axial positions are occupied by two molecules of pyridine, while the three aryloxo groups lie in the equatorial plain. All of the bond angles and distances are normal, and no significant V–C contact has been detected within 3.6 Å. The magnetic moment $\mu_{\text{eff}} = 2.71\ \mu_B$ is in agreement with a V(III) d^2 high-spin configuration. A study on the reactivity of vanadium aryloxides is currently in progress.

Acknowledgment. This work has been supported by the University of Groningen Chemistry Department and by a NATO travel grant (0402/87). We are indebted to the generosity of the Chemistry Department, Columbia University.

Supplementary Material Available: Stereoview of complex **3** and tables of crystal data, anisotropic thermal parameters, positional parameters, bond distances, bond angles, torsional angles, and rms thermal vibration amplitudes for complex **3** and crystal data, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom parameters for complex **4** (25 pages); listings of calculated and observed structure factors for complexes **3** and **4** (42 pages). Ordering information is given on any current masthead page.

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(17) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Coordination Complexes of Polyoxomolybdate Anions. Characterization of a Tetranuclear Core from Reactions in Methanol: Syntheses and Structures of Two Polyoxomolybdate Alcoholates, $(\text{MePPh}_3)_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]$ and $(n\text{-Bu}_4\text{N})_2[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_2(\text{OC}_6\text{H}_4\text{O})_2]$, and Their Relationship to a General Class of Tetranuclear Cluster Types $[\text{Mo}_4\text{O}_x(\text{OMe})_2(\text{L})_y(\text{LL})_z]^{2-}$

Sir:

Organic derivatives of isopolymolybdate anions are of fundamental chemical interest as models for the interactions of substrates with metal oxide surfaces and in the photooxidation of organic compounds.[1,2] In recent years a variety of oxygen-[3-7] or nitrogen-containing[8-13] organic derivatives of polyoxomolybdate anions have been synthesized and structurally characterized. In the specific case of the selective oxidation of methanol to formaldehyde over molybdate catalysts, the molybdenum oxy–methoxide complex $[\text{Mo}_2\text{O}_5(\text{OCH}_3)_2]$[6] and the methoxy–isopolymolybdate complex $\text{Na}_4[\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4]\cdot 8\text{CH}_3\text{OH}$[5] provide adequate chemical models and structural information relevant to surface coordination geometry.[7] Furthermore, isopolymolybdate

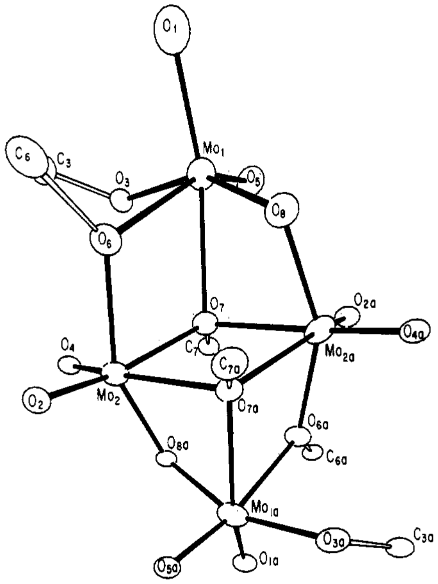

Figure 1. ORTEP view of the structure of $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]^{2-}$, showing the atom-labeling scheme. Selected bond lengths (Å): Mo1–O1, 1.708 (2); Mo1–O3, 1.919 (3); Mo1–O5, 1.708 (2); Mo1–O6, 2.248 (2); Mo1–O7, 2.261 (2); Mo1–O8, 1.976 (2); Mo2–O2, 1.701 (3); Mo2–O4, 1.702 (2); Mo2–O6, 2.033 (2); Mo2–O7, 2.286 (2); Mo2–O7a, 2.415 (2); Mo2–O8, 1.870 (2).

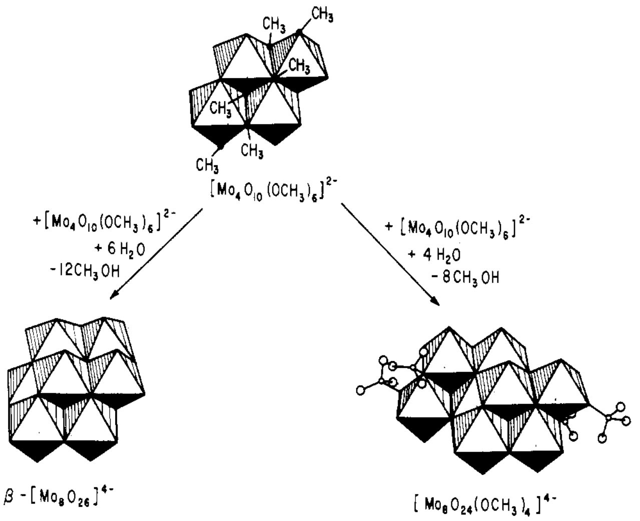

Figure 2. Idealized polyhedron representation of the structure of $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]^{2-}$ and of the formal relationship to the structures of β-$[\text{Mo}_8\text{O}_{26}]^{4-}$ and of $[\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4]^{4-}$. Condensation of two $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]^{2-}$ units by sharing of four edges of each unit and loss of CH_3OH produces the β-$[\text{Mo}_8\text{O}_{26}]^{4-}$ structure while the $[\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4]^{4-}$ structure results either from shearing of $[\text{Mo}_4\text{O}_{13}]^{2-}$ asymmetric units of β-$[\text{Mo}_8\text{O}_{26}]^{4-}$ parallel to one other or from condensation of two $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]^{2-}$ units along two edges of each unit and partial loss of CH_3OH.

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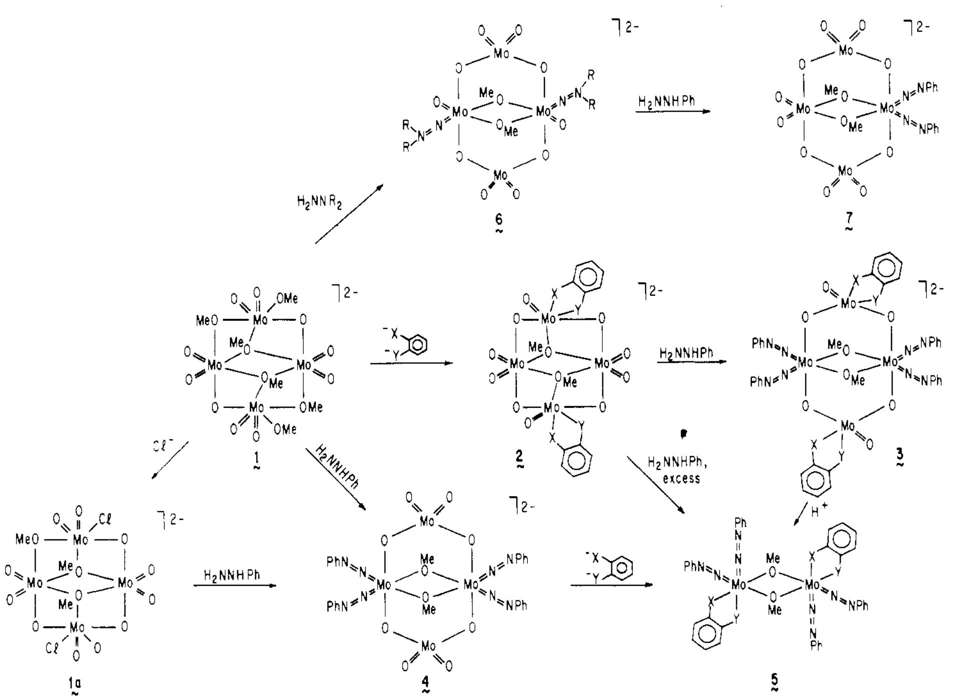

Figure 3. Schematic representation of the reaction chemistry of $[Mo_4O_{10}(OCH_3)_6]^{2-}$ and of derivative tetranuclear complexes that have been structurally identified.[9-13,19] The $[Mo_2(\mu\text{-}OCH_3)_2X_4]^{2+}$ core, where X is a strong π-ligand such as O^{2-} or $-N_2Ph$, persists in methanolic solutions. The substitution of the electronegative and strongly π-bonding terminal oxo groups by the three-electron donor diazenido ligands $-N_2R$ is compensated by the cleavage of Mo–O(methoxy) bonds from the $[Mo_2(\mu\text{-}OCH_3)_2X_4]^{2+}$ core methoxy group to the bridging $[MoO_4]^{2-}$ or $[MoO_3(XC_6H_4Y)]^{2-}$, resulting in the tetrahedral bridging $[MoO_4]^{2-}$ units of **4** and the bridging square pyramidal $[MoO_3(XC_6H_4Y)]^{2-}$ units of structures of type **3**.

anions incorporating alkoxide ligands have been invoked as models for selective hydrolysis of ethylene oxide to monoethylene glycol[14,15] and for the general oxidation of primary and secondary alcohols.[16] In the course of our investigations of the coordination chemistry of isopolyoxomolybdates with small organic molecules, we have isolated an oxo–methoxy cluster of molybdenum (VI), $[Mo_4O_{10}(OCH_3)_6]^{2-}$ (**1**), a species which is structurally related to the asymmetric tetranuclear core of the β-$[Mo_8O_{26}]^{4-}$ and $[(X)_2Mo_8O_{26}]^{(2n-4)}$ cluster types[17,18] and to the oxomolybdenum alkoxide $[Mo_4O_8(OC_2H_5)_2(CH_3C(CH_2O)_3)]^{22}$ and which provides a synthetic precursor in the preparation of a variety of structurally related organohydrazines,[9-13] alkoxide, and halide derivatives.

Reaction of α-$(MePPh_3)_4[Mo_8O_{26}]$[20] with 2 equiv of *N*-methyl-*N*-phenylhydrazine in methanol yields a bright red solution of $[Mo_4O_{10}(OMe)_2(NNMePh)_2]^{2-}$ [12] and a pale yellow powder. Recrystallization of the powder from CH_3OH/CH_2Cl_2 affords light yellow crystals of $(MePPh_3)_2[Mo_4O_{10}(OCH_3)_6]$ (**1**).[21] The infrared spectrum of **1** exhibits absorbances in the 885 to 930 cm⁻¹ region characteristic of the presence of both terminal and bridging oxo groups and bands at 2900–3000 cm⁻¹, assigned to C–H stretch features of the coordinated methoxy groups. The ^{17}O NMR spectrum revealed resonances at 946 and 881 ppm, associated with terminal oxo groups in significantly different environments and a resonance at 572 ppm assigned to a bridging oxo ligand. The crystal structure of **1** confirms the presence of coordinated methoxy groups and nonequivalent *cis*-dioxomolybdenum $[MoO_2]$ units.

The structure of the dinegative anion of **1** consists of discrete tetranuclear clusters $[Mo_4O_{10}(OMe)_6]^{2-}$, constructed from edge-sharing $[MoO_6]$ octahedra, as illustrated by the conventional structure in Figure 1 and the polyhedron model shown in Figure 2. The cluster is located at a crystallographic center of symmetry, which relates the symmetry-independent $[Mo_2O_4(\mu\text{-}O)(OCH_3)(\mu\text{-}OCH_3)(\mu'\text{-}OCH_3)]^-$ binuclear units. The unique molybdenum centers display pseudooctahedral geometry: $[MoO_2(\mu\text{-}O)(OCH_3)(\mu\text{-}OCH_3)(\mu_3\text{-}OCH_3)]$ and $[MoO_2(\mu\text{-}O)(\mu\text{-}OCH_3)(\mu_3\text{-}OCH_2)_2]$.

The overall cluster geometry is similar to that described for the neutral tetramolybdate $[Mo_4O_8(OEt)_2(tme)_2]$[22] and closely related to the asymmetric unit common to the $[(X)_2Mo_8O_{26}]^{(2n-4)}$ clusters and to their parent structure β-$[Mo_8O_{26}]^{4-}$. Figure 2 illustrates the relationship between the $[Mo_4O_{10}(OCH_3)_6]^{2-}$ structure and those of β-$[Mo_8O_{26}]^{4-}$ and $[Mo_8O_{24}(OCH_3)_4]^{4-}$, which may be generated, in a formal sense, from the tetranuclear core through hydrolysis and aggregation of two units and which, in turn, are related to each other through parallel shearing of the asymmetric $[Mo_4O_{13}]^{2-}$ units.

As illustrated by the reaction scheme of Figure 3, complex **1** provides a useful synthetic precursor for substitution reactions involving displacement of terminal and bridging methoxy groups and/or terminal oxo units and, furthermore, serves as the structural prototype for the entire class of tetranuclear and binuclear structures thus derived. Thus, reactions with organohydrazine ligands yield complexes **4**, **6**, and **7**,[9,10,12] while reaction with

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[21] Experimental: (a) All reactions and measurements were carried out anaerobically. Anal. Calcd for $C_{44}H_{54}P_2Mo_4O_{16}$: C, 41.1; H, 4.21. Found: C, 41.4; H, 4.06. IR spectrum (KBr pellet, cm⁻¹): 3000 (m), 2940 (m), 2902 (m), 1437 (ms), 1111 (ms), 1060 (w), 1006 (ms), 926 (sh), 906 (vs), 885 (sh), 746 (s), 710 (br), 682 (s), 556 (ms), 510 (ms). ^{17}O NMR spectra were obtained in CD_2Cl_2; chemical shifts are relative to $^{17}OH_2$ (ppm [line width at half-height in Hz]): 946 [73], 881 [450], 572 [152]. (b) X-ray diffraction data of **1** were collected at ca. 21 °C by using monochromatized Mo Kα radiation. The structure was solved by Patterson and difference Fourier maps, and all non-hydrogen atoms of the anion were refined anisotropically. Crystal data: space group $P\bar{1}$, $a = 10.185$ (2) Å, $b = 10.848$ (2) Å, $c = 11.686$ (2) Å, $\alpha = 92.55$ (1)°, $\beta = 107.15$ (1)°, $\gamma = 96.79$ (1)°, $V = 1220.8$ (11) Å³, $Z = 1$, $D_{calcd} = 1.75$ g cm⁻³; crystal dimensions, 0.32 × 0.28 × 0.37 mm; 2θ scan range; 2–50° using variable scan speeds of 1–15° min⁻¹ to collect a total of 2742 reflections. Absorption correction was based on ψ scans of five reflections near $\chi = 90$ or 270°. Structure solution and refinement were based upon 2798 reflections ($F_o \geq 6\sigma(F_o)$) Mo Kα, $\lambda = 0.71073$ Å) and converged at a conventional discrepancy value of 0.0245.
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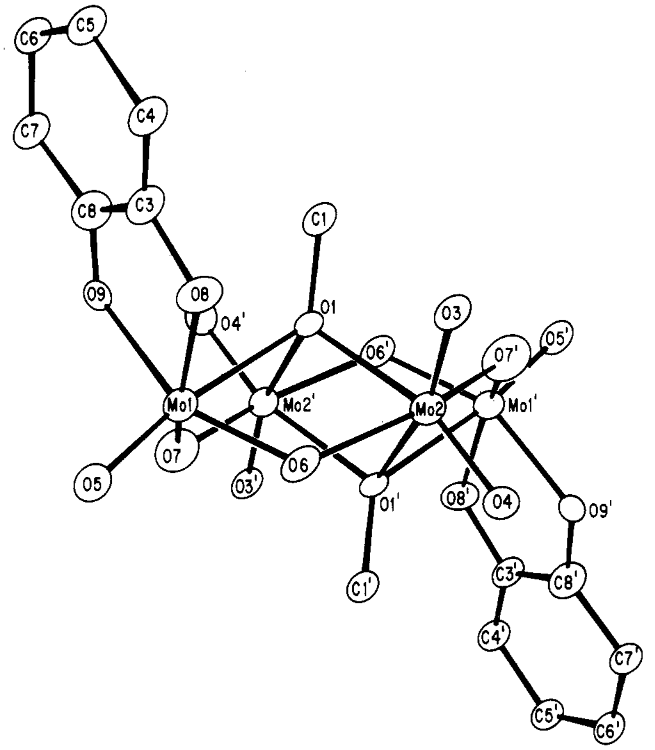

Figure 4. ORTEP view of the structure of $[Mo_4O_{10}(OCH_3)_2(OC_6H_4O)_2]^{2-}$ (**2**), showing the atom-labeling scheme. Selected bond lengths (Å): Mo1–O1, 2.416 (7); Mo1–O5, 1.699 (8); Mo1–O6, 1.817 (7); Mo1–O7, 1.824 (9); Mo1–O8, 1.981 (9); Mo1–O9, 1.982 (7); Mo2–O1, 2.270 (7); Mo2–O3, 1.682 (11); Mo2–O4, 1.677 (8); Mo2–O6, 1.983 (7); Mo2–O1′, 2.248 (8); Mo2–O7′, 1.990 (8).

chloride yields the structurally analogous **1a**.[23] Reaction of the $(Bu_4N)^+$ salt of **1** with 2 equiv of catechol in methanol[24] yields, when allowed to stand for several days, bright green crystals of $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]$ (**2**).[25]

The key feature of structure **2** is the retention of the tetranuclear core with pseudooctahedral $[MoO_6]$ coordination geometries, as shown in Figure 4. Although a number of Mo–catecholato complexes have been previously structurally characterized,[26-30] none have displayed the tetranuclear core, which persists in reactions carried out in methanol and which appears to be a characteristic structural type under these reaction conditions.

Complexes **1** and **2** display contrasting behavior upon thermal decomposition. While thermal decomposition of **1** at 150 °C yields dimethyl ether, formaldehyde, methanol, and water as gaseous products, the decomposition of **2** produces only water and methanol as volatile products. This result is consistent with the presence of significant intramolecular C–H···O contacts in **1**, providing a mechanism for C–H bond activation,[7] and with absence of close C–H···O contacts in **2**.[31] These observations lend further support to the model proposed by McCarron et al. for C–H bond activation in the oxidation of methanol to formaldehyde.[5-7]

Complex **2** and analogous species of the general type $[Mo_4O_{10}(OCH_3)_2(XC_6H_4Y)_2]^{2-}$ react readily with organohydrazine ligands.[19] Thus, in the reactions with phenylhydrazine, complex **2a**, $[Mo_4O_{10}(OCH_3)_2(HNC_6H_4O)_2]^{2-}$, yields $[Mo_4O_6(OCH_3)_2(NNPh)_4(HNC_6H_4O)_2]^{2-}$ (**3**) or $[Mo_2(OCH_3)_2(HNC_6H_4O)_2(NNPh)_4]$ (**5**), depending upon reaction conditions. As illustrated by Figure 3, structurally analogous tetranuclear cores are observed for a range of chemical transformations.

Acknowledgment. This work was supported by a grant from the National Science Foundation to J.Z. (CHE8514634).

Supplementary Material Available: Tables of atom coordinates, bond lengths, bond angles, and thermal parameters for **1** and **2** (21 pages); tables of observed and calculated structure factors for both compounds (78 pages). Ordering information is given on any current masthead page.

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(23) (a) Anal. Calcd for $C_{36}H_{84}N_2Mo_4Cl_2O_{14}$: C, 35.3; H, 6.93; N, 2.29. Found: C, 35.4; H, 7.19; N, 2.26. (b) Crystal data: space group $P\bar{1}$, $a = 10.186$ (2) Å, $b = 11.722$ (2) Å, $c = 13.173$ (2) Å, $\alpha = 109.35$ (1)°, $\beta = 107.43$ (1)°, $\gamma = 96.99$ (1)°, $Z = 1$, $D_{calcd} = 1.45$ g cm^{-3}; 3020 reflections with $F_o \geq 6\sigma(F_o)$; $R = 0.0407$.

(24) Similar reactions have been carried out by using 2-aminophenol and 2-aminothiophenol.

(25) (a) Anal. Calcd for $C_{46}H_{86}N_2Mo_4O_{16}$: C, 42.3; H, 6.58. Found: C, 42.7; H, 6.47. The IR spectrum of **2** in KBr shows a complex pattern of absorbances in the 830–920-cm^{-1} Mo=O region and in the 2950-cm^{-1} methoxy C—H stretching region. (b) X-ray diffraction studies were carried out at ca. 20 °C with monochromatized Mo Kα radiation. Crystal data: space group $P2_1/a$, $a = 18.474$ (3) Å, $b = 16.192$ (3) Å, $c = 20.411$ (4) Å, $\beta = 107.51$ (2)°, $V = 5822.6$ (12) Å^3, $Z = 4$; crystal dimensions, 0.22 × 0.18 × 0.26 mm; the conditions of data collection and reduction were identical with those for **1**. Of 5645 reflections collected, 3832 were used in the structure refinement ($F_o \geq 6\sigma(F_o)$; Mo Kα, $\lambda = 0.71073$ Å; $R = 0.0539$). The $n\text{-}Bu_4N^+$ cations were somewhat disordered as indicated by C–C bond distances in the range 1.32 (2)–1.59 (4) Å and thermal parameters in the range 0.070–0.603 Å^2. Since only the anion was of interest and it behaved quite well, the disorder of the cations was modeled by placing the carbon atoms at the peak of highest density consistent with an atom position.

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(31) Hydrogen atom positions were located and refined for **1**. Although H atoms were not located for **2**, C···O contact distances precluded significant C–H···O interactions. C–H···O contacts for **1**: (C3)H3c···O6, 2.63 Å; (C6)H6a···O4, 2.64 Å; (C3)H3c···O2, 2.75 Å; (C3)H3b···O5, 2.75 Å; (C7)H7c···O3, 2.74 Å.

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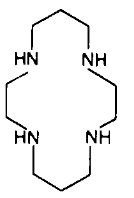
Received September 4, 1987

Unusually Rapid Homolysis of the Cobalt-Carbon Bond in a Macrocyclic Benzylcobalt Complex

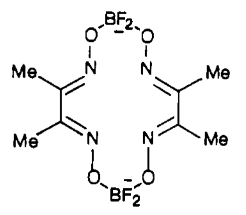
Sir:

The highest rate constant reported for homolysis of a cobalt–carbon bond in a series of macrocyclic benzylcobalt complexes is that for benzylcobalamin, $k = 2.7 \times 10^{-3}$ s^{-1} at 25.5 °C.[1] The ready homolysis of this complex as compared to other $C_6H_5CH_2Co(N_4\text{-macrocycle})$ complexes has been attributed in part to configurational motions of the corrin ligand,[1a] and to steric interactions that cause the angular distortion of the Co–C bond.[1c] We now report that a newly prepared benzylcobalt complex of a synthetic macrocycle, $C_6H_5CH_2Co([14]aneN_4)(H_2O)^{2+}$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane), homolyzes in aqueous solutions even more rapidly than benzylcobalamin does.

The structures of the ligands $[14]aneN_4$ and $(dmgBF_2)_2$ (see later) are



$[14]aneN_4$



$(dmgBF_2)_2$

The organocobalt complex $C_6H_5CH_2Co([14]aneN_4)(H_2O)^{2+}$ was prepared by photolysis of $C_6H_5CH_2Co(dmgH)_2H_2O$ in the presence of $Co([14]aneN_4)(H_2O)_n^{2+}$ (n = 1 or 2),[2] followed by

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