Synthesis and Characterization of $[Mo_2O_5]^{2+}$-Bridged Complexes Containing Cofacially-Oriented, Catechol-Functionalized Macrocyclic and SALPHEN Ligands

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The synthesis of multinuclear supermolecules, using catechol-functionalized macrocyclic complexes as ligands, has been a subject of recent studies in our laboratory.[1] The metal-complexed "ligands" include derivatives of the macrocyclic tetraazacyclotetradecacatechol $[H_2TAD\text{-}(OH)_2]$[1] and of the salicylideneaminocatechols obtained by condensation of 4,5-diaminocatechol with various salicylaldehydes, $[H_2(R_2R'_2\text{-}SALPHEN)\text{-}(OH)_2]$[2] (Figure 1).

In this communication, we report on the synthesis and properties of complexes that contain cofacially-oriented, $[Mo_2O_5]^{2+}$-bridged, macrocyclic and SALPHEN ligands and on the structural characterization of the $(Bu_4N)_2[Mo_2O_5[Ni(TAD\text{-}(O)_2)]_2]$ and $(Bu_4N)_2[Mo_2O_5[Cu(EtO_2SALPHEN\text{-}(O)_2)]_2]$ complexes. Interest in these compounds derives from the possible combination of the unique properties of the previously studied cofacial porphyrin complexes[3,4] and the redox characteristics of the metallocatecholate ligands.[1]

The synthesis of the macrocyclic-catechol $[Mo_2O_5]$-derivatives was inspired by the known $[Mo_2O_5(3,5\text{-}R_2cat)_2]^{2-}$ and $[Mo_2O_5(PQ)_2]$ complexes (cat = catechol, R = H[5] or R = *tert*-butyl (^{t}Bu)[6]; PQ = phenanthrenequinone[7]) that contain cofacially-oriented phenyl rings. A reaction that uses $[Mo_2O_7]^{2-}$ as a source of the $[Mo_2O_5]^{2+}$ unit for the synthesis of these catecholate compounds has been developed in our laboratory (eq 1) and appears to be of general synthetic utility. Thus the

$$[Mo_2O_7]^{2-} + 2\,H_2L \rightarrow [L(Mo_2O_5)L^{2-} + 2\,H_2O \qquad (1)$$

previously reported $(Bu_4N)_2[Mo_2O_5(^tBu_2cat)_2]$ complex was obtained[8] in 90% yield from the reaction of $(Bu_4N)_2[Mo_2O_7]$[9] with 2 equiv of 3,5-di-*tert*-butylcatechol (^{t}Bu$_2$cat) in oxygen-free CH_2Cl_2 at ambient temperature.

The synthesis of the supermolecular $(Bu_4N)_2[Mo_2O_5[Ni(TAD\text{-}(O)_2)]_2]$ (**I**) and $(Bu_4N)_2[Mo_2O_5[H_2(EtO)_2SALPHEN\text{-}(O)_2]_2]$ (**II**) has been accomplished in oxygen-free CH_2Cl_2 at ambient temperature according to eq 1 (H_2L = $[NiTAD\text{-}(OH)_2]$ and $[H_2(EtO)_2SALPHEN\text{-}(OH)_2]$, respectively). In a subsequent step, **II** can be metalated with 2 molar equiv of $M(OAc)_2$ in methanol at room temperature to yield $(Bu_4N)_2[Mo_2O_5[M(EtO)_2\text{-}SALPHEN\text{-}(O)_2]_2]$ in nearly quantitative yield (M = Cu(II), **III**, or Ni(II), **IV**).[8]

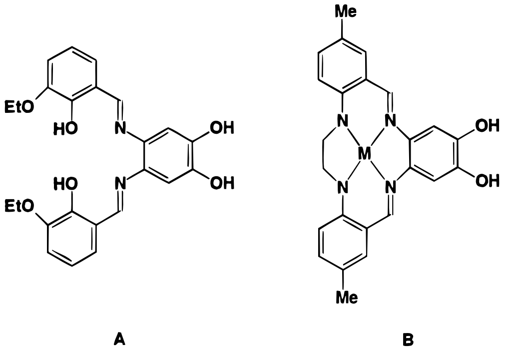

Figure 1. Catechol-functionalized ligands employed in this communication: (A) the $[H_2(EtO)_2SALPHEN\text{-}(OH)_2]$ SALPHEN catechol and (B) the $[M(TAD\text{-}(OH)_2)]$ macrocyclic catechol (M = Ni).

The crystal and molecular structures of **I**[8,10] and **III**[8,11] have been determined (Figure 2). In both structures the catecholate subunits are cofacially oriented and the $[Mo_2O_5]^{2+}$ unit assumes a bridging mode essentially identical to that observed in the structures of the $[Mo_2O_5(^tBu_2cat)_2]^{2-}$ (**V**) and $[Mo_2O_5(cat)_2]^{2-}$ (**VI**) complexes. In the latter the catechol phenyl rings are found in a cofacial, staggered arrangement. The Mo(1)−Mo(2) distances at 3.179(2) Å in **I** and 3.237(4) Å in **III** are slightly longer than those reported in **V** (3.132(4) Å) and **VI** (3.13(1) Å). The Mo(1)−O(1)−Mo(2) angles in **I** and **III** are 112.1(3) and 116.2(6)°, respectively, similar to that in **V** (109.4(4)°). The intramolecular Ni(1)−Ni(2) distance in **I** is 3.938 Å, and the corresponding Cu(1)−Cu(2) distance in **III** is 4.110 Å. These distances are within the range reported for a variety of cofacial metalated porphyrin systems, from 3.417 Å in $Co_2(FTF4)$[12] to 6.33 Å in $Cu_2(FTF6)$.[13] The macrocyclic subunits in **I** are nearly planar,[14] with rms deviations for all atoms of 0.110 and 0.144 Å, respectively. The angle between these planes is 6.5(2)°, which is small compared to the angle reported between the phenyl rings in **V** at 50.0(4)°. The lateral displacement of Ni-

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(8) Please see the Supporting Information section for complete details on the characterization of this complex.

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(10) Anal. Calculated for $C_{80}H_{112}N_{10}O_9Ni_2Mo_2$: C, 57.63; H, 6.78; N, 8.40. Found: C, 57.53; H, 6.83; N, 8.39. Crystal and refinement data: Dark green plates of **I** are triclinic, space group $P\bar{1}$, with a = 12.324(3) Å, b = 17.740(4) Å, c = 20.920(4) Å, α = 108.79(3)°, β = 98.20(3)°, and γ = 103.12(3)°. The refinement of the structure by full-matrix least-squares methods was based on 10686 unique reflections ($2\theta_{max}$ = 45°, $I > 2\sigma(I)$). The refinement of 826 parameters with all atoms present has converged to R1 = 9.7 and wR2 = 23.4, respectively.

(11) Anal. Calcd for $C_{80}H_{112}N_6O_{17}Mo_2Cu_2$: C, 54.94; H, 6.47; N, 4.81. Found: C, 54.62; H, 6.56; N, 5.08. Crystal and refinement data: Dark red "arrowheads" of **III** are monoclinic, space group $P2_1/c$, with a = 20.821(4) Å, b = 23.133(5) Å, c = 20.056(4) Å, and β = 117.71(3)°. The refinement of the structure by full-matrix least-squares methods was based on 8018 unique reflections ($2\theta_{max}$ = 40°, $I > 2\sigma(I)$). The refinement of 558 parameters with all atoms present has converged to R1 = 9.95 and wR2 = 20.57, respectively.

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(14) For ligands A and B of **I**, the atoms with the largest deviation from planarity are O(4) (0.308(8) Å) and O(8) (0.352(8) Å), respectively.

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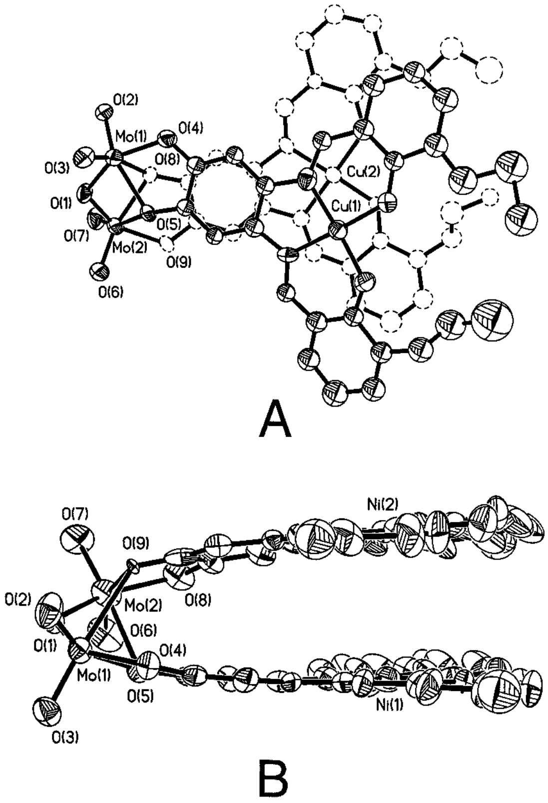

Figure 2. ORTEP plots (showing 30% probability ellipsoids) for the anions of (A) $(\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_5[\text{Cu(EtO)}_2\text{SALPHEN-(O)}_2]_2]$ (**III**) and (B) $(\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_5[\text{Ni(TAD-(O)}_2)]_2]$ (**I**). Complimentary views of **I** and **III** and additional metric features are available in the Supporting Information.

(1) relative to Ni(2) at 1.6 Å compares with similar "lateral slip" values for Ni_2(DPA) (2.40 Å),[4c] Cu_2(DPB) (1.60 Å),[4c] and Co_2(DPB) (1.57 Å).[3] The SALPHEN subunits in **III** define a dihedral angle of 9.7(1)° and are slightly puckered with rms deviations from the best planes[15] of 0.165 and 0.137 Å. The "lateral slip" between the Cu atoms in **III** is only 0.6 Å.

Complexes **I, II,** and **IV** are diamagnetic. Complex **III** has magnetic moments (μ_{eff}corr) of 4.09 μ_{M} (2.05 per Cu(II)) and 2.48 μ_{M} at 300 and 4 K, respectively, consistent with weak antiferromagnetic exchange coupling between the Cu(II) centers.

The $\eta 1\text{-O}_1;\eta 1,\mu 2\text{-O}_2$ bridging mode of the catecholate ligands accounts in part for the "hairpin" structure of the anions in **I**−**VI**. The last two of these compounds can be envisioned as structural precursors to the $(\text{pyH})_2[[(\text{Cl}_4\text{-cat})(\text{py})\text{MoO}_2]_2(\mu\text{-O})]$ complex (**VII**, Figure 3) which has been isolated and structurally characterized previously in an unrelated synthesis.[16] In this molecule, the six-coordinate Mo(VI) ions in the bridging $[\text{Mo}_2\text{O}_5]^{2+}$ unit are each coordinated by a pyridine molecule rather than by a bridging catecholate oxygen lone pair, and the catecholate phenyl rings are still cofacially oriented. By comparison to **V**, the Mo−O−Mo angle in **VII** opens to 168.7(4)° and the Mo−Mo separation is rather long at 3.77 Å.

The addition of 2 equiv of pyridine to $(\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_5(\text{Cl}_4\text{-cat})_2]$[8] ($\text{Cl}_4$-cat = tetrachlorocatecholate, **VIII**) did not result in any change in the electronic spectrum. Upon addition of pyH^+ (2 equiv) a change in the electronic spectrum was apparent and the isolated product was found to be identical to **VII**. The electronic spectra of **II**−**IV** are also perturbed upon addition of pyH^+ cations. Apparently, cations that are sufficiently acidic are capable of hydrogen-bonding to the catecholate oxygen atoms and "tie-up" the lone pair used for bridging (Figure 3). This hydrogen-bonding interaction, evident in the crystal structure of **VII**, is necessary for the structural change from **VIII** to **VII**. The change in the catecholate binding mode from bridging $\eta 1\text{-O}_1;\eta 1,\mu 2\text{-O}_2$ to chelating $\eta 1\text{-O}_1,\text{O}_2$ and the opening of the Mo−O−Mo angle that may accompany such a change impart flexibility to the possible distance between the catecholate subunits.

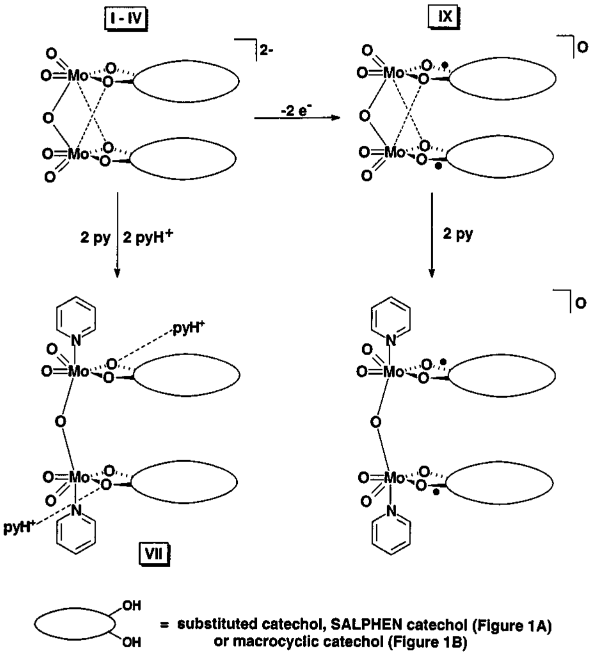

Figure 3. General scheme showing the reactions of the $[\text{Mo}_2\text{O}_5]$-bridged catecholate systems.

The oxidation[17] of **IV** with 2 equiv of ferrocenium has yielded the neutral bis(semiquinone) complex $[\text{Mo}_2\text{O}_5[\text{Ni(EtO)}_2\text{-SALPHENSQ-(O)}_2]_2]$ (**IX**).[8] This complex is paramagnetic ($\mu_{\text{eff}}^{\text{corr}} = 3.4\ \mu_{\text{M}}$ at 300 K, or 1.7 μ_{M} per SALPHEN unit) and reacts with pyridine in the absence of added acid. Whether pyridine affects the coordination mode of the semiquinone ligands and causes a structural change similar to that shown in **VII** remains to be established.

The ability to chemically manipulate both the redox state of these molecules and the relative spatial separation of the cofacial catecholates within molecules such as **I, III, IV,** and **IX** represents an unusually attractive feature. The possible use of these complexes in the binding and activation of small molecules is presently under investigation.

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Supporting Information Available: Text giving analytical and spectroscopic characterization for compounds **I**−**IX**, including some preparative information, and X-ray diffraction characterization of **I** and **III**, tables of data collection and structure refinement parameters, anisotropic displacement parameters, and of bond lengths and angles for **I** and **III**, figures showing alternate views of **I** and **III** and connectivity diagrams of the disordered cations of **I**, and a listing of the deviations of each macrocyclic atom in **I** and **III** from the calculated least-square planes (40 pages). Ordering information is given on any current masthead page.

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[15] For ligands A and B of **III**, the atoms with the largest deviation from planarity are C(12) (0.39(2) Å) and O(8) (0.30(1) Å), respectively.

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[17] Cyclic voltamograms in acetonitrile solution (vs Ag/AgCl, Bu_4NClO_4 added as supporting electrolyte) show multiple broad, poorly defined oxidation waves between 0.0 and 1.5 V which are inconclusive and will not be discussed here.