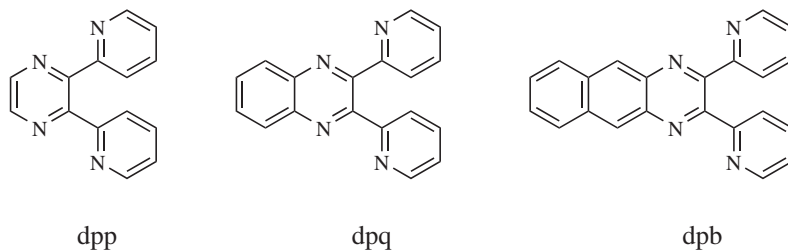
Checked by D. SENIVERATNE and J. F. ENDICOTT[‡]

Interest in osmium(II) and ruthenium(II) polypyridyl complexes originally developed because of their extreme stability and intense colors.¹⁻³ Later they were shown to possess very interesting excited-state properties and undergo facile energy and electron transfer.⁴⁻⁷ A more recent trend in this area of chemistry is to attach a variety of polyazine ligands capable of bridging to allow for the construction of supramolecular systems.⁸⁻¹³ One useful series of polyazine bridging ligands is that of dpp [2,3-bis(2-pyridyl)pyrazine], dpq [2,3-bis(2-pyridyl)quinoxaline], and dpb [2,3-bis(2-pyridyl)benzoquinoxaline]^{8,14,15} (Fig. 1).

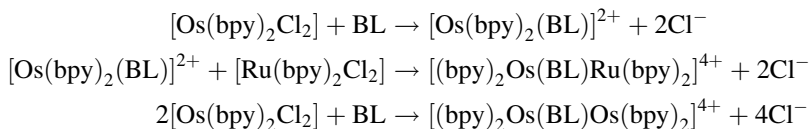
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**Figure 1**

This procedure describes the preparation of the dpq and dpb ligand and a series of general synthetic methods for the synthesis of osmium(II) and mixed-metal osmium(II) and ruthenium(II) bipyridine complexes of these polyazine bridging ligands. The procedures for the preparation of the starting complexes $[M(\text{bpy})_2\text{Cl}_2]$, $M = \text{Os}^{\text{II}}$ ^{2,17} or Ru^{II} ^{1,16,17} have been reported in previous *Inorganic Syntheses* volumes. The dpq ^{11,14} and dpb ^{11,15} ligands are prepared by a modification of the earlier literature preparations and purified by adsorption chromatography. The metal complexes are prepared by the reaction of the appropriate $[M(\text{bpy})_2\text{Cl}_2]$ with either the free BL (BL = bridging ligand), to prepare the monometallic ¹¹ and symmetric bimetallic systems ¹² or BL already bound to the osmium, $[\text{Os}(\text{bpy})_2(\text{BL})]^{2+}$, to prepare the following mixed-metal bimetallic complexes: ¹³



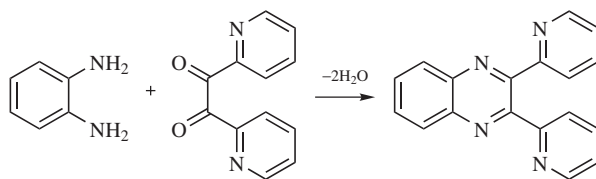
General Chromatographic Procedures

All the ligands and complexes reported herein are purified by column chromatography using Fisher Scientific adsorption alumina. Most other types of alumina and sources of alumina possess more active surfaces, and this often results in either the need for more polar solvents to elute the system of interest or an irreversible adsorption of the compounds to the chromatographic support. Columns are typically 2–3 cm in diameter and 40–50 cm in length. The columns are prepared by first loading with the solvent of interest and then adding the dry adsorption alumina with the solvent flowing through the column. This enhances the packing of the column and eliminates air bubbles within the alumina base.

Sufficient adsorption alumina is added to fill the column approximately two-thirds full, allowing for dead volume on the top to load solutions of compounds and for solvent addition as the compound passes through the column. The solvent used varies with each system and is specified in the synthetic procedure. The total volume of solvent needed depends on many factors, including water content of solvents and humidity of the laboratory and vary from ~ 100 – 500 mL for the purifications described below. The compound is dissolved in a minimal amount of the solvent used for the column preparation, filtered, and loaded on the column. The solvent is then added for the chromatographic step and the products collected as they elute from the column. Most of the systems studied are colored and visual inspection is used to separate product bands. For the purification of the colorless dpq ligand a handheld UV lamp makes it possible to see the blue emission of the dpq ligand. Alternatively, the ligand can be detected by electronic absorption spectroscopy as dpq absorbs highly in the UV region. In all chromatographic separations the product band is collected and the solvent is removed by rotary evaporation. The product is then redissolved in a minimal amount of methylene chloride for dpq and dpb and CH_3CN for the metal complexes and precipitated by the addition to ~ 250 mL of diethyl ether while stirring. The product is removed by vacuum filtration and dried under vacuum. Specific solvent conditions and visual observations of product colors are described below.

■ **Caution.** *2,2'-pyridil is toxic and an irritant. 1,2-diaminobenzene is toxic and an irritant. 2,3-diaminonaphthalene is highly toxic and a suspected carcinogen. 2,3-bis(2-pyridyl)pyrazine is toxic and an irritant. 2,3-bis(2-pyridyl)quinoxaline is toxic. 2,3-bis(2-pyridyl)benzoquinoxaline is toxic. Potassium hexafluorophosphate is toxic and corrosive. Avoid contact with skin or inhalation for all of these chemicals. Ethanol is flammable. This procedure should be performed in a fume hood. Ethylene glycol is toxic and flammable. Toluene is toxic and flammable. Acetonitrile is toxic and flammable. Diethyl ether is toxic and highly flammable. Avoid contact with skin, inhalation, and breathing vapors for all chemicals. All procedures should be performed in a fume hood. Refluxing ethylene glycol is very hot, use a heat-resistant glove to remove the reaction mixture from the heat.*

A. 2,3-BIS(2-PYRIDYL)QUINOXALINE (dpq)



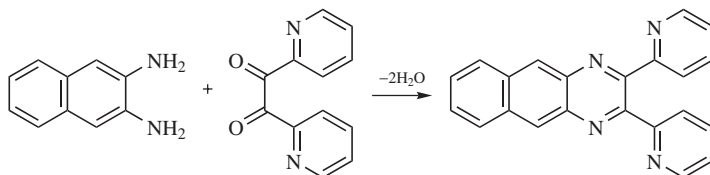
Procedure

The total time for the preparation and purification of this product is about 10 h. The ligand dpq is prepared by the method of Goodwin and Lions as described below.¹⁴

Solid 2,2'-pyridyl (available from Aldrich Chemicals) (1.09 g, 5.12 mmol) is combined with 0.56 g (5.2 mmol) of 1,2-diaminobenzene in a 100-mL round-bottomed flask containing a magnetic stir bar. To this is added 30 mL of absolute ethanol. The flask is equipped with a reflux condenser and the solution is stirred and heated at reflux for 5 h. The flask is removed from the heating mantle and the solution is allowed to cool to room temperature, at which time solid colorless crystals of the dpq product form. The product is removed by vacuum filtration. Purification can be achieved by recrystallization from hot ethanol or by chromatography on adsorption alumina using methylene chloride as the eluent as described above. The chromatographic purification of the crude dpq ligand yields the desired colorless band containing the purified product as the first band that elutes prior to the unreacted starting materials. The chromatographic procedure can be monitored by UV spectroscopy or with the use of a UV lamp as the dpq ligand displays a blue emission. Purification by recrystallization is also possible. The crude product is dissolved in a minimum amount of boiling EtOH. The EtOH is allowed to cool to RT and the product removed by vacuum filtration. Two recrystallizations are typically required to produce the pure, colorless dpq ligand. The purified product is washed with 50 mL of diethylether and dried under vacuum for 4 h. Yield: 0.96 g, 66%.

Anal. Calc. for $C_{18}H_{12}N_4$: C, 76.03; H, 4.26; N, 19.71. Found: C, 75.11; H, 4.06; N, 19.52. ^{13}C NMR $d(CDCl_3)$: 157.4, 152.5, 148.6, 141.1, 136.6, 130.5, 129.4, 124.2, 123.0. $E_{1/2}^{red}$ (0.1 M Bu_4NPF_6 in CH_3CN) = -1.43 V versus Ag/AgCl.

B. 2,3-BIS(2-PYRIDYL)BENZOQUINOXALINE (dph)



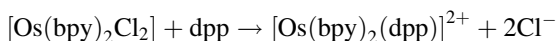
Procedure

The total time for the preparation and purification of this product is about 10 h. The ligand dpb was prepared by a modification of the method of Buu-Hoi and Saint-Ruf.¹⁵ (*Note:* This procedure should be performed in a fume hood.)

Solid 2,2'-pyridil (1.08 g 5.10 mmol) is combined with 0.82 g (5.2 mmol) of 2,3-diaminonaphthalene in a 100-mL round-bottomed flask containing a magnetic stir bar. To this is added 30 mL of absolute ethanol. The flask is equipped with a reflux condenser. This solution is then stirred and heated at reflux for 5 h. The round bottom is removed from the heat and the solution is allowed to cool to room temperature, at which time solid yellow crystals of the dpb product form. The product is removed by vacuum filtration. Purification is achieved by chromatography on adsorption alumina using methylene chloride as the eluent as described above. The desired yellow band containing the dpb product elutes prior to the unreacted starting materials. The purified product is then washed with 50 mL of diethylether and dried under vacuum for 4 h. Yield: 1.14 g, 67%.

Anal. Calc. for C₂₂H₁₄N₄: C, 79.02; H, 4.22; N, 16.76. Found: C, 77.74; H, 4.20; N, 16.08. ¹³C NMR *d*(CDCl₃) 157.5, 153.1, 148.4, 137.7, 136.7, 134.3, 128.6, 127.9, 127.0, 124.0, 123.0. *E*_{1/2}^{red} (0.1 M Bu₄NPF₆ in CH₃CN) = −1.14 V versus Ag/AgCl.

**C. *cis*-BIS(2,2'-BIPYRIDINE)2,3-BIS(2-PYRIDYL)PYRAZINEOSMIUM
(II)HEXAFLUOROPHOSPHATE HYDRATE
{[Os(bpy)₂(dpp)](PF₆)₂·H₂O}**



Procedure

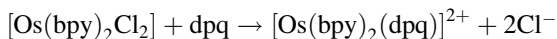
The total time required for the preparation and purification of this product is about 3 h. The procedure is a modification of a published synthesis by Kalyanasundaram.⁹

The ligand dpp (0.23 g, 1.0 mmol) and [Os(bpy)₂Cl₂] (0.28 g, 0.48 mmol) are added to a 100-mL round-bottomed flask. To this is added 10 mL of ethylene glycol. The round-bottomed flask is equipped with a reflux condenser and a magnetic stir bar and stirrer and a heating mantle. While the reaction mixture is being stirred, it is heated to reflux for 60 min. The heat is removed and the reaction mixture is allowed to cool to room temperature. A saturated, aqueous solution of KPF₆ is prepared by adding an excess of KPF₆ to 30 mL of deionized water and stirring to ensure saturation. The solution is allowed to sit for 5 min and then 20 mL of the supernatant is decanted into a 100-mL beaker. The reaction mixture is added dropwise to this saturated, aqueous KPF₆ to induce precipitation of the brown crude product. The solid is removed by vacuum filtration and washed with

two 30 mL portions of diethyl ether. The crude product is purified by chromatography on adsorption-type alumina using a 2 : 1 v/v toluene/acetonitrile eluent as described above. The first visible band to elute is the desired brown product. It is important to discard any solvent that elutes prior to this product as it contains some unreacted dpp ligand that is not visible to the eye. A small amount of the purple bimetallic species can be seen to follow the desired brown product on the alumina column. The product obtained from this first column is rechromatographed on a new adsorption alumina column using the same procedure and 2 : 1 toluene/acetonitrile eluent. Again the brown band is collected. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield 0.42 g, 85%.

Anal. Calc. for $C_{34}H_{28}N_8OP_2F_{12}Os$: C, 39.08; H, 2.70; N, 10.73. Found: C, 39.21; H, 2.60; N, 10.75.

**D. *cis*-BIS(2,2'-BIPYRIDINE)2,3-BIS(2-PYRIDYL)
QUINOXALINEOSMIUM(II) HEXAFLUOROPHOSPHATE
{[Os(bpy)₂(dpq)](PF₆)₂}**



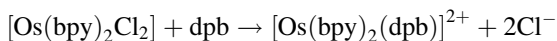
Procedure

The total time required for the preparation and purification of this product is about 3 h. This complex is prepared as above for [Os(bpy)₂(dpp)](PF₆)₂·H₂O substituting dpq (0.29 g, 1.0 mmol) for the dpp used above.

The crude product is purified by chromatography on adsorption alumina using a 2 : 1 toluene/acetonitrile solvent mixture as described above. The first visible band to elute from the column is the desired red-purple product band. It is important to discard any solvent that elutes prior to this product as it contains some unreacted dpq ligand that is not visible to the eye. A small amount of the dark purple bimetallic species can be seen to follow the desired red-purple product on the alumina column. This red-purple solid obtained from this chromatographic separation is rechromatographed on a new adsorption alumina column using the same procedure and 2 : 1 toluene/acetonitrile solvent mixture. Again the red-purple band is collected. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.42 g, 80%.

Anal. Calc. for $C_{38}H_{28}N_8P_2F_{12}Os$: C, 42.38; H, 2.62; N, 10.41. Found: C, 42.99; H, 2.86; N, 10.65.

E. *cis*-BIS(2,2'-BIPYRIDINE)2,3-BIS(2-PYRIDYL) BENZOQUINOXALINEOSMIUM(II) HEXAFLUOROPHOSPHATE
{[Os(bpy)₂(dpb)](PF₆)₂}

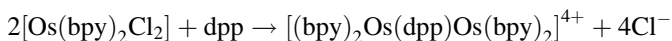


Procedure

The total time required for the preparation and purification of this product is about 3 h. This complex is prepared as described above for [Os(bpy)₂(dpp)](PF₆)₂·H₂O by substituting dpb (0.34 g, 1.0 mmol) for dpp. Purification is achieved again by chromatography on adsorption alumina as described above using a 2 : 1 toluene/acetonitrile eluent. The first visible band to elute from the column is typically unreacted dpb ligand that is yellow in color and elutes with the solvent front. This should be discarded. The desired product comes next and is purple. A small amount of the green bimetallic species can be seen to follow the desired purple product on the alumina column. The desired purple product is collected. This product is rechromatographed using the same procedure and 2 : 1 toluene/acetonitrile solvent mixture. Again the purple band is collected. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.41 g, 75%.

Anal. Calc. for C₄₂H₃₀N₈P₂F₁₂Os: C, 44.76; H, 2.68; N, 9.95. Found: C, 44.74; H, 2.88; N, 9.87.

F. *cis*-TETRAKIS(2,2'-BIPYRIDINE)-μ-[2,3-BIS(2-PYRIDYL) PYRAZINE]DIOSMIUM(II) HEXAFLUOROPHOSPHATE
DIHYDRATE {[Os(bpy)₂Os(dpp)Os(bpy)₂](PF₆)₄·2H₂O}



Procedure

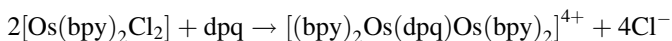
The total time required for the preparation and purification of this product is about 3 h, and the product is prepared by a modification of the published procedure of Campagna.¹⁰ The ligand dpp (0.056 g, 0.24 mmol) and [Os(bpy)₂Cl₂] (0.34 g, 0.60 mmol) are added to a 100-mL round-bottomed flask. To this is

added 30 mL of ethylene glycol. The round-bottomed flask is equipped with a reflux condenser and a magnetic stir bar and stirrer. While the reaction mixture is being stirred it is heated at reflux for 45 min.

The heat is removed and reaction allowed to cool to room temperature. A saturated, aqueous solution of KPF_6 is prepared by adding an excess of KPF_6 to 90 mL of deionized water and stirring to ensure saturation. The solution is allowed to sit for 5 min and then 75 mL of the supernatant is decanted into a 150-mL beaker. The reaction mixture is added dropwise to this saturated, aqueous KPF_6 to induce precipitation of the purple-brown crude product. The solid is removed by vacuum filtration and washed with two 30-mL portions of diethyl ether. The crude product is purified by chromatography on adsorption alumina as described above using a 2 : 1 toluene/acetonitrile eluent. The first visible band to elute is a small amount of the brown monometallic. Occasionally a small amount of unreacted $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ will elute prior to the brown monometallic. After the monometallic band is eluted, the solvent is changed to 1 : 2 toluene/acetonitrile to elute the desired purple product. The purple product band is collected. This product is then rechromatographed on a new alumina column using the same procedure and solvent mixtures. Again the purple product band is collected. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.25 g, 56%.

Anal. Calc. for $\text{C}_{54}\text{H}_{46}\text{N}_{12}\text{O}_2\text{P}_4\text{F}_{24}\text{Os}_2$: C, 34.96; H, 2.50; N, 9.06. Found: C, 35.05; H, 2.58; N, 9.00.

G. *cis*-TETRAKIS(2,2'-BIPYRIDINE)- μ -[2,3-BIS(2-PYRIDYL)QUINOXALINE]DIOSMIUM(II) HEXAFLUOROPHOSPHATE DIHYDRATE $\{[(\text{bpy})_2\text{Os}(\text{dpq})\text{Os}(\text{bpy})_2](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}\}$



Procedure

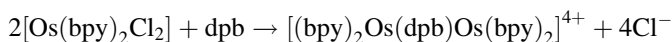
The total time required for the preparation and purification of this product is about 3 h. This product is prepared as above for $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Os}(\text{bpy})_2](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}$ substituting dpq (0.068 g, 0.24 mmol) for the dpp above.

This crude product is purified by chromatography using adsorption alumina as described above initially using a 2 : 1 toluene/acetonitrile solvent mixture and changing solvents as described below. The first visible band to elute from this column is a small amount of the red-purple monometallic complex. After this band is eluted the solvent is changed to 1 : 2 toluene/acetonitrile to elute the

desired purple product. This band elutes second. This purple product is rechromatographed on a new adsorption alumina column using the same 2 : 1 toluene/acetonitrile solvent mixture followed by the change to 1 : 2 toluene/acetonitrile after elution of the red-purple monometallic. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.46 g, 58%.

Anal. Calc. for $C_{58}H_{48}N_{12}O_2P_4F_{24}Os_2$: C, 36.56; H, 2.54; N, 8.82. Found: C, 36.61; H, 2.65; N, 8.98.

H. *cis*-TETRAKIS(2,2'-BIPYRIDINE)- μ -[2,3-BIS(2-PYRIDYL)BENZO-QUINOXALINE]DIOSMIUM(II) HEXAFLUOROPHOSPHATE TRIHYDRATE{[(bpy)₂Os(dpb)Os(bpy)₂](PF₆)₄·3H₂O}



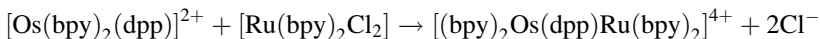
Procedure

The total time required for the preparation and purification of this product is about 3 h. This product is prepared as above for [(bpy)₂Os(dpp)Os(bpy)₂](PF₆)₄·2H₂O substituting dpb (0.081 g, 0.24 mmol) for the dpp described above.

The product is purified by chromatography on adsorption alumina using the procedure described above and a 2 : 1 toluene/acetonitrile solvent mixture. The first visible band to elute from this column is unreacted dpb that is yellow in color and elutes with the solvent front. Next a small amount of the purple monometallic elutes. After this band is eluted, the solvent is changed to 1 : 2 toluene/acetonitrile to elute the desired green product. The green product is rechromatographed on a new alumina column using the same procedure and solvent mixtures. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.20 g, 43%.

Anal. Calc. for $C_{62}H_{52}N_{12}O_3P_4F_{24}Os_2$: C, 37.73; H, 2.65; N, 8.52. Found: C, 37.60; H, 2.56; N, 8.32.

I. *cis*-TETRAKIS(2,2'-BIPYRIDINE)- μ -[2,3-BIS(2-PYRIDYL)PYRAZINE]RUTHENIUM(II)-OSMIUM(II) HEXAFLUOROPHOSPHATE DIHYDRATE {[(bpy)₂Os(dpp)Ru(bpy)₂](PF₆)₄·2H₂O}



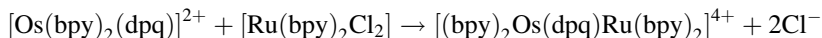
Procedure

The total time required for the preparation and purification of this product is about 3 days, and the product is prepared by a modification of the published procedure of Kalyanasundaram.⁹

The osmium complex $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ (0.11 g, 0.10 mmol) and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (0.24 g, 0.50 mmol) are added to a 500-mL round-bottomed flask. To this is added 300 mL of 2 : 1 v/v ethanol/water. The round-bottom flask is equipped with a reflux condenser and a magnetic stir bar and stirrer. While the reaction mixture is being stirred it is heated at reflux for 48 h. The heat is removed and reaction allowed to cool to room temperature. The volume is reduced to 75 mL by rotary evaporation. A saturated, aqueous solution of KPF_6 is prepared by adding an excess of KPF_6 to 80 mL of deionized water and stirring to ensure saturation. The solution is allowed to sit for 5 min, and then 60 mL of the supernatant is decanted into a 250-mL beaker. The reaction mixture is added dropwise to this saturated, aqueous KPF_6 to induce precipitation of the purple-brown crude product. The solid is removed by vacuum filtration and washed with two 30-mL portions of diethyl ether. The crude product is purified by chromatography on adsorption alumina as described above using a 1 : 1 v/v toluene/acetonitrile eluant. The first visible band to elute is a small amount of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. Next a small amount of the brown osmium monometallic is eluted. After this band is eluted, the solvent is changed to 1 : 3 toluene/acetonitrile to elute the desired purple product. The purple product band is collected. This product is then rechromatographed on a new alumina column using the same procedure and solvent mixtures. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.13 g, 70%.

Anal. Calc. for $\text{C}_{54}\text{H}_{46}\text{N}_{12}\text{O}_2\text{P}_4\text{F}_{24}\text{OsRu}$: C, 36.72; H, 2.62; N, 9.52. Found: C, 36.66; H, 2.73; N, 9.52.

J. *cis*-TETRAKIS(2,2'-BIPYRIDINE)- μ -[2,3-BIS(2-PYRIDYL)QUINOXALINE]RUTHENIUM(II)-OSMIUM(II) HEXAFLUOROPHOSPHATE TRIHYDRATE $\{[(\text{bpy})_2\text{Os}(\text{dpq})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4 \cdot 3\text{H}_2\text{O}\}$



Procedure

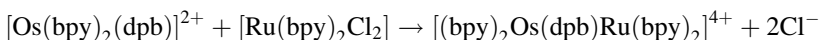
The total time required for the preparation and purification of this product is about 3 days. This product is prepared as described above for $[(\text{bpy})_2\text{Os}(\text{dpp})]$

$\text{Ru}(\text{bpy})_2](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}$ substituting $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ (0.12 g, 0.11 mmol) for the $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$.

The product is purified by chromatography on adsorption alumina using the procedure described above and a 2 : 1 toluene/acetonitrile solvent mixture initially. The first visible band to elute from this column is a small amount of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. Next a small amount of the red-purple osmium monometallic is eluted. After this band is eluted, the solvent is changed to 1 : 3 toluene/acetonitrile to elute the desired blue-green product. The blue-green product is rechromatographed on a new alumina column using the same procedure and solvent mixtures. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.18 g, 85%.

Anal. Calc. for $\text{C}_{58}\text{H}_{50}\text{N}_{12}\text{O}_3\text{P}_4\text{F}_{24}\text{OsRu}$: C, 37.98; H, 2.75; N, 9.17. Found: C, 37.82; H, 2.94; N, 9.46.

K. *cis*-TETRAKIS(2,2'-BIPYRIDINE)- μ -[2,3-BIS(2-PYRIDYL)BENZOQUINOXALINE]RUTHENIUM(II)-OSMIUM(II) HEXAFLUOROPHOSPHATE DIHYDRATE
 $\{[(\text{bpy})_2\text{Os}(\text{dpb})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}\}$



Procedure

The total time required for the preparation and purification of this product is about 3 days. This product is prepared as described above for $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}$ substituting $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$ (0.11 g, 0.10 mmol) for the $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$.

The product is purified by chromatography on adsorption alumina using the procedure described above and an initial 2:1 toluene/acetonitrile solvent mixture. The first visible band to elute from this column is a small amount of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. Next a small amount of the purple osmium monometallic is eluted. After this band is eluted the solvent is changed to 1 : 3 toluene/acetonitrile to elute the desired green product. The green product is rechromatographed on a new alumina column using the same procedures and solvent mixtures. The purified product is washed with two 30-mL portions of diethylether and dried under vacuum overnight. Yield: 0.16 g, 87%.

Anal. Calc. for $\text{C}_{62}\text{H}_{50}\text{N}_{12}\text{O}_2\text{P}_4\text{F}_{24}\text{OsRu}$: C, 39.90; H, 2.70; N, 9.01. Found: C, 40.25; H, 2.95; N, 9.18.

TABLE I. Electronic Spectral Properties^a of [Os(bpy)₂(BL)]²⁺,¹¹ [(bpy)₂Os(BL)Os(bpy)₂]⁴⁺,¹² and [(bpy)₂Os(BL)Ru(bpy)₂]⁴⁺¹³ (BL = dpp, dpq or dpb)^b

Complex	$\lambda_{\text{max}}^{\text{abs}}$, nm (ϵ , M ⁻¹ cm ⁻¹)
[Os(bpy) ₂ (dpp)] ²⁺	290 (67,300), 432 (11,000), 486 (12,700)
[Os(bpy) ₂ (dpq)] ²⁺	286 (73,200), 346 (25,100), 428 (11,000), 536 (13,400)
[Os(bpy) ₂ (dpb)] ²⁺	290 (70,000), 366 (24,400), 408 (17,300), 446 (12,800), 570 (13,800)
[(bpy) ₂ Os(dpp)Os(bpy) ₂] ⁴⁺	286 (96,700), 356 (26,400), 432 (19,800), 552 (25,200)
[(bpy) ₂ Os(dpq)Os(bpy) ₂] ⁴⁺	286 (90,500), 356 (21,700), 398 (19,600), 428 (14,300), 630 (20,900)
[(bpy) ₂ Os(dpb)Os(bpy) ₂] ⁴⁺	286 (90,700), 354 (35,300), 422(16,600), 510 (8,160), 610 (12,900), 670 (16,800)
[(bpy) ₂ Os(dpp)Ru(bpy) ₂] ⁴⁺	286 (102,700), 348 (31,300), 430 (22,300), 542 (28,500)
[(bpy) ₂ Os(dpq)Ru(bpy) ₂] ⁴⁺	286 (118,600), 398 (28,400), 424 (19,100), 616 (28,500)
[(bpy) ₂ Os(dpb)Ru(bpy) ₂] ⁴⁺	286 (100,300), 344 (40,700), 408 (20,600), 424 (20,500), 658 (18,500)

^a CH₃CN solution at RT.

^b Abbreviations: dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline; dpb = 2,3-bis(2-pyridyl)benzoquinoxaline.

Properties

Spectral and electrochemical properties are listed in Tables I and II. The complexes are all quite stable as solids and as acetonitrile solutions. They all display intense electronic transitions in the ultraviolet that represent bpy and BL-based $\pi \rightarrow \pi^*$ transitions. In the visible spectrum they display metal-to-ligand charge transfer (MLCT) transitions associated with each metal center and its coordinated ligands. The lowest-lying electronic transition in all the complexes reported is a Os $\rightarrow$ BL CT transition.

All the complexes display reversible metal-based oxidations M^{II/III} with the osmium oxidizing prior to the ruthenium in the mixed-metal bimetallic complexes. They also possess reversible ligand-based reductions with the monometallic complexes displaying BL^{0/-}, bpy^{0/-}, and bpy^{0/-} couples and the bimetallics displaying BL^{0/-}, BL^{-1/2-}, and four bpy^{0/-} couples.

TABLE II. Electrochemical Data^a for [Os(bpy)₂(BL)]²⁺, ¹¹ [(bpy)₂Os(BL)Os(bpy)₂]⁴⁺, ¹² and [(bpy)₂Os(BL)Ru(bpy)₂]⁴⁺ ¹³ (BL = dpp, dpq or dpb)^b

Complex	$E_{1/2}$ (V vs. Ag/AgCl)
[Os(bpy) ₂ (dpp)] ²⁺	0.94, -1.02, -1.38, -1.58
[Os(bpy) ₂ (dpq)] ²⁺	0.99, -0.76, -1.26, -1.57
[Os(bpy) ₂ (dpb)] ²⁺	1.00, -0.61, -1.16, -1.55
[(bpy) ₂ Os(dpp)Os(bpy) ₂] ⁴⁺	1.22, 0.91, -0.61, -1.00, -1.28, -1.38, -1.58, -1.76
[(bpy) ₂ Os(dpq)Os(bpy) ₂] ⁴⁺	1.28, 0.98, -0.34, -0.90, -1.26, -1.36, -1.54, -1.72
[(bpy) ₂ Os(dpb)Os(bpy) ₂] ⁴⁺	1.30, 0.98, -0.25, -0.76, -1.31, -1.39, -1.58, -1.74
[(bpy) ₂ Os(dpp)Ru(bpy) ₂] ⁴⁺	1.56, 1.01, -0.62, -1.03, -1.34, -1.41, -1.61, -1.74
[(bpy) ₂ Os(dpq)Ru(bpy) ₂] ⁴⁺	1.61, 1.09, -0.33, -0.94, -1.32, -1.42, -1.56, -1.73
[(bpy) ₂ Os(dpb)Ru(bpy) ₂] ⁴⁺	1.62, 1.09, -0.21, -0.76, -1.34, -1.42, -1.59, -1.75

^aRecorded in CH₃CN for monometallics and oxidative couples and DMF for bimetallic reductive couples with 0.1 MBu₄NPF₆ supporting electrolyte and potentials are reported versus Ag/AgCl (0.27 V vs. NHE).

^bAbbreviations: dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline; dpb = 2,3-bis(2-pyridyl)benzoquinoxaline.

Acknowledgments

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5. BINUCLEAR OXOMOLYBDENUM–METALLOPORPHYRIN COMPLEXES

Submitted by PARTHA BASU,^{*} MICHAEL VALEK,[†] and JOHN H. ENEMARK[‡]
 Checked by H. TETSUO UYEDA and M. J. THERIEN[‡]

In this section, syntheses of {5-(*m,n*-catecholato[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]oxomolybdenum(V)}-10,15,20-tri-*p*-tolylporphinatometal [ML (*m,n*-Mo-TTP)], [ML = Zn(II), Fe(III)Cl, Cu; *m,n* = 2,3 or 3,4] are described.

Supramolecular assemblies of metal complexes are of considerable interest because of their versatile chemistry that can be adapted to produce materials with applications in several areas such as separation, electron transfer, catalysis, magnetic devices, and optical devices.^{1,2} Transition metal complexes with the ability to shuttle between multiple redox states are playing a pivotal role in developing such materials. Moreover, some of these complexes are important in understanding the complex clusters in biological macromolecules.

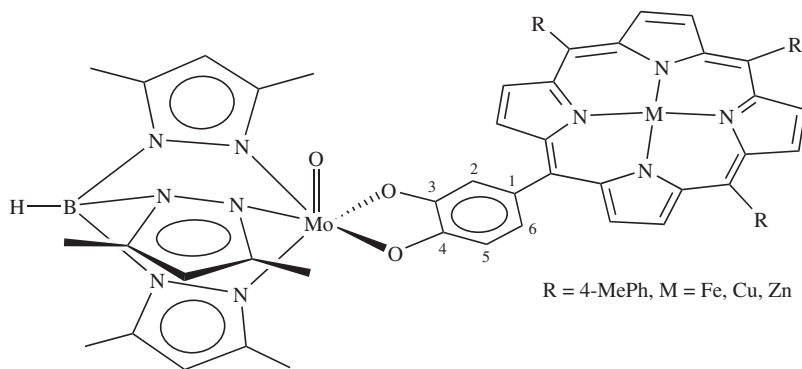
The multinuclear assemblies described here were developed as models for understanding the interprosthetic group interaction between the molybdenum and heme centers in sulfite oxidase.

The ligand system of Fig. 1 is designed to coordinate two metal centers at constrained distances and is well suited for studying weak magnetic interactions

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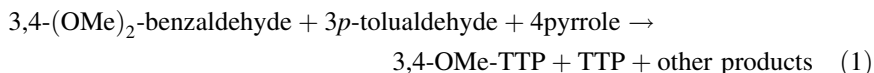
[‡]Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

**Figure 1**

between Mo(V) and a paramagnetic metalloporphyrin center.^{3–6} The corresponding Zn(II) derivatives exhibit interesting photoinduced electron transfer processes.⁷ The synthetic approach to preparation of these complexes is outlined in Scheme 1.

The free-base porphyrins 3,4-OH-TTP and 2,3-OH-TTP are synthesized by demethylating the corresponding dimethoxy porphyrins.⁸ The dimethoxy porphyrins are prepared by direct condensation of pyrrole and an appropriate mixture of aldehydes following Adler's method.⁹

A. 5-(3,4-DIMETHOXYPHENYL)-10,15,20-TRI-*p*-TOLYLPORPHYRIN (3,4-OME-TTP)



Procedure

3,4-Dimethoxybenzaldehyde (8.3 g, 50 mmol) and *p*-tolualdehyde (18 g, 150 mmol) are dissolved in propionic acid (500 mL) and brought to reflux. Freshly distilled pyrrole (13.4 g, 200 mmol) is added to the solution and reflux continued for 45 min. The reaction mixture is cooled overnight at 11°C and filtered, and the purple-black precipitate washed with cold absolute ethanol. The crude product is purified in 500-mg batches. Tar and other insoluble impurities are removed by addition of 50 mL of dichloromethane and rapid elution through a 4×5-cm silica column with dichloromethane until the eluted product is no longer purple. Evaporation of the solvent gives a purple solid that is purified by chromatography on a 4×15-cm column using 230–400-mesh 60 Å silica gel. Up to 500 mg of crude product can be loaded on the column, and the major TTP component



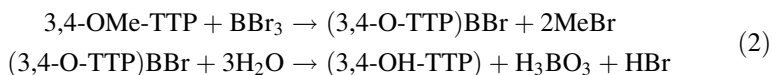
Anal. Calcd. for 3,4-OMe-TTP: C, 82.07; H, 5.62; N, 7.85. Found: C, 80.90; H, 5.75; N, 7.72. Mass spectrum: calcd. molecular ion: 716.32 amu; found (FAB, nitrobenzyl alcohol): 717.00 amu. Proton NMR in CDCl₃ at 22°C: δ 2.69(s) (9H); δ 3.97(s) (3H); δ 4.16(s) (3H); δ 7.23(d)=8 Hz (1H); δ 7.54(d)=8 Hz (6H); δ 7.74(d)=8 Hz (1H); δ 7.76(s) (1H); δ 8.1(d)=8 Hz (6H); δ 8.85(m) (8H). Electronic spectrum in toluene at 25°C (λ in nm, ϵ in L mol⁻¹ cm⁻¹): 516 (17,400), 552 (9330), 594 (5010), 649 (4370).

B. 5-(2,3-DIMETHOXYPHENYL)-10,15,20-TRI-*p*-TOLYLPORPHYRIN (2,3-OME-TTP)

This compound is prepared from 2,3-dimethoxybenzaldehyde (8.3 g, 50 mmol) with 3 equiv of *p*-tolualdehyde (10.8 g, 90 mmol) and 4 equiv of freshly distilled pyrrole (8.1 g, 120 mmol) by the procedure used for 3,4-OME-TTP. The crude product is purified by adsorption chromatography on silica gel with dichloromethane–hexane as the elutant, as described for 3,4-OME-TTP. The product is recrystallized from dichloromethane–heptane. Yield: 0.55 g (2.6%). Mass spectrum: calcd. molecular ion: 716.32 amu; found (FAB, nitrobenzyl alcohol): 716.60. Proton NMR in CDCl₃ at 22°C: δ 2.70(s) (9H); δ 3.18(s) (3H); δ 4.13(s) (3H); δ 7.38(m) (2H); δ 7.55(d) = 8 Hz (6H); δ 7.65(m) (1H); δ 8.1(m) (6H); δ 8.3(m) (8H). Electronic spectrum in toluene at 25°C (λ in nm, ϵ in L mol^{−1} cm^{−1}): 516 (19,500), 550 (8510), 592 (5370), 652 (5620).

C. 5-(3,4-DIHYDROXYPHENYL)-10,15,20-TRI-*p*-TOLYLPORPHYRIN (3,4-OH-TTP)

This compound is synthesized from 3,4-OME-TTP by demethylating with boron tribromide.¹⁰

*Procedure*

First, 0.2 g (2.8×10^{-4} mol) of 3,4-OME-TTP dissolved in a minimum volume of freshly distilled dry dichloromethane is added dropwise to a BBr₃ solution (2 mL BBr₃ in 5 mL dichloromethane) at −80°C. The solution is stirred for 1 h, slowly brought to room temperature, and then stirred for an additional 24 h. Water is added slowly to the green solution to hydrolyze any excess BBr₃ present, and the solution is neutralized with triethylamine to precipitate the target compounds as a purple solid. The solid mass is filtered, washed with water, dried, and recrystallized from dichloromethane–heptane solution.¹¹ Yield: 0.17 g (90%).

Anal. Calcd. for 3,4-OH-TTP (1): C, 81.92; H, 5.27; N, 8.17. Found: C, 81.49; H, 5.56; N, 7.92. Mass spectrum: calcd. molecular ion 688.28 amu; found (FAB, nitrobenzyl alcohol): 688.20 amu. Proton NMR in CD₂Cl₂ at 22°C: δ 2.70(s) (9H); 7.12(d) = 8 Hz (1H); 7.49(s) (1H), 7.57(d) = 8 Hz (7H); 8.09(d) = 8 Hz (6H); 8.87(s) (8H). Electronic spectrum in toluene at 25°C (λ in nm, ϵ in L mol^{−1} cm^{−1}): 516 (17,800), 551 (9550), 594 (5250), 652 (7590).

D. 5-(2,3-DIHYDROXYPHENYL)-10,15,20-TRI-*p*-TOLYLPORPHYRIN (2,3-OH-TTP)

This compound is synthesized from 2,3-OMe-TTP by the method described above. Yield: (88%).

Anal. Calcd. for 2,3-OH-TTP (**2**): C, 81.92; H, 5.27; N, 8.17. Found: C, 80.86; H, 5.62; N, 7.87. Mass spectrum: calcd. molecular ion 688.28 amu; found (FAB, nitrobenzyl alcohol): 689.45 amu. Proton NMR in CD₂Cl₂ at 22°C: δ 2.71(s) (9H); 7.23(t) = 8 Hz (1H); 7.33(d) = 8 Hz (1H); 7.59(d) = 8 Hz (7H); 8.10(d) = 8 Hz (6H); 8.89(m) (8H). Electronic spectrum in toluene at 25°C (λ in nm; ϵ in L mol⁻¹ cm⁻¹): 515 (18,600), 550 (8710), 592 (6030), 651 (9550).

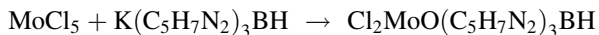
Properties

Compounds 3,4-OMe-TTP; 2,3-OMe-TTP; 3,4-OH-TTP, and 2,3-OH-TTP are bright purple crystalline substances that are stable in air in the solid state. However, their solutions, which are purple in color, are light-sensitive. The solids almost always contain solvents of crystallization that interfere with the elemental analyses. They are highly soluble in organic solvents such as chloroform and dichloromethane. They are also slightly to moderately soluble in methanol and ethanol.

Materials and General Procedures

A convenient source of the molybdenum center is LMoO(eth-gly)¹² (where L = 3,5-dimethyl-1-pyrazolylborate and eth-gly = ethylene glycolate). The low acidity of ethylene glycol makes it a good leaving group from LMoO(eth-gly) that can be easily replaced by stronger acids, such as the pendant catechol function of the porphyrin catecholate ligands.

E. [HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO] OXOMOLYBDENUM(V)DICHLORIDE (LMoOCl₂)

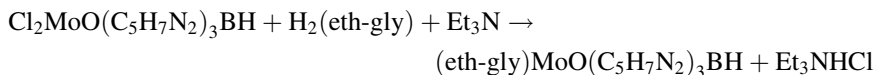


Procedure

To 16.4 g (60 mmol) of MoCl₅ in a 200-mL airless flask at -77°C is slowly added 120 mL of tetrahydrofuran (also at -77°C) with vigorous stirring. The reaction mixture is gradually brought to room temperature with continuous

stirring. Near room temperature an exothermic reaction begins and the color changes from dark red-brown to green, and a green precipitate subsequently forms. To the resulting slurry is added 20 g (59.5 mmol) of potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate^{13,14} (KL), and the mixture is heated at 50°C for 12 h with stirring. The resultant green precipitate is separated from the dark red supernatant by filtration, washed several times with acetonitrile, and dried in vacuo. The crude product is dissolved in ~1 L of refluxing 1,2-dichloroethane; the solution is filtered to remove potassium chloride and evaporated to dryness in vacuo. The green product, LMoOCl₂, is washed several times with acetonitrile to remove a red impurity. This green material is suitable for subsequent syntheses; additional purification can be effected by recrystallization from 1,2-dichloroethane. Yield of LMoOCl₂ (C₁₅H₂₂N₆OCl₂BMo): 20 g (70%). IR (KBr pellet): ν (MoO) 960 cm⁻¹. Electronic spectrum in dichloroethane (λ in nm; ϵ in L mol⁻¹ cm⁻¹): 337 (5200), 435 (1000), 705 (50).

F. [HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V) ETHYLENEGLYCOLATE [LMoO(Eth-Gly)]



Procedure

To a stirring slurry of 2 g (4.2 mmol) of LMoOCl₂ in 50 mL of toluene at 70°C is added a mixture of 0.6 mL (8.4 mmol) of triethylamine and 0.5 mL (8.4 mmol) of ethylene glycol in 5 mL of toluene. The progress of the reaction can be monitored by thin-layer chromatography (TLC). After the reaction is complete (~1.5 h) the mixture is cooled to room temperature, filtered, and evaporated to dryness in vacuo. The crude product is dissolved in toluene and the solution filtered to remove Et₃NHCl. Evaporation of the filtrate gives a blue powder that is dissolved in a minimum volume of dichloromethane and purified by column chromatography on a neutral alumina column (mesh 80–200) with dichloromethane as eluant. The solvent is removed under vacuum to give blue LMoO(eth-gly). Yield of LMoO(eth-gly) (C₁₇H₂₆N₆O₃BMo): 1.0 g (50%). IR: ν (MoO) 938 cm⁻¹. Electronic spectrum in 1,2-dichloroethane (λ in nm; ϵ in L mol⁻¹ cm⁻¹): 348 (3940), 525 (200), 640 (200).

G. 5-{3,4-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHYRIN (3,4-Mo-TTP)



Attachment of the molybdenum center to the pendant catecholato group is described in this section and Section H.

Procedure

Amounts of 3,4-OH-TTP (0.5 g, 0.7 mmol) and $\text{LMo}^{\text{VO}}(\text{eth-gly})$ (0.7 g, 1.5 mmol) are placed in an evacuated Schlenk flask (250 mL). Degassed dry toluene (100 mL) is added and the mixture is stirred at 70°C. Heating the solution to ~100°C lowers the yield. Heating is continued until the reaction is complete as evidenced by TLC; the organic solvent is removed under vacuum. Dichloromethane/toluene (1 : 1) (25 mL) is added to yield a purple-brown solution. The solution is purified by chromatography on a silica gel column (3 × 30 cm) with dichloromethane/toluene (1 : 1) as eluant. The solvent is removed under vacuum. Recrystallization from dichloromethane–heptane gives dark purple microcrystals. Yield: 0.65 g (82%).

Anal. Calcd. for 3,4-Mo-TTP (**3**) ($\text{C}_{62}\text{H}_{56}\text{N}_{10}\text{O}_3\text{BMo}$): C, 67.95; H, 5.15; N, 12.78. Found: C, 67.88; H, 5.64; N, 12.24. Mass spectrum: calculated molecular ion: 1097.37 amu; found (FAB, nitrobenzyl alcohol): 1098.41 amu. IR (KBr): $\nu_{\text{B-H}}$ 2545(w); $\nu_{\text{Mo=O}}$ 941(s) cm^{-1} . Electronic spectrum in toluene at 25°C (λ in nm; ε in $\text{L mol}^{-1} \text{cm}^{-1}$): 518 (19,100), 554 (12,600), 595 (5890), 653 (7590).

H. 5-{2,3-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHYRIN (2,3-Mo-TTP)

This synthesis follows the procedure described above for 3,4-Mo-TTP but utilizing the 2,3-OH-TTP porphyrin. Yield: 0.70 g (88%).

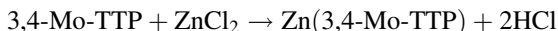
Anal. Calcd. for 2,3-Mo-TTP ($\text{C}_{62}\text{H}_{56}\text{N}_{10}\text{O}_3\text{BMo}$): C, 67.95; H, 5.15; N, 12.78. Found: C, 68.10; H, 5.33; N, 12.62. Mass spectrum: calculated molecular ion: 1097.37 amu; found (FAB, nitrobenzyl alcohol): 1096.52 amu. IR (KBr): $\nu_{\text{B-H}}$ 2547(w); $\nu_{\text{Mo=O}}$ 939(s) cm^{-1} . Electronic spectrum in toluene at 25°C (λ in nm; ε in $\text{L mol}^{-1} \text{cm}^{-1}$): 516 (18,200), 551 (9550), 594 (5370), 652 (7240).

Properties

Both 3,4-Mo-TTP and 2,3-Mo-TTP are purple in color in the solid state as well as in solution. Both compounds are moderately sensitive to acid and show a strong Mo=O and a weak B—H stretch in the IR. The electronic spectra show strong bands due to the porphyrin center that obscure weak absorptions originating from the molybdenyl fragment. Because of the long electronic relaxation time of the molybdenyl center, the ^1H NMR spectra of the molybdenyl fragment is too broad to be meaningfully interpreted.

We now discuss metalation of the porphyrin. Insertion of a metal ion into the porphyrin generates binuclear metal complexes. Metalation of a free-base porphyrin generates 2 equiv of protons per mole of porphyrin. The hydrolytic sensitivity of the molybdenum center necessitates removal of the acid from the reaction mixture as it is generated. This is achieved by bubbling argon or dinitrogen through the solution during the course of the reaction.¹⁵

I. 5-{3,4-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOZINC(II) [Zn(3,4-Mo-TTP)]



In this section we describe insertion of zinc to produce binuclear zinc–molybdenum compounds.

Procedure

The compound 3,4-Mo-TTP (0.175 g, 0.16 mmol) is dissolved in dimethylformamide (100 mL) and brought to reflux. ZnCl_2 (0.30 g, 2.2 mmol) is added to the solution with vigorous stirring. Reflux is maintained until zinc insertion is complete as evidenced by the loss of the band at 652 nm from the electronic spectrum of **3**. The reaction mixture is diluted with 200 mL of water and extracted with dichloromethane (3×50 mL) to yield a pink-purple solution. This solution is washed with 3×200 -mL portions of water to remove inorganic zinc salts and the organic solvent removed by rotary evaporation. The purple residue is dissolved in a minimum amount of dichloromethane and purified by chromatography on silica gel with dichloromethane/methanol (20 : 1) as eluant. Removal of the solvent in vacuo gives a purple solid. This solid can be recrystallized by dissolving in a minimum amount of toluene at ambient temperature and adding heptane until incipient crystallization. Yield: 0.12 g (65%).

Anal. Calcd. for Zn(3,4-Mo-TTP) (**5**) (C₆₂H₅₄N₁₀O₃BMoZn): C, 64.20; H, 4.69; N, 12.13. Found: C, 65.73; H, 5.18; N, 11.17. Mass spectrum: calculated molecular ion: 1159.29 amu; found (FAB, nitrobenzyl alcohol): 1159.43 amu. IR (KBr): $\nu_{\text{B-H}}$ 2545(w); $\nu_{\text{Mo=O}}$ 940(s) cm⁻¹. Electronic spectrum in toluene at 25°C: (λ in nm; ϵ in L mol⁻¹ cm⁻¹): 515 (4470), 552 (24,000), 592 (6920).

J. 5-{2,3-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOZINC(II) [Zn(2,3-Mo-TTP)]

The compound Zn(2,3-Mo-TTP) is synthesized from 2,3-Mo-TTP following the procedure outlined above for Zn(3,4-Mo-TTP). Yield: 0.10 g (60%).

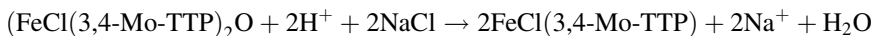
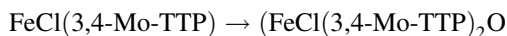
Anal. Calcd. for Zn(2,3-Mo-TTP) (**6**) (C₆₂H₅₄N₁₀O₃BMoZn): C, 64.20; H, 4.69; N, 12.13. Found: C, 65.28; H, 5.03; N, 11.28. Mass spectrum: calculated molecular ion: 1159.27 amu; found (FAB, nitrobenzyl alcohol): 1159.43 amu. IR (KBr): $\nu_{\text{B-H}}$ 2542(w); $\nu_{\text{Mo=O}}$ 940(s) cm⁻¹. Electronic spectrum in toluene at 25°C: (λ in nm; ϵ in L mol⁻¹ cm⁻¹): 513 (3020), 551 (22,900), 590 (4900).

Properties

Compounds Zn(3,4-Mo-TTP) and Zn(2,3-Mo-TTP) are purple in the solid state and readily dissolve in organic solvents such as dichloromethane, chloroform, and toluene to give pink solutions. Both compounds are photosensitive, and syntheses and manipulations should be performed in low light or with reaction vessels and columns individually wrapped to minimize exposure to ambient light. Their dimethylformamide and dichloromethane solutions are unstable on prolonged heating. The compounds should be stored in an inert atmosphere and in the dark.

Next, we discuss insertion of iron to synthesize binuclear high-spin iron(III) ($S = \frac{5}{2}$)-molybdenum compounds. Iron insertion into the porphyrin core is more complicated and requires strict exclusion of HCl from the reaction mixture and product complexes to avoid the acid hydrolysis of the catecholato ligand from the molybdenyl group. The μ -oxo dimer generated during purification is cleaved by aqueous NaCl in a biphasic reaction.

K. 5-{3,4-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOIRON(III)CHLORIDE [FeCl(3,4-Mo-TTP)]



An amount of 3,4-Mo-TTP (0.2 g, 1.82×10^{-4} mol) is dissolved in 20 mL of dichloromethane, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 1.08×10^{-3} mol) is dissolved in a 15-mL methanol/dichloromethane mixture. After the addition of the iron solution to the porphyrin solution, the mixture is refluxed until iron insertion is complete as evidenced by the electronic spectra. The solution is evaporated to dryness under vacuo and dissolved in dichloromethane (50 mL) to yield a brown solution. After washing with three 100-mL portions of water, the organic phase is purified by chromatography on a silica gel column (2.5×50 cm, 70–230 mesh) using 400 mL dichloromethane/MeOH (10 : 1) as eluant. This procedure converts the chloro iron species to a μ -oxo dimer that is greenish brown in solution. The greenish brown solution is evaporated, redissolved in dichloromethane (25 mL), and reacted with two 200-mL portions of aqueous NaCl (1 M) with vigorous stirring [addition of 3–5 drops of 6(N) HCl in each liter of NaCl solution facilitates the reaction]. The remaining dichloromethane solution is washed with water (100 mL), and the solvent is removed in vacuo. Recrystallization from dichloromethane–heptane gives dark black microcrystals. Yield: 0.14 g (65%).

Anal. Calcd. for $\text{FeCl}(\text{3,4-Mo-TTP})$ ($\text{C}_{62}\text{H}_{54}\text{N}_{10}\text{O}_3\text{BMoFeCl}$): C, 62.79; H, 4.59; N, 11.86; Cl, 2.99. Found: C, 63.97; H, 5.40; N, 11.00; Cl, 2.82. Mass spectrum: calculated molecular ion: 1186.26 amu; found (FAB, nitrobenzyl alcohol): 1150.63 amu ($\text{M}-\text{Cl}=1151.29$ amu). IR (KBr): $\nu_{\text{B-H}}$ 2545(w); $\nu_{\text{Mo=O}}$ 940(s) cm^{-1} . Electronic spectrum in toluene at 25°C: (λ in nm; ϵ in $\text{L mol}^{-1} \text{cm}^{-1}$): 509 (14,100), 571 (5500), 693 (3720).

L. 5-(2,3-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOIRON(III)CHLORIDE [$\text{FeCl}(\text{2,3-Mo-TTP})$]

This compound is synthesized by the same procedure used for $\text{FeCl}(\text{3,4-Mo-TTP})$, utilizing 2,3-Mo-TTP as the molybdenum-containing porphyrin. Recrystallization from dichloromethane–heptane gives a purple powder. Yield: (75%).

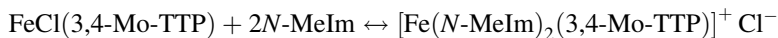
Anal. Calcd. for $\text{FeCl}(\text{2,3-Mo-TTP})$ ($\text{C}_{62}\text{H}_{54}\text{N}_{10}\text{O}_3\text{BMoFeCl}$): C, 62.79; H, 4.59; N, 11.86; Cl, 2.99. Found: C, 62.69; H, 4.78; N, 11.88; Cl, 3.06. Mass spectrum: calculated molecular ion: 1186.26 amu; found (FAB, nitrobenzyl alcohol): 1149.51 amu ($\text{M}-\text{HCl}=1150.28$ amu). IR (KBr): $\nu_{\text{B-H}}$ 2550(w); $\nu_{\text{Mo=O}}$ 943(s) cm^{-1} . Electronic spectrum in toluene at 25°C: (λ in nm; ϵ in $\text{L mol}^{-1} \text{cm}^{-1}$): 509 (15,100), 573 (4170), 690 (3630).

Properties

Compounds (FeCl(3,4-Mo-TTP) and (FeCl(2,3-Mo-TTP) are dark-colored solids that are stable in the solid state. They are soluble in most organic solvents, giving brown-colored solutions. Both compounds are acid/alkali-sensitive.

Next we discuss preparation of binuclear low-spin iron(III) ($S = \frac{1}{2}$)-molybdenum compounds. The low-spin iron(III) compounds are generated in solution by adding excess base to the corresponding high-spin complexes.¹⁶

M. 5-{3,4-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOIRON(III)BIS(*N*-METHYLIMIDAZOLE) ADDUCT {Fe(*N*-MeIm)₂[(3,4-Mo-TTP)]Cl}



Procedure

[Fe(*N*-MeIm)₂(3,4-Mo-TTP)]Cl ($\sim 1 \times 10^{-5}$ mol) is generated in solution by addition of 0.4 mL (0.41 g, $d = 1.03$) of *N*-methylimidazole (5×10^{-3} mol) to 10 mg of FeCl(3,4-Mo-TTP) (7.41×10^{-6} mol), and making the final volume of the solution to 10 mL. The solvents are either dimethylformamide/methylene chloride or methylene chloride/toluene (1 : 1). Mass spectrum: calculated molecular ion for the cation [Fe(*N*-MeIm)₂(3,4-Mo-TTP)]⁺: 1314 amu; found (ESI in dimethylformamide): 1313.75. Electronic spectrum in dimethylformamide (λ in nm; ε in L mol⁻¹ cm⁻¹): 556 (7240), 581(sh) (6610), 644(sh) (2500), [where (sh) represents a shoulder].

N. 5-{2,3-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOIRON(III)BIS(*N*-METHYLIMIDAZOLE) ADDUCT {Fe(*N*-MeIm)₂[(2,3-Mo-TTP)]Cl}

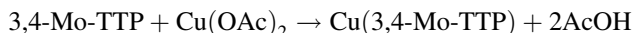
[Fe(*N*-MeIm)₂(2,3-Mo-TTP)]Cl is prepared in solution following the procedure for [Fe(*N*-MeIm)₂(3,4-Mo-TTP)]Cl. Electronic spectrum in dimethylformamide (λ in nm; ε in L mol⁻¹ cm⁻¹): 555 (7240), 579 (6170), 647(sh) (1580).

Properties

The solutions of [Fe(*N*-MeIm)₂(3,4-Mo-TTP)]Cl and [Fe(*N*-MeIm)₂(2,3-Mo-TTP)]Cl are red in color and show distinctive paramagnetically shifted pyrrole ¹H resonances centered about -17 ppm at 23°C.¹⁷ At 500 MHz [Fe(*N*-MeIm)₂(3,4-Mo-TTP)]Cl shows four peaks in the -15- to -18-ppm range,

whereas $[\text{Fe}(N\text{-MeIm})_2(2,3\text{-Mo-TTP})]\text{Cl}$ shows eight peaks in the -10 - to -24 -ppm range.

O. 5-{3,4-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOCOPPER(II) $[\text{Cu}(3,4\text{-Mo-TTP})]$



This synthesis and the procedure described in Section P involve insertion of copper to produce bimetallic copper–molybdenum compounds.

Procedure

An amount of 3,4-Mo-TTP (58 mg, 0.05 mmol) is dissolved in 20 mL of dichloromethane and the solution is degassed thoroughly with argon. This solution is brought to reflux, and a dichloromethane/methanol (3 : 1) solution (10 mL) of copper acetate (35 mg, 0.16 mmol) is added [use of copper chloride instead of copper acetate leads to demolybdated product(s)]. Refluxing is continued until the electronic spectrum indicates complete insertion of the copper (~ 30 min). After removal of the solvents under vacuum, the remaining solid mass is dissolved in dichloromethane and washed with water in order to remove excess inorganic material. The organic layer is evaporated to dryness, the solid redissolved in dichloromethane, and chromatographed on a silica gel column. The target compound is eluted as a reddish brown band with dichloromethane. The compound is isolated by the evaporation of the organic solvent and further purified by recrystallization from dichloromethane–heptane. Yield: 45 mg (80%). Mass spectrum: calculated molecular ion, 1158.3 amu; found (FAB, nitrobenzyl alcohol): 1156.7 amu. IR (KBr): $\nu_{\text{B-H}}$ 2542(w); $\nu_{\text{Mo=O}}$ 940(s). Electronic spectrum in toluene at 25°C (λ in nm; ε in $\text{L mol}^{-1} \text{cm}^{-1}$): 501 (4300), 542 (18,300), 580 (3700), 617 (2200).

P. 5-{2,3-CATECHOLATO[HYDROTRIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATO]OXOMOLYBDENUM(V)}-10,15,20-TRI-*p*-TOLYLPORPHINATOCOPPER(II) $[\text{Cu}(2,3\text{-Mo-TTP})]$

This compound is synthesized according to the procedure for $\text{Cu}(3,4\text{-Mo-TTP})$ described above but using 2,3-Mo-TTP instead of 3,4-Mo-TTP.

Mass spectrum: calculated molecular ion, 1158.3 amu; found (FAB, nitrobenzyl alcohol), 1158 amu. IR (KBr): $\nu_{\text{B-H}}$ 2540(w); $\nu_{\text{Mo=O}}$ 940(s). Electronic spectrum in toluene at 25°C (λ in nm; ε in $\text{L mol}^{-1} \text{cm}^{-1}$): 507 (2300), 540 (10,800), 575 (2200), 617 (3500).

Properties

Both Cu(3,4-Mo-TTP) and Cu(2,3-Mo-TTP) are dark brown in the solid state and dissolve in most organic solvents to give brown solutions.

Acknowledgments

We thank Mr. J. Weibrecht for experimental assistance and Dr. J. McMaster for helpful discussions. Partial support of this research by the National Institutes of Health (GM-37773) and the Materials Characterization Program of the University of Arizona is gratefully acknowledged. MV thanks the DuPont-Arizona Research Experience (DARE) program for a summer undergraduate research fellowship.

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11. The checkers isolated **1** and **2** by extracting the neutralized reaction mixture into 2 × 100 mL of dichloromethane, rather than by filtration of the purple solid. Removal of the solvent gives a purple powder that is purified by column chromatography (SiO₂, 3 : 1 dichloromethane/hexane).
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15. The checkers obtained similar yields without purging the solution with argon to remove stoichiometric amounts of HCl formed in the reaction.
16. (a) Low-spin complexes were prepared in proper concentration according to the equilibrium constant for individual complexes: P. Basu, A. M. Raitsimring, J. H. Enemark, and F. A. Walker, *Inorg. Chem.* **36**, 1088–1094 (1997); (b) F. A. Walker, V. L. Balke, and J. T. West, *J. Am. Chem. Soc.* **107**, 1226–1233 (1985). For the equation that follows Synthesis M.
17. P. Basu, N. V. Shokhirev, F. A. Walker, and J. H. Enemark, *J. Am. Chem. Soc.* **117**, 9042 (1995).

6. IRON SANDWICH POLYOXOANION COMPOUNDS

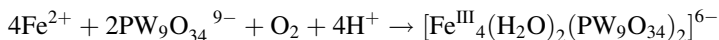
Submitted by XUAN ZHANG, DEAN C. DUNCAN,
QIN CHEN, and CRAIG L. HILL*

Checked by H. WEINER and R. FINKE†

The title complexes are the first well-characterized multiiron sandwich compounds prepared via rational synthesis from lacunary or defect species. They have possible applications as catalysts for the oxidation of organic compounds with the environmentally friendly oxidant $\text{H}_2\text{O}_2^{1-3}$ and constitute a well-defined multiiron species to facilitate the further investigation and delineation of magnetic interactions in such systems.^{4,5}

The most prevalent and studied sandwich polyoxoanions are those derived from trivacant forms of the Keggin and Wells-Dawson parent polyoxoanion structures, in which two such d^0 polyanion fragments sandwich four d electron-containing transition metal ions. The first family of formula $[(\text{M})_4(\text{PW}_9\text{O}_{34})_2]^{10-}$, initially prepared by Weakley et al.,⁶ and the second family, of formula $[(\text{M})_4(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$, first prepared by Finke et al.,⁷ are known only for some divalent first-row transition metal ions ($\text{M} = \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$), however. The literature procedure does not work well with Fe^{3+} because of the acidity of the solution. Related iron-containing sandwich compounds that have been reported include $[(\text{Fe}_2\text{Cu}_2)(\text{FeW}_9\text{O}_{34})_2\text{H}_2]^{10-8}$ and $[(\text{Zn}_x\text{Fe}_{3-x}\text{W})(\text{ZnW}_9\text{O}_{34})_2]^{(9+x)-}$ ($n = 0, 1$).⁹ The procedure reported here provides routes to both Keggin and Wells-Dawson-derived Fe_4 sandwich polyanions.

A. HEXAKISTETRABUTYLAMMONIUM OCTADECATUNGSTOTETRAIRONDIPHOSPHATE $\{(\text{TBA})_6[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]\}$



Procedure

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.48 g) is dissolved in 25 mL of H_2O in a 60-mL beaker, and 3.0 g (1.09 mmol) of $\Delta\text{-Na}_8\text{HPW}_9\text{O}_{34} \cdot 19\text{H}_2\text{O}^{10}$ is added

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slowly as a solid at room temperature with vigorous stirring. The solution is heated to 60°C for 5–10 min and filtered hot through a medium-porosity sintered-glass frit. Potassium chloride (3.6 g; 48.29 mmol) is added and an immediate dark precipitate forms. The solution is stirred as it cools to ambient temperature. The precipitate is collected on a 50-mL medium-porosity sintered-glass frit, washed with 3×25 mL (i.e., three 25-mL portions) of ethanol and dried at 40°C in vacuum for 1 h. About 3 g of this precipitate is dissolved in 100 mL of H₂O (pH ~ 7 without adjustments). Tetrabutylammonium (TBA) chloride (2.4 g; 8.64 mmol) dissolved in 90 mL of CH₂Cl₂ is added to the aqueous solution. The resulting two-layer mixture is transferred to and shaken in a separatory funnel to produce a dark-chocolate-colored upper layer and yellowish-green bottom layer. The bottom layer is removed, an additional 90 mL of CH₂Cl₂ is added, and the mixture is shaken again. A yellow precipitate forms in the upper layer while the bottom layer remains a dark greenish-brown solution. The bottom organic layer is removed, placed in a 400-mL recrystallizing dish, covered with parafilm containing several holes, and allowed to oxidize in the air overnight (the color changes from dark brown to light brown). The next day the remaining oil organic phase is washed with 150 mL of H₂O to give a greenish yellow solid. This solid is collected on a medium-porosity frit, washed with 3×25 mL of H₂O and then dried at 40°C under vacuum overnight. The powder is dissolved in a minimum amount (~1–3 mL) of CH₃CN in a 250-mL beaker to form a dark brownish-green solution. Diethyl ether (100 mL) is added and a light yellow powder precipitates. After the mixture is stirred for 2–3 h, the precipitate is collected on a 50-mL medium porosity sintered-glass frit and dried at 40°C under vacuum overnight. The yield is 0.8–1.2 g. The compound can be recrystallized by dissolving 0.05 g (8.1×10^{-3} mmol) of the crude product in a 10-mL vial containing 4 mL of a 5 : 1 v/v mixture of CH₂Cl₂ and CH₃CN, then placing this vial into a 20-mL vial containing 5 mL of diethyl ether. This two-vial assembly is then capped and placed in a freezer at –20°C for several days. For X-ray-quality crystals, the compound is recrystallized by dissolving 0.02 g (3.2×10^{-3} mmol) of the crude product in a 20-mL vial containing 10 mL of a 9 : 1 v/v mixture of CH₂Cl₂ and CH₃CN, then placing this vial in a 50-ml vial or jar containing 5 mL of diethyl ether. This two-vial assembly is then capped and placed in a freezer at –20°C for approximately one week.

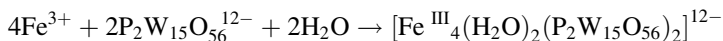
Properties

The tetrabutylammonium salt, (TBA)₆[Fe^{III}₄(H₂O)₂(PW₉O₃₄)₂], is a light yellow solid. It is soluble in acetonitrile, *N,N*-dimethylformamide, and dimethylsulfoxide. It is slightly soluble in acetone and methylene chloride. It is characterized in the solid state by its IR spectrum (2% KBr pellet, 1300–400 cm^{–1}): 1066(m), 1014(w), 970(m), 957(m), 932(m, sh), 868(s), 823(s), 769(vs), 699(s), 623(w),

589(w,sh), 520(w), 496(w,sh), and 454(w). No IR bands arising from the presence of solvent molecules are visible as the crystals lose solvent molecules of crystallization quickly on exposure to the air. The crystal data for $(\text{TBA})_6[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 4\text{CH}_3\text{CN} \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ are orthorhombic, space group *Pbca*, with $a = 25.3330(3)$ Å, $b = 24.9326(4)$ Å, $c = 28.4164(3)$ Å, $V = 17948.30$ Å³, $Z = 4$.

Anal. Calcd. for $\text{C}_{96}\text{H}_{220}\text{Fe}_4\text{N}_6\text{O}_{70}\text{P}_2\text{W}_{18}$ or $(\text{TBA})_6[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$: C, 18.68; H, 3.59; Fe, 3.62; N, 1.36; P, 1.00; W, 53.60. Found: C, 18.73; H, 3.55; Fe, 3.35; N, 1.33; P, 0.89; W, 53.24.

B. DODECASODIUM TRIACONTATUNGSTOTETRAIRON TETRA PHOSPHATE HYDRATE $\{\text{Na}_{12}[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 58\text{H}_2\text{O}\}$



Procedure

To a solution of 0.82 g (3 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 30 mL of a 1 M NaCl solution in a 60-mL beaker is added slowly with vigorous stirring 6.0 g (1.4 mmol) of solid $\alpha\text{-Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56} \cdot 18\text{H}_2\text{O}$.¹⁰ The solution is heated to 80°C for 5–10 min and filtered hot. The solution is left to stand. After several days, yellow crystalline solid precipitates (1.8 g, ~30% yield); the filtrate is discarded. X-ray-quality crystals can be obtained by recrystallizing 1 g of this yellow crystalline solid in 5 mL of a 2 M NaCl solution. The needle-shaped crystals are dichroic: yellow along the thin axis and brown along the long axis.

Properties

The sodium salt of this Wells-Dawson-derived sandwich polyoxoanion is a yellow crystalline solid that is soluble in water. It is characterized in solution by ³¹P NMR (9 mM solution in H₂O, D₂O in a capillary insert): one resonance for the distal P atoms at –11.1 ppm ($\Delta\nu_{1/2} = 70$ Hz). In the solid state the compound always contains NaCl as it must be crystallized from aqueous NaCl solution. If NaBr is substituted for NaCl in the aqueous crystallization process, crystals of the compound still form but now contain NaBr in place of NaCl. This sandwich complex is characterized in the solid state by IR (2% KBr pellet, 1300–400 cm^{–1}): 1091(s), 1017(w), 951(s,sh), 917(m), 826(s), 757(s), 695(s), 630(m,sh), 526(w). The crystal data for $\text{Na}_{12}[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 58\text{H}_2\text{O}$

are triclinic, space group $P\bar{1}$, with $a = 12.536 \text{ \AA}$, $b = 16.150 \text{ \AA}$, $c = 18.980 \text{ \AA}$, $\alpha = 87.618^\circ$, $\beta = 79.895^\circ$, $\gamma = 74.926^\circ$, $V = 3633.9 \text{ \AA}^3$, $Z = 1$.

Anal. Calcd. for $\text{H}_{120}\text{ClFe}_4\text{Na}_{13}\text{P}_4\text{O}_{172}\text{W}_{30}$ or $\text{Na}_{12}[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot \text{NaCl} \cdot 58\text{H}_2\text{O}$: Na, 3.30; Fe, 2.46; P, 1.37; W, 60.81; Cl, 0.39. Found: Na, 3.30; Fe, 2.35; P, 1.24; W, 60.93; Cl, 0.48.

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7. DIPYRRYL AND PORPHYRINIC PRECURSORS TO SUPRAMOLECULAR CONJUGATED (PORPHINATO)METAL ARRAYS: SYNTHESIS OF DIPYRRYLMETHANE AND (5,15-DIPHENYLPORPHINATO)ZINC(II)

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Checked by STEVE MALINAK and DIMITRI COUCOUVANIS

Metal-mediated cross-coupling reactions involving *meso*-haloporphyrins enable the fabrication of porphyrin arrays that exhibit exceptional electronic interactions between their constituent porphyrinic building blocks.¹⁻³ Because *meso*-haloporphyrins derive from direct halogenation of the porphyrinic aromatic macrocycle, porphyrins bearing unsubstituted *meso* positions are important synthetic precursors to these supramolecular, multichromophoric systems.

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Archetypal examples of these strongly coupled (porphinato)metal assemblies are highlighted by a *meso*-to-*meso* ethynyl or butadiynyl linkage topology between the porphyrin units of the array and feature a linear arrangement of chromophores, typified by structures **I** and **II** (Fig. 1).

Similar design elements can be incorporated into more elaborate supramolecular structures (**III** and **IV**, Fig. 1),⁴ which serve as models in which to probe ground- and excited-state electronic interactions along multiple conjugation

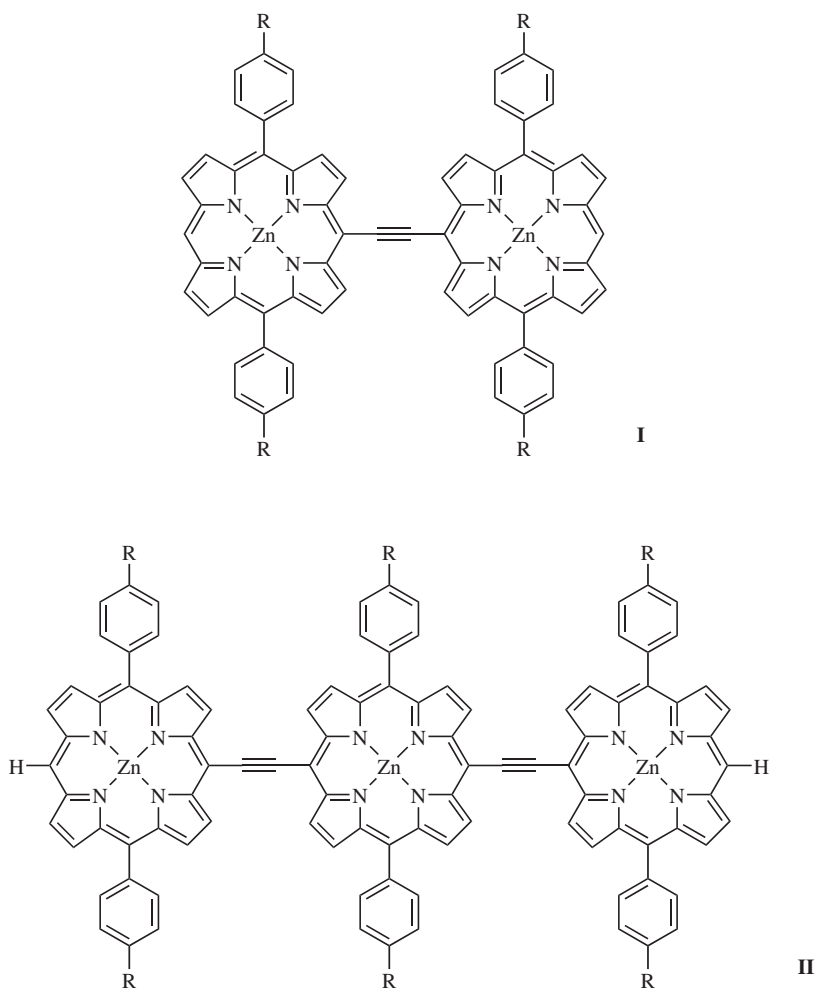
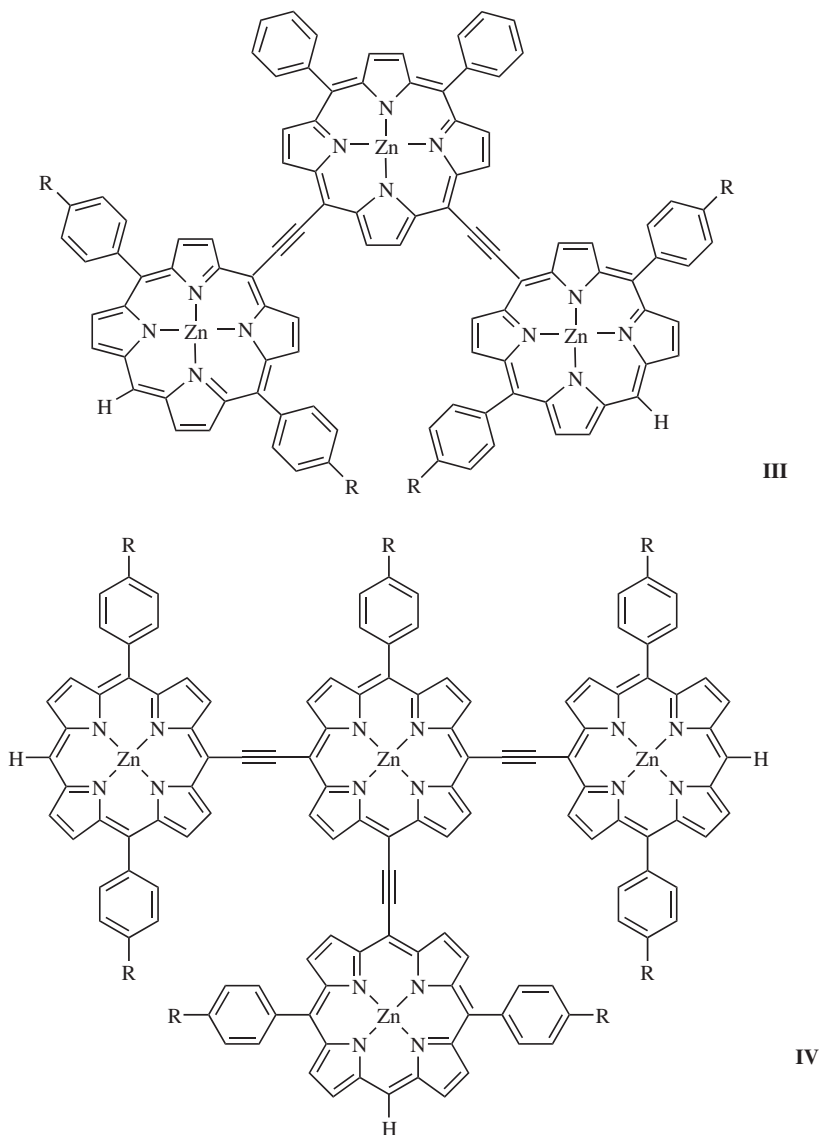
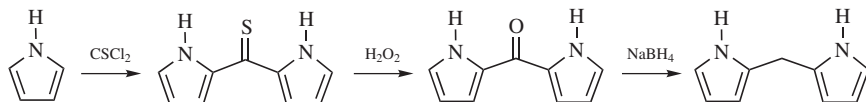


Figure 1. Highly conjugated ethyne-bridged (porphinato)zinc(II) arrays **I–IV**.

**Figure 1** (Continued)

pathways as well as important oligochromophoric precursors to higher-order structures.

While the 5-phenylporphyrin and 5,10-diphenylporphyrin components of conjugated porphyrin arrays **III** and **IV** can be prepared by a number of methods,



Scheme 1. Clezy's synthetic route to dipyrromethane.⁶

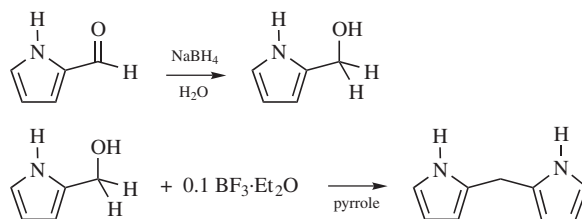
routes exploiting McDonald-type 2+2 acid-catalyzed condensations of dipyrrolyl precursors to such asymmetrically *meso*-substituted parent porphyrin complexes offer numerous advantages with respect to syntheses that rely on the direct reaction of organic aldehydes with monopyrroles, the most important of which is significantly simplified chromatographic purification of products. As such, dipyrromethane along with its α -substituted and α,α' -disubstituted derivatives, are key building blocks for these highly conjugated multiporphyrin structures.

Although a variety of synthetic methods for β -unsubstituted-*meso*-substituted, β -substituted-*meso*-substituted, and β -substituted-*meso*-unsubstituted dipyrromethanes have been reported in the past,⁵ the preparation of the parent compound dipyrromethane has generally been accomplished using a three-step synthesis developed by Clezy (Scheme 1).⁶ Drawbacks to this method include the toxicity of thiophosgene as well as the difficult isolation of the thioketone and its tendency to polymerize; such difficulties make large-scale preparations of dipyrromethane problematic. Recently, Bruce published an improved procedure for dipyrromethane synthesis involving a one-step reaction of excess pyrrole and paraformaldehyde in a mixture of methanol and acetic acid.⁷ The poor solubility of paraformaldehyde in most organic solvents coupled with the required chromatographic purification of the product, however, likewise precluded large-scale preparations of this compound.

We report herein a significantly improved and simplified preparation of dipyrromethane, which is based on Lindsey's route to *meso*-substituted dipyrrolyl porphyrin precursors,⁸ as well as the syntheses of (5,15-diphenylporphinato)-zinc(II), a key building block of conjugated porphyrin arrays **I–IV** (Fig. 1).

Experimental Procedure

Standard Schlenk techniques were employed to manipulate air-sensitive solutions. All manipulations involving air-sensitive materials were carried out under nitrogen previously passed through an O₂ scrubbing tower (Schweizerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves). All solvents utilized in this work were obtained from Fisher Scientific (HPLC Grade). Methylene chloride was distilled from calcium hydride under N₂. Chromatographic purification (Silica Gel 60, 230–400 mesh, EM Science) of products, when required, was accomplished on the bench top. Reagents were obtained from Aldrich Chemical Company.

A. 2,2'-DIPYRRYLMETHANE (C₉H₁₀N₂)*Procedure*

Pyrrole-2-carboxaldehyde (10 g, 0.1 mol) was dissolved in 300 mL of water in an Erlenmeyer flask. NaBH₄ (11 g, 0.3 mol) was dissolved in 100 mL of water and added to the pyrrole-2-carboxaldehyde solution dropwise over a 10-min period. The mixture was allowed to stir at room temperature for 1 h. The reaction solution was then extracted with diethylether (3 × 100 mL), washed with satd Na₂CO₃ (3 × 100 mL), and dried over MgSO₄ (anhydrous). The solvent was evaporated to yield 9 g of 2-(hydroxymethyl)pyrrole, isolated as a colorless oil (90% yield based on 10 g of the pyrrole-2-carboxaldehyde starting material).

The 2-(hydroxymethyl)pyrrole was added to a Schlenk flask containing 70 mL of pyrrole which served as the solvent for the reaction. The solution was immediately purged with N₂ for 5 min, following which BF₃·Et₂O (1.23 mL) was slowly added via syringe. The color of the solution changed from light yellow to dark brown over a period of 2 h. Stirring at room temperature under N₂ was continued for 12 h; the reaction mixture was then diluted with 200 mL of CH₂Cl₂, thrice washed with 100-mL of 0.1 N NaOH(aq), and neutralized with saturated aqueous Na₂CO₃. The organic layer was isolated, dried over MgSO₄, and evaporated to give a dark brown oil which contained both the dipyrrolylmethane product and unreacted pyrrole. The pyrrole was removed by vacuum transfer (10 μm Hg, 50°C) to give an oily mixture which was placed under high vacuum for an additional 3 h to completely remove any remaining pyrrole. Hexane (600 mL) was added and the solution was refluxed for 15 min prior to carrying out a hot filtration on the bench top. The filtrate was evaporated to give a light yellow pale solid product. The hexane extraction procedure was repeated 3 times, giving a total 7.5 g of pure dipyrrolylmethane [56% yield based on 9 g of the 2-(hydroxymethyl)pyrrole starting material]. The dipyrrolylmethane is stored at -40°C under inert conditions. The compound, under these conditions, is stable in excess of 6 months. ¹H NMR (250 MHz, CDCl₃): δ 7.89 ppm (bs, 2H, NH), 6.65 (q, 2H, β-H), 6.13 (q, 2H, β-H), 6.02 (q, 2H, β-H), 3.97 (s, 2H, meso-H). All other characterization data was consistent with that previously reported.^{6,7}

B. 5,15-DIPHENYLPORPHYRIN^{9,10}*Procedure*

A flame-dried 1000-mL flask equipped with a magnetic stirring bar was charged with 2,2'-dipyrrylmethane (458 mg, 3.1 mmol), benzaldehyde (315 μ L, 3.1 mmol), and 600 mL of freshly distilled methylene chloride. The solution was degassed with a stream of dry nitrogen for 10 min. Trifluoroacetic acid (150 μ L, 1.95 mmol) was added via syringe, the flask was shielded from light with aluminum foil, and the solution was stirred for 3 h at room temperature. The reaction was quenched by the addition of 900 mg (3.96 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), and the solution was stirred for an additional 30 min. Pyridine (3 mL) was then added, which serves two purposes: (i) it neutralizes excess acid and 1,4-dihydroxy-2,3-dichloro-5,6-dicyanobenzene, and (ii) it reacts with excess DDQ to form an insoluble precipitate which can be filtered from the solution prior to chromatographic work up. After reducing the volume of the filtrate, it was poured directly on top of a silica gel column (20 $\times$ 2 cm) packed in CH_2Cl_2 . The product was eluted in 700 mL of CH_2Cl_2 . The solvent was evaporated leaving purple crystals that were washed once with hexane, filtered, and dried. This compound (518 mg, 1.12 mmol, 72.2%) was sufficiently pure for further reactions.

C. (5,15-DIPHENYLPORPHINATO)ZINC(II)*Procedure*

A 500-mL round-bottom flask was charged with 5,15-diphenylporphyrin (518 mg, 1.12 mmol), zinc acetate (1 g, 5.5 mmol), and 300 mL of a 9:1 CHCl_3 :THF solution and refluxed. The porphyrin metalation reaction was monitored by optical spectroscopy and was completed within 2 h. The solution was washed with water (3 $\times$), dried over calcium chloride, and filtered. Evaporation of the solvent gave 562 mg of 5,15-(diphenylporphinato)zinc(II) (95% yield, based on 518 mg of the porphyrin starting material). No further purification was necessary.

Anal. ^1H NMR (500 MHz, CDCl_3): δ 10.17 ppm (s, 2H, *meso*-H), δ 9.32 (d, 4H, J = 4.4 Hz, β -H), δ 9.04 (d, 4H, J = 4.4 Hz, β -H), δ 8.22 (m, 4H, *o*-phenyl), 7.72 (m, 6H, *m,p*-phenyl). ^{13}C NMR (500 MHz, CDCl_3): 105.61 ppm, 119.35, 126.30, 127.04, 131.33, 132.02, 134.74, 143.29, 149.32, 149.90. HRMS: Calcd. 524.0979; Found: 524.0973 [MH^+].

References and Notes

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8. SYNTHESIS OF DODECAOXOHEXADECACARBOXY-LATOTETRAAQUO-DODECAMANGANESE [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] (R = Me, Et, Ph, Cr) COMPLEXES

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Great interest and excitement have developed since the late 1980s among members of the chemistry and physics communities about complexes with the formula [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄].^{1–7} In these dodecanuclear complexes, a central Mn₄^{IV} cubane moiety is surrounded by a nonplanar ring of alternating Mn^{III} and oxide ions (Fig. 1). These complexes have shown unusual bulklike magnetic

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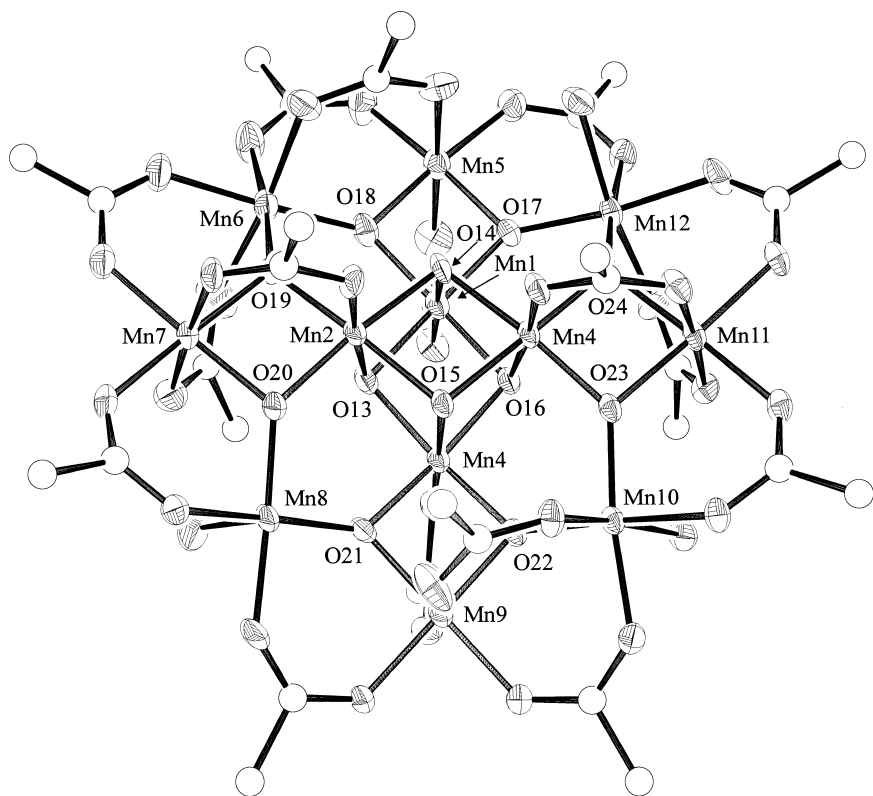


Figure 1. The structure of the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]$ family of complexes.

properties and have been a source of novel discoveries at the interface of the quantum and classical regimes. The Mn_{12} complexes are well-characterized, single-molecule models for superparamagnets and have exhibited abnormally slow magnetic relaxation for a molecular species, resulting in hysteresis of magnetization and out-of-phase components in the AC magnetic susceptibility.^{1,2,7} Rather than resulting from a magnetic phase transition, these unusual magnetic properties result from a large ground-state spin value of $S = 9$ or 10 and a high degree of molecular anisotropy in the complexes, the latter due to near-parallel alignment of the Jahn–Teller elongation axes of the eight Mn^{III} ions. In addition to these fascinating properties, the Mn_{12} molecules can also serve as models for the investigation of quantum tunneling of magnetization, which is of particular interest to physicists.^{4,5} These complexes, despite their structural complexity, are nevertheless quite easy to synthesize.^{1,6,7} Syntheses of four examples of the dodecanuclear complexes are given herein.

Procedure

All reagents were used as purchased. All reactions were carried out under ambient atmospheric conditions. The procedure is a slightly modified version of the original synthesis reported by T. Lis.⁶

A. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{HO}_2\text{CMe}$

Distilled water (16 mL) and glacial acetic acid (24 mL) are mixed in a 125-mL Erlenmeyer flask at room temperature (20°C). To this solution 4.04 g (16.5 mmol) $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ is added with vigorous stirring using a very large stir bar (5 cm). When the $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ has dissolved, 1.00 g (6.33 mmol) of finely crushed KMnO_4 solid is added all at once with continued vigorous stirring. A gradual color change occurs from light pink to red-brown, and finally to a very dark brown. The solution is stirred vigorously until all the KMnO_4 has dissolved. It is quite difficult to observe whether complete dissolution has occurred because the solution is so dark, and accurate evaluation of the reaction's progress requires inspection of the bottom of the flask with a flashlight. The reaction should not stir longer than 20 min; longer reaction times produce a powder that has nearly the same IR spectrum as the desired product but is insoluble. The stirring is halted when the KMnO_4 has all reacted, and the solution is allowed to stand at room temperature for 24–72 h. Black rectangular crystals are collected by filtration through a Büchner funnel with a coarse fritted glass disk, and excess powder and reaction solution is washed away with copious amounts of acetone (100 mL). Yield is 3.12 g (~80% based on Mn).

Anal. Calcd. for $\text{C}_{36}\text{H}_{72}\text{O}_{56}\text{Mn}_{12}$: C, 21.0; H, 3.5; Mn 32.0. Found: C, 21.3; H, 3.2; Mn, 31.2

Properties

Solubility: $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{HO}_2\text{CMe}$ is soluble in CH_3CN . Although the bulk material is analytically pure, a small amount of material will remain insoluble. The proportion of this insoluble form increases with an increased rate of crystallization of **A**, and appears to be a different solvate form. The complex is stable indefinitely in air and atmospheric moisture but decomposes into amorphous manganese oxides when exposed to a large amount of H_2O . The lattice MeCO_2H cannot be easily removed by drying in vacuo, but it can be removed by recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. Selected IR peaks (KBr, cm^{-1}): 3650(w), 3300(w,b), 1709(w). 1586(s), 1561(s), 1527(s), 1450(s), 1389(s), 1334(m), 1258(s), 1049(w), 1026(w), 959(w), 935(w), 714(m), 673(m), 640(m), 611(m), 563(m), 553(m), 518(w). ^1H NMR in CD_3CN (ppm):

48.2, 41.8, 13.9 (plus a peak due to an average of coordinated and free H₂O, which varies significantly in broadness and shift depending on sample concentration). All peaks are very broad because of the presence of unpaired electrons in the complex.

B. [Mn₁₂O₁₂(O₂C*Et*)₁₆(H₂O)₃](H₂O)

Procedure

The synthesis is an optimized version of the published synthesis of B.⁷ To a slurry containing 1.00 g (0.49 mmol) [Mn₁₂O₁₂(O₂C*Me*)₁₆(H₂O)₄]·4H₂O·2HO₂C*Me* (A) and 50 mL of toluene in a 250-mL round-bottomed flask is added 3 mL (40 mmol) of EtCO₂H. The slurry is concentrated using a rotary evaporator at reduced pressure (water aspiration) with gentle warming (40°C) to remove acetic acid as the toluene azeotrope. The synthesis may also be performed successfully using a vacuum pump to remove the solvent. The slurry of Mn₁₂ dissolves as ligand substitution occurs, forming a dark brown solution. When the solution has been concentrated to only a few milliliters (2–4 mL), 50 mL of toluene is added, and removed at reduced pressure as stated previously, and then another 50 mL of toluene is added to the flask and the solution is filtered to remove insoluble material (~0.2 g). Another 3 mL of HO₂C*Et* is added to the dark brown oil. Toluene (15 mL) is added to the oil and the solution filtered. To the dark brown filtrate 400 mL of hexanes is added with mixing and the solution allowed to stand overnight, whereupon small black crystals form. The solution is filtered to isolate the crystals, which are then washed with three 30-mL portions of hexane. The product is dried in vacuo, giving 850 mg of compound (~84% based on Mn).

Anal. Calcd. for C₄₈H₈₈O₄₈Mn₁₂: C, 27.63; H, 4.27; Mn, 30.52. Found: C, 27.90; H, 4.27; Mn, 31.51.

Properties

Solubility: [Mn₁₂O₁₂(O₂C*Et*)₁₆(H₂O)₃](H₂O) is soluble in a variety of organic solvents, including toluene, diethyl ether, dichloromethane, acetonitrile, benzonitrile, dichloroethane, and others, making it well suited for solution-state characterization. The product can be recrystallized from CH₂Cl₂/hexanes to give well-formed crystals containing no lattice H₂O. Selected IR bands (KBr, cm⁻¹): 3370(m,b), 1586(s), 1575(s), 1466(s), 1432(vs), 1379(s), 812(m), 719(m), 650(s,b), 559(m,b). Conductivity (25°C): 4.1 and 0.3 S cm² mol⁻¹ in CH₃CN and CH₂Cl₂, respectively. ¹H NMR in CD₃CN (ppm): 52.7, 47.3, 46.7, 12.2, 11.1, 3.7, -4.9 (plus a peak due to an average of coordinated and free H₂O, which varies significantly in broadness and shift depending on sample concentration).

All peaks are broadened because of the presence of unpaired electrons in the complex.

C. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$

Procedure

This procedure is based on a published preparation.¹ To a slurry of crystalline $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ from **A** (3.00 g, 1.5 mmol) in CH_2Cl_2 (90 mL) is added 6.00 g (48 mmol) of HO_2CPh , and the reaction is stirred for 24 h. As the slurry is stirred and ligand substitution progresses, the insoluble starting material dissolves. After 24 h, the solution is filtered by gravity through filter paper to remove the unreacted starting material. To the filtrate 2 : 1 Et_2O /hexanes (v/v) is added to precipitate the crude product, which is collected by filtration and washed with two 15-mL portions of hexane. In our syntheses, this requires 400 mL of solvent and results in precipitation of the product within 30 min. However, more solvent may be required to precipitate the product depending on the exact volume of dichloromethane remaining at this stage. The crude product is redissolved in 100 mL of CH_2Cl_2 containing an additional 6.00 g of benzoic acid and the solution is stirred overnight. The solution is filtered and then 400 mL (or more) 2 : 1 Et_2O /hexanes is added carefully, until a slight cloudiness in the solution indicates saturation. The solution is then allowed to stand overnight, during which time the product precipitates from solution. The brown-black microcrystals are filtered, washed with two 40-mL portions of 2 : 1 Et_2O /hexanes, and dried in vacuo. The yield is 2.63 g (~57% based on Mn).

Anal. Calcd. for $\text{C}_{112}\text{H}_{88}\text{O}_{48}\text{Mn}_{12}$: C, 47.0; H, 3.1; Mn, 21.5. Found; C, 46.5; H, 3.4; Mn, 21.2.

Properties

Solubility: $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4$ is soluble in dichloromethane and similar solvents, but relatively insoluble in CH_3CN . Selected IR peaks (KBr, cm^{-1}): 1599(m), 1561(m), 1525(m), 1493(m), 1448(m), 1418(s), 1350(m), 1308(w), 1179(w), 1159(w), 1140(w), 1070(w), 1026(w), 718(m), 677(m), 652(m), 615(m), 550(w), 513(m).

D. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}=\text{CHCH}_3)_{16}(\text{H}_2\text{O})_3]$

Procedure

To a slurry containing 1.00 g of **A** (0.49 mmol) in 50 mL of toluene in a 250-mL round-bottomed flask is added 1.00 g (11.6 mmol) of crotonic acid. The solution

is concentrated using rotary evaporation at reduced pressure (water aspiration) with gentle warming ($\sim 40^\circ\text{C}$). The solid slowly dissolves as ligand substitution occurs, giving a dark brown solution. This solution is evaporated to an oil, and then another 50 mL of toluene is added. The solvent removal process is repeated twice more with additional 50-mL aliquots of toluene. To the final oil, 15 mL of toluene is added and the dark brown solution is filtered to remove any insoluble material. To the filtrate, 125 mL of hexane is added to precipitate the product as a dark brown solid. This is collected by filtration and washed with five 15-mL hexane aliquots. The yield of the product is 780 mg ($\sim 70\%$).

Anal. Calcd. for $\text{C}_{64}\text{H}_{86}\text{O}_{47}\text{Mn}_{12}$: C, 33.9; H, 3.8. Found: C, 34.1; H, 4.1.

Properties

Solubility: $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}=\text{CHCH}_3)_{16}(\text{H}_2\text{O})_3$ is soluble in a variety of organic solvents, including CH_2Cl_2 , CH_3CN , toluene, Et_2O , and benzonitrile. Excess ligand can be easily separated from the product by washing with hexanes (crotonic acid is quite soluble in hexanes). Selected IR bands (KBr, cm^{-1}): 3044(w), 2967(w), 2938(w), 2913(w), 2851(w), 1657(s), 1568(s), 1495(s), 1425(vs), 1354(s), 1296(m), 1256(m), 1233(m), 1103(w), 1020(w), 966(m), 916(w), 849(w), 731(w), 702(m), 654(m), 612(m), 552(w), 517(w). ^1H NMR in CD_3CN (ppm): 51.8, 27.8, 23.8, 14.2, 6.6, 4.9, 3.1, -5.6 , -12.5 (plus a peak due to an average of coordinated and free H_2O , which varies significantly in broadness and chemical shift depending on sample concentration). All peaks are broad because of the unpaired electrons in the complex.

All the reactions (**A–D**) may be scaled up, but the yields are somewhat reduced. If reactions **B–D** do not yield completely substituted product (as evidenced by the presence of peaks from **A** in the ^1H NMR spectrum), the ligand substitution process can be repeated until the product is pure. All products are stable in air for extended periods of time.

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**9. USE OF PICOLINEHYDROXIMATE COMPLEXES IN
PREPARATION OF URANYL AND LANTHANIDE
15-METALLACROWN-5: $\text{UO}_2(\text{NO}_3)_2[\text{15-MCCu(II)N(PIC)-15}]$
AND $\{\text{Eu}(\text{NO}_3)_3[\text{15-MCCu(II)N(PIC)-15}]\}_3\text{NO}_3$**

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Checked by MINSHENG HUANG and D. COUCOUVANIS*

Metallacrowns are a new class of molecular recognition agents that selectively bind cations and/or anions in structures that are similar to organic crown ethers.¹⁻¹⁵ Metallacrowns in the 9-MC-3, 12-MC-4, and 15-MC-5 structure motifs were prepared using variants of the ligand salicylhydroxamic acid. This and related ligands form five- and six-membered chelate rings to the ring metals of the metallacrown. While nonplanar 15-metallacrown-5⁸ structure types were prepared with these ligands, planar structures that would form a pentagonal coordination environment around the captured metal could not be realized by this approach.

The strategy we used to prepare planar 15-MC-5 chelating agents required the use of a ligand such as picoline hydroximate (H_2picHA), which forms two 5 membered chelate rings. Five of these ligands can be accommodated into a planar structure to achieve the desired structure. In these new metallacrowns, metals with higher preferred coordination geometries can be sequestered. Herein we provide syntheses for uranyl⁻¹³ and lanthanide⁻¹⁰ encapsulated 15-MC-5 (Fig. 1).

Materials and General Procedures

Planar 15-metallacrown-5 molecules can be synthesized in a one-step reaction, by the self-assembly of a simple ligand and metal salts. The ligand that is used is picoline hydroxamic acid, H_2PicHA . This ligand was easily prepared by the reaction of hydroxylamine hydrochloride with ethyl picolinate in ethanol using a well-documented procedure for the preparation of hydroxamic acids from esters.^{16,17} Reagents used are ethyl picolinate, copper(II) acetate, uranyl(II) nitrate, hydroxyl amine hydrochloride, and potassium hydroxide, which were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent-grade.

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A. $\text{UO}_2(\text{NO}_3)_2[15\text{-MC}_{\text{Cu(II)N(pic)}-15]$ *Procedure*

The metallacrown complex $\text{UO}_2(\text{NO}_3)_2[15\text{-MC}_{\text{Cu(II)N(picHA)}-15]$ is synthesized by dissolving $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.40 g, 2 mmol) in 50 mL of DMF in a 500-mL Erlenmeyer flask. To this solution is added H_2picHA (0.28g, 2 mmol) dissolved

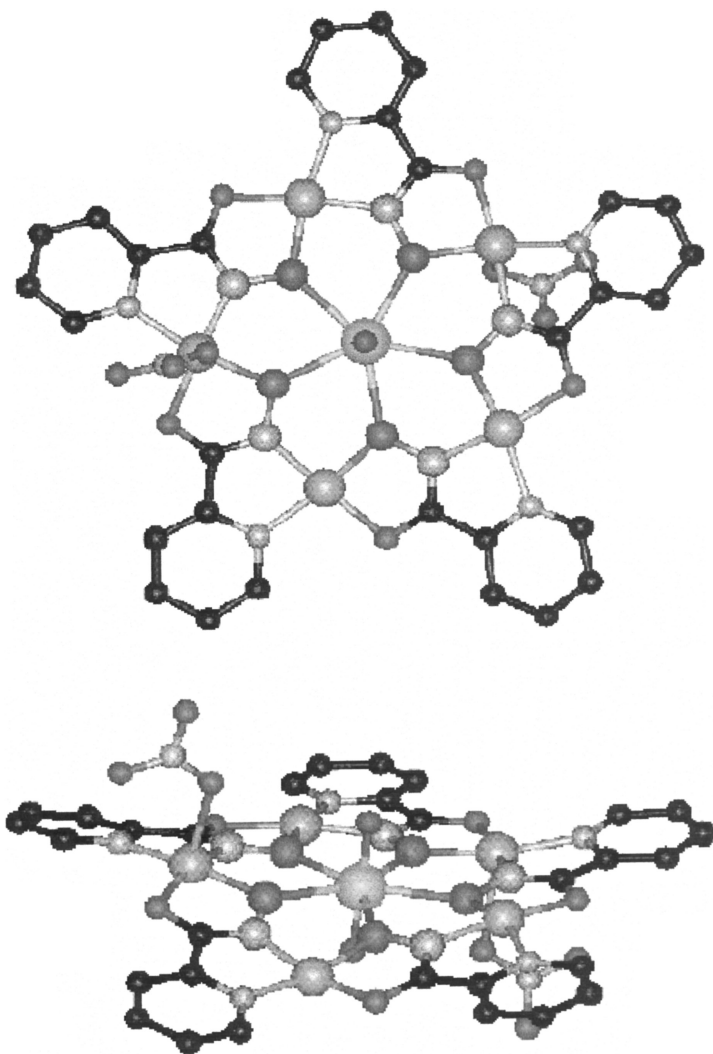


Figure 1. The structure of the $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4$ family of complexes.

in 50 mL of DMF. The solution is allowed to stir for 1 hour, at which point solid $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.20 g, 2/5 mmol) is added and the solution is stirred for several hours. Vapor diffusion of ether into the DMF solution resulted in a 69% yield of dark green, rhombic crystals.

Characterization: elemental analysis calculated for $\text{Cu}_5\text{C}_{33}\text{H}_{29}\text{N}_{13}\text{O}_{20}\text{U}$: Cu, 21.1; C, 26.92; H, 2.31; N, 11.89. Found: Cu, 21.4; C, 26.72; H, 1.97; N, 12.27. ESI+MS in methanol gave a molecular ion of 1330 *m/e* and 634 *m/e*. The ^1H NMR spectrum had four resonances at 108, 41.87, 40.97, and 13.21 ppm in d^4 methanol. An infrared spectrum (KBr) exhibits the characteristic $\text{O}=\text{U}=\text{O}$ stretch at 920 cm^{-1} .

B. $\{\text{Eu}(\text{NO}_3)_2[\text{15-MC}_{\text{Cu(II)N(picHA)}-15}]\}\text{NO}_3$

Procedure

The metallacrown complex $\{\text{Eu}(\text{NO}_3)_2[\text{15-MC}_{\text{Cu(II)N(pic)}-15}]\}\text{NO}_3$ is synthesized by dissolving $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.40 g, 2 mmol) in 50 mL of DMF in a 500 mL Erlenmeyer flask. To this solution is added H_2picHA (0.28g, 2 mmol) dissolved in 50 mL of DMF. The solution is allowed to stir for one hour, at which point solid $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.18 g, 0.4 mmol) is added, and the solution is stirred for several hours. Slow evaporation of the solvent results in a 79% yield of dark green, rhombic crystals. (The checkers found it necessary to reduce the volume of the solution to a third of the original volume before crystals formed.) These crystals, obtained in 71% yield, were washed with ether, were dried, and gave satisfactory elemental analysis.

Characterization: Elemental analysis calculated for $\text{Cu}_5\text{C}_{45}\text{H}_{55}\text{N}_{18}\text{O}_{24}\text{Eu}$: Cu, 18.68; C, 33.175; H, 3.23; N, 14.82. Found: Cu, 19.6; C, 31.81; H, 3.25; N, 14.51. FAB+MS in methanol gave a molecular ion of $[\text{M}]^+ 1273\text{ m/e}$ and $[\text{M}]^{2+} 606\text{ m/e}$. The UV-vis spectrum in methanol has a maximum at 580 nm ($\epsilon = 340\text{ cm}^{-1}\text{ M}^{-1}$). The ^1H NMR spectrum had four resonances at 90.75, 37.14, 36.88, and 12.28 ppm in d^4 methanol. Magnetic moment at 300 K is 5.34 BM. The molecule is soluble and stable in lower alcohols and water. The compound will decompose in moderately ($\text{pH} < 6$) acidic solutions.

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**10. USE OF SALICYL- AND NAPHTHOYLHYDROXIMATE
COMPLEXES IN PREPARATION OF MANGANESE AND
COPPER 12-METALLACROWN-4 COMPLEXES:
Mn(II)(ACETATE)₂[Mn(III)(SALICYLHYDROXIMATE)]₄
AND (TETRAMETHYLAMMONIUM)₂[Cu(II)5
(NAPHTHOYLHYDROXIMATE)₄]**

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Checked by MINSHENG HUANG, D. COUCOUVANIS,* WYNDHAM
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The “metallacrown analogy” is a powerful synthetic methodology for the design and preparation of moderate-valence multinuclear complexes from hydroxamic acid and oxime ligands in straightforward high-yield syntheses.^{1,2}

Using the salicylhydroxamic acid ligand, complexes with V(V),^{3,4} Mn(III),^{5–8} Fe(III),⁹ Ni(II),¹⁰ Cu(II)¹¹ and Ga(III)¹² in the ring positions and encapsulated Li(I), Na(I), K(I), Mn(II), Mg(II), Fe(III), Ni(II), Cu(II), and lanthanides¹³ ions have been prepared in a variety of structural motifs, 9-MC-3,^{3,4,9} 12-MC-4 (Fig. 1), 15-MC-5,⁸ and metallacryptates.¹² Added complex stability can be obtained by anions such as acetate, sulfate, or chloride, which serve to bridge

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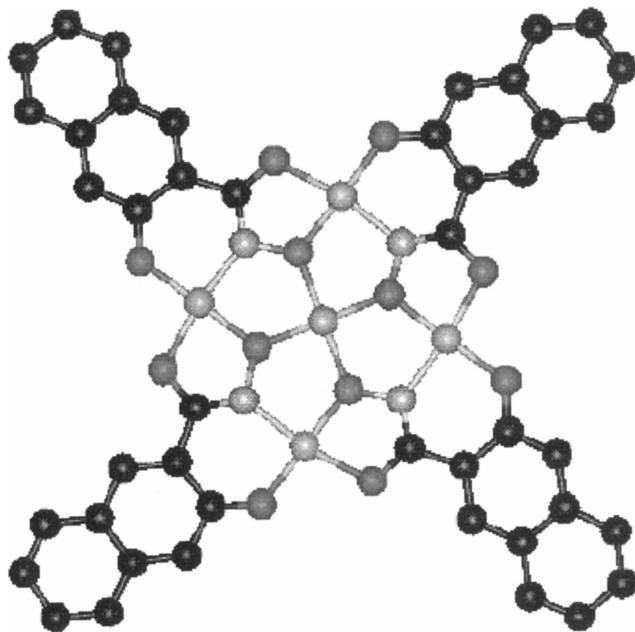


Figure 1. Molecular structure of the dianion, $\text{Cu(II)[12-MC}_{\text{Cu(II)N(nha)}}^{-4}$].

between the encapsulated and ring metals, resulting in metal salt selectivity rather than simple metal selectivity. Predictable metallacrown syntheses provide a plethora of coordination complexes by controlled variation in the metallacrown ring metal, encapsulated metal, ring size, bridging anion, and ligand architecture. This also leads to controllable methods for incorporating chirality into macrocycles.^{13–15}

A. PREPARATION OF FREE-BASE HYDROXYLAMINE: KOH SOLUTION

Materials and General Procedures

Hydroxylamine hydrochloride (34.8 g, 500 mmol) is dissolved with rapid stirring in 185 mL of hot methanol. Potassium hydroxide (42.0 g, 750 mmol) is dissolved in 115 mL of room-temperature methanol. After cooling both solutions to ambient temperature the potassium hydroxide solution is added with stirring to the hydroxylamine hydrochloride (an exothermic process!). The resulting solution and precipitated potassium chloride are cooled to -20°C in a methanol ice bath before vacuum filtration. The clear colorless supernatant hydroxylamine: KOH solution is immediately used in the preparation of the hydroxamic acid ligands.

B. 3-HYDROXY-2-NAPHTHOHYDROXAMIC ACID (H₃NHA)*Materials and General Procedures*

An amount of 3-hydroxy-2-naphthoic acid (18.8 g, 100 mmol) is refluxed in 500 mL of absolute ethanol with 5 mL concentrated sulfuric acid for 18 h. Periodic water removal is achieved via a Dean–Stark trap (8 × 15 mL). The resulting solution is cooled to room temperature and solvent is removed by flash evaporation. Ethyl-3-hydroxy-2-naphthoate crystallizes during this process. Recrystallization from methanol gives 14.0 g (64.8% yield) of ethyl 3-hydroxy-2-naphthoate. If crystals are not obtained by this procedure, one can purify the material by adding 300 mL of an aqueous Na₂CO₃ (pH 9–10) solution to the green-brown oil. The resulting aqueous solution is washed 4 times with 200 mL of diethyl ether. The diethylether is removed under reduced pressure to reveal an orange solid. This solid can be crystallized from hot methanol solutions, on cooling, to afford a tan, crystalline solid (13.6 g, 63 mmol, 63% yield). Free-base hydroxylamine:KOH solution (138 mL, 230 mmoles) is added to a 300-mL methanol solution of 3-hydroxy-2-naphthoate (24.5g, 115 mmol) and stirred for 5 h. The golden potassium salt of 3-hydroxy-2-naphthohydroxamic acid precipitates on standing in a fume hood. This salt is collected by gravity filtration, allowed to dry, and dissolved in warm 1.25 M acetic acid in methanol to crystallize. Yield: 18.7 g of H₃nha (46% yield based on ester). A higher yield of product (6.84 g, 80.6%) is achieved starting with 7.13 g of 3-hydroxy-2-naphthoate (33 mmol).²

Properties

¹H-NMR (CD₃OD, 300 MHz) δ 7.12 (s, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H). Mass spectroscopic molecular weight calculated for C₁₁H₉N₁O₃: 203.0582, observed 203.0580 *m/e*.

**C. (TETRAETHYLAMMONIUM)₂[Cu(II)₅
(NAPHTHOYLHYDROXIMATE)₄]DIMETHYLFORMAMIDE
{(Et₄N)₂[Cu(II)12-MC_{Cu(II)N(nha)}-4]}·DMF}**



An amount of Cu(OAc)₂·H₂O (1.25 g, 6.25 mmol) and tetraethylammonium acetate·4H₂O (2.60 g, 10 mmol) are dissolved in 50 mL of DMF. A 50-mL solution of DMF containing H₃nha (1.01 g, 5 mmol) is added. The solution immediately turns deep green on addition of the H₃nha and is allowed to stir for 2 h prior

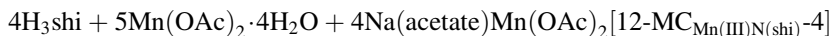
to gravity filtration. Vapor diffusion of diethyl ether to the filtrate affords 1.320 g (77%) of forest green crystalline rods. A second recrystallization gives the final product in 74.2% yield.

Properties

(Tetraethylammonium) $_2$ [Cu(II)12-MC_{Cu(II)N(nha)}-4] shows an electronic absorption at $\lambda_{\max}$ 616 nm ($\epsilon = 237 \text{ M}^{-1} \text{ cm}^{-1}$).

Anal. Calcd for Cu₅C₆₀H₆₄N₆O₁₂: Cu, 23.0; C, 52.2; H, 4.7; N, 6.1. Found: Cu, 22.4; C, 51.6; H, 5.1; N, 6.1. FAB-MS(–) molecular ion 1118 *m/z* (88% of base).

D. Mn(II)(ACETATE) $_2$ [Mn(III)(SALICYLHYDROXIMATE)] $_4$ {Mn(OAc) $_2$ [12-MC_{Mn(III)N(shi)}-4]}



A 50-mL solution of *N,N*-dimethylformamide containing Mn(OAc) $_2 \cdot 4\text{H}_2\text{O}$ (1.53 g, 6.25 mmol) is added to a 50-mL solution of DMF containing salicylhydroxamic acid, H₃shi, (0.77 g, 5.0 mmol, Aldrich) and sodium acetate (0.41 g, 5.0 mmol). The solution immediately turns olive green and is gravity-filtered following 3 h of continuous stirring. Within a day, slow evaporation of solvent lead to 1.11 g (81% yield) of dark green crystals that were collected by gravity filtration. (The checkers reduced the volume of the solution to a third of its original volume to obtain the green crystalline product in 84% yield.)

Properties

Elemental analysis calculated for the metallacrown with six bound and one lattice DMF, Mn₅C₅₆H₇₈N₁₂O₂₄: Mn, 17.4; C, 42.6; H, 4.9; N, 10.6. Found: Mn, 17.8; C, 42.2; H, 4.5; N, 10.2. The ESI-MS(+) molecular ion is observed because of loss of one of the two bridging acetate ions, (M-OAc)⁺: 934 *m/e* (base).

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