Macrocyclic Catechol Complexes as Ligands in the Synthesis of Heterometallic Supramolecules

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In a preceding communication[1] we reported on the synthesis of a new class of binucleating macrocyclic ligands that, in addition to a tetraaza cavity, contain an appended catechol group. Complexes of the 2,3-ethylene-5,6:13,14-di(5′-MeBzo)-9,10-(4′,5′-$(OH)_2$Bzo)-[14]-1,4,8,11-$[N_4]$-7,12-diene ligand, ETC, with the tetraaza cavity occupied by a metal ion (Figure 1), are expected to display not only the chemistry associated with the tetraaza-coordinated metal ion but also the diverse chemistry that characterizes the simpler catechols and in particular the coordination properties of the catecholate anions.[2] The use of these functionalized macrocycles as ligands for metal ions, or coordinatively unsaturated complexes, holds much promise for the synthesis of supramolecules with a high degree of complexity and with a host of unusual redox, electronic, or magnetic properties. Recently, the design of specific supramolecules that can be described as "multicomponent electronic systems" is receiving attention as a route to possible precursors for the generation of molecular devices with applications in photoswitching, light energy conversion, on charge separation.[3] The functionalization of catechols or quinones in the synthesis of various potentially multinucleating ligands has been reported previously, and the chemistry of such ligands as 9,10-phenanthroline-5,6-quinone,[4,5] $(NQ)_2en$[6] (a naphthoquinone-substituted SALEN type of a ligand), 2,3-dihydroxyterephthalamide,[7] and multidentate ligands containing three 2,3-dihydroxybenzoyl groups[8] has been explored in considerable detail.

In this communication, we demonstrate the use of the metal macrocycle-catecholates as ligands for the $[Mo_2O_2S_2]^{2+}$ cation, and we report on the crystal structure of the $\{[NiETC][Mo_2O_2S_2(S_2)]\}^{2-}$complex.

The deprotonation of the catechol group in the NiETC or CoETC complexes (Figure 1, M = Ni, Co) by n-Bu_4NOH, KOMe, or Et_4NOH in the presence of the $[(DMF)_3Mo_2O_2S_2(S_2)]$ complex[9] (in DMF or THF solution) results in the formation of black precipitates that can be recrystallized from DMF/ether mixtures to give microcrystalline solids of K^+, $[Et_4N]^+$, or $[Bu_4N]^+$ salts of the $\{[NiETC][Mo_2O_2S_2(S_2)]\}^{2-}$ (I)[10] and $\{[CoETC][Mo_2O_2S_2(S_2)]\}^{2-}$ (II)[11] anions. Similar reactions of the NiETC or CoETC macrocycles, in THF or DMF, with the $[(DMF)_3Mo_2O_2S_2(DMF)_3]^{2+}$ cation[9] in a 2:1 molar ratio and with 4 equiv of base afford microcrystalline salts of the $\{[NiETC]_2[Mo_2O_2S_2]\}^{2-}$ (III)[12] and $\{[CoETC]_2[Mo_2O_2S_2]\}^{2-}$ (IV)[13] anions, where two functionalized macrocycles are bridged by the $[Mo_2O_2S_2]^{2+}$ unit.

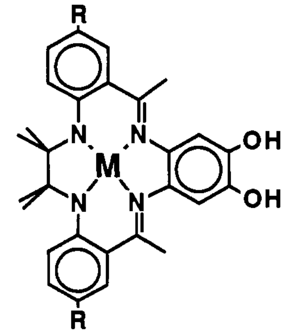

Figure 1. M{2,3-ethylene-5,6:13,14-di(5′-CH_3Bzo)-9,10-(4′,5′-$(OH)_2$Bzo)-[14]-1,4,8,11-$[N_4]$-7,12-diene} (ETC) macrocyclic metallocatechols.

Single crystals of the mixed K^+/Et_4N^+ salt of I, as a tris-DMF solvate, were obtained by diffusion of diethyl ether into a DMF solution of the compound.[14] In the structure of K^+/Et_4N^+(I) the potassium cation is coordinated to the oxygen atoms of three DMF molecules, the catecholate oxygen atoms, and the oxygen atom of one molybdenum-oxo group to achieve a six-coordinate geometry. The planarity of the macrocyclic Ni^{2+} complex is retained upon coordination to the $[Mo_2O_2S_2(S_2)]$ unit (Figure 2), and the Ni–N bonds span the range from 1.851(13) to 1.888-

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(10) Data for $(Et_4N)_2\{[NiETC](Mo_2O_2S_2(S_2))\}$ (I) are as follows. Anal. Calc for $C_{40}H_{60}N_6O_4S_4Mo_2Ni$: C, 45.0; H, 5.62; N, 7.87. Found: C, 44.75; H, 5.43; N, 7.76. ^{1}H-NMR in DMSO-d_6 [δ (ppm)]: 1.10 (q, 24H), 2.21 (s, 6H), 3.14 (t, 16H), 3.47 (s, 4H), 6.92 (d, 2H), 7.05 (d, 2H), 7.40 (s, 2H), 7.45 (s, 2H), 8.61 (s, 2H). Electronic spectrum in DMF (2.67×10^{-4} M) [nm (ϵ, M^{-1} cm^{-1})]: 651 (8923), 584 (10 273), 550 (sh), 460 (35 769), 438 (33 144), 415 (sh), 390 (sh), 355 (sh), 332 (sh), 304 (47 303), 274 (40 793). IR spectrum (CsI pellet, cm^{-1}): 1520 (m, ν(C=N)), 1473 (vs, ν(C=C)), 1284 (vs, ν(C–O)), 949 (m, ν(Mo=O)), 521 (w, $\nu(M–S_2)$, 476 (w, $\nu(M–S_b)$.

(11) Data for $(Et_4N)_2\{[CoETC](Mo_2O_2S_2(S_2))\}$ (II) are as follows. Anal. Calc for $C_{40}H_{60}N_6O_4S_4Mo_2Co$: C, 45.0; H, 5.62; N, 7.87. Found: C, 45.08; H, 5.58; N, 7.88. Electronic spectrum in DMF (2.0×10^{-4} M) [nm (ϵ, M^{-1} cm^{-1})]: 690 (sh), 630 (sh), 554 (6550), 480 (sh), 444 (46 000), 436 (sh), 400 (sh), 346 (sh), 320 (34 200), 265 (39 050). IR spectrum (CsI pellet, cm^{-1}): 1520 (m, ν(C=N)), 1476 (vs, ν(C=C)), 1282 (vs, ν(C–O)), 949 (m, ν(Mo=O)), 520 (w, $\nu(M–S_2)_t$), 473 (w, $\nu(M–S_b)$. Magnetic susceptibility (300 K): $\mu_{eff}^{corr} = 2.36\ \mu_B$. EPR in DMF at 77 K shows a typical low-spin Co^{2+} signal.

(12) Data for $(Bu_4N)_2\{[NiETC]_2(Mo_2O_2S_2)\}$ (III) are as follows. Anal. Calc for $C_{80}H_{112}N_{10}O_6S_2Mo_2Ni_2$: C, 57.09; H, 6.66; N, 8.33. Found: C, 55.76; H, 6.47; N, 8.16. ^{1}H-NMR in DMSO-d_6 [δ (ppm)]: 0.90 (t, 24H), 1.27 (q, 16H), 1.57 (m, 16H), 2.22 (s, 12H), 3.11 (m, 16H), 3.49 (s, 8H), 6.94 (d, 4H), 7.04 (d, 4H), 7.40 (s, 4H), 7.51 (s, 4H), 8.63 (s, 4H). Electronic spectrum in DMF (3.8×10^{-4} M) [nm (ϵ, M^{-1} cm^{-1})]: 650 (11 000), 584 (12 175), 542 (sh), 462 (42 483), 442 (sh), 418 (sh), 394 (sh), 350 (sh), 330 (sh), 302 (55 059), 274 (44 303). IR spectrum (CsI pellet, cm^{-1}): 1520 (m, ν(C=N)), 1472 (vs, ν(C=C)), 1283 (vs, ν(C–O)), 950 (m, ν(Mo=O)), 476 (vw, $\nu(S)_b$).

(13) Data for $(Bu_4N)_2\{[CoETC]_2(Mo_2O_2S_2)\}\cdot 3DMF$ (IV) are as follows. Anal. Calc for $C_{89}H_{133}N_{13}O_6S_2Mo_2Co_2$: C, 56.19; H, 7.00; N, 9.58. Found: C, 55.98; H, 7.08; N, 9.51. Electronic spectrum in DMF (2.22×10^{-4} M) [nm (ϵ, M^{-1} cm^{-1})]: 638 (sh), 564 (sh), 470 (sh), 446 (69 595), 438 (sh), 406 (sh), 346 (sh), 324 (42 838), 264 (52 748). IR spectrum (CsI pellet, cm^{-1}): 1520 (m, ν(C=N)), 1475 (vs, ν(C=C)), 1280 (vs, ν(C–O)), 950 (m, ν(Mo=O)), 476 (vw, $\nu(S)_b$).

(14) This salt was obtained by the reaction of NiETC with 2 equiv of base of a 1:1 mixture of KOMe and Et_4NOH in the presence of the $[(DMF)_3Mo_2O_2S_2(S_2)]$ complex. Crystal and refinement data: Black crystals of $\{[Et_4N]K[C_{24}H_{20}N_4O_2Ni][Mo_2O_2S_2(S_2)]\}(DMF)_3$, I, are monoclinic, space group $P2_1/a$ with $a = 9.350(6)$ Å, $b = 32.19(2)$ Å, $c = 17.603(8)$ Å, $\beta = 104.29(5)°$, and $Z = 4$. The solution of the structure was carried out by direct methods, and the heavy-atom positions were verified in the Patterson map. All non-hydrogen atoms of the anion as well as the potassium cation and the oxygen and nitrogen atoms of solvents and the Et_4N^+ cations were refined with anisotropic temperature factors. The refinement of 492 parameters by using 3599 unique reflections ($2\theta_{max} = 45°$ $I > 3\sigma(I)$) and employing full-matrix least-squares methods has converged to final values of R_w and R of 0.080 and 0.081, respectively. The maximum residual electron density is 0.98 e/Å^3 and is found around the metal atoms. In view of the small value for μ ($\mu = 10.9$ cm^{-1}) no absorption correction was applied to the data.

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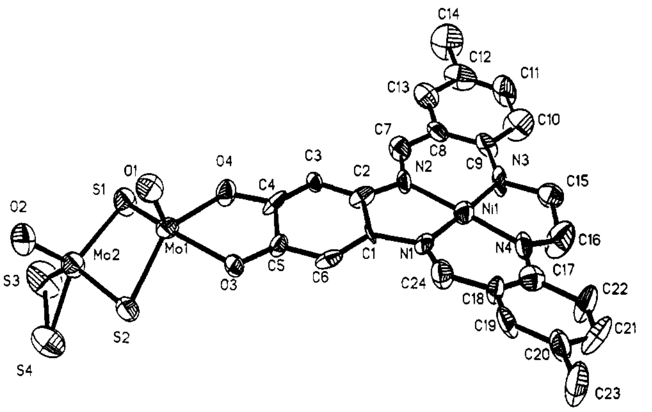

Figure 2. Structure of the $\{[\text{NiETC}][\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)]\}^{2-}$ anion showing the atom-labeling scheme and 40% probability ellipsoids as drawn by ORTEP. Selected structural parameters: Mo(1)–Mo(2), 2.853(2) Å; Mo–S_b, 2.322(5) Å; Mo(1)–O(1), 1.656(11) Å; Mo(2)–O(2), 1.685(12) Å; Mo–O_L, 2.056(12) Å; Mo(2)–S(3), 2.385(6) Å; Mo(2)–S(4), 2.376(7) Å. Ni–N, 1.87(1) Å; C–O, 1.33(2) Å.

(15) Å with a mean value of 1.87(1) Å. These values are indistinguishable from those in the "parent" NiETC complex.[1] The metric details and coordination geometry of the Mo atoms in I are similar to a number of other complexes that contain the *syn*-$[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ cores.[15] The Mo^V–O_cat bond lengths in I at 2.054(12) and 2.059(10) Å are of intermediate length by comparison to the Mo^VI–O bond lengths in the $\text{Mo}_2(o\text{-Cl}_4\text{Cat})_6$ complex[16] (1.919(6) Å) and the Mo^IV–O bond lengths in the $[\text{MoO}_2(\text{Cat})_2]^{2-}$ anion (2.05, 2.17 Å).[17] The intramolecular Mo(1)–Ni and Mo(2)–Ni distances are 7.87 and 10.43 Å, respectively.

The EPR spectra of II and IV were obtained in DMF glasses at 77 K. The spectra are very similar and show rhombic symmetry for the Co^{2+} ion (for IV, $g_1 = 2.68$, $g_2 = 2.02$, and $g_3 = 1.97$, with $A = 29.0 \times 10^{-4}\ \text{cm}^{-1}$).[22] By comparison the EPR spectrum of the "parent" CoETC complex (Figure 1) has $g_1 = 2.65$, $g_2 = 2.19$, and $g_3 = 1.97$, with $A = 28.0 \times 10^{-4}\ \text{cm}^{-1}$.

The distinctive features in the electronic spectra of the complexes I–IV are very similar but the extinction coefficients of the 2:1 complexes (III, IV) are considerably larger, and this effect is more pronounced in the case of the cobalt complex (IV). The major absorption in the electronic spectra of the "parent" metallocatecholate complexes (at 428 and 424 nm, respectively, for the Ni^{2+} and Co^{2+} complexes) appears bathochromically shifted by 30–50 nm in the $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ 2:1 and 1:1 adducts (I–IV). The same electronic absorption in the metal-free macrocyclic catechol ligands is found at 392 nm ($\epsilon = 2.1 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$). The data suggest that the absorption around 400 nm, of the macrocyclic ligands and complexes reported herein, is due to a ligand-centered π–π^* transition. In the electronic spectra of organic molecules with π systems, bathochromic shifts with increasing solvent polarity usually are associated with π–π^* transitions.[18] The effect of metal ions on the π systems of either the macrocyclic ligands or their metallomacrocycle derivatives would be qualitatively similar to the effects associated with increasing solvent polarity.

The infrared spectra of I–IV exhibit characteristic vibrations near 521 cm^{-1} and near 476 cm^{-1} that are attributed to terminal disulfide and bridging sulfide ligands, respectively, and the characteristic Mo=O vibrations around 950 cm^{-1}.

The cyclic voltammetry[19] shows much complexity with a number of redox-active couples. Two to three reversible or quasireversible oxidations are observed for II, IV and I, III between 0 and +0.50 V and are considered to be ligand-based. Poorly defined, irreversible reduction waves are observed for I and III at high potentials (–1.50 to –1.75 V). Two reversible reduction waves are found for each of the Co complexes at –1.15, –1.50 V and –1.00, –1.35 V, respectively, for II and IV. The reversibility of the waves observed with the Co-containing compounds suggests that the orbitals involved in both the reduction and oxidation processes in II and IV have appreciable Co character. The potential of the reversible oxidation wave of II (+0.180 mV) is 200 mV less positive than the potential of the corresponding wave in IV (+0.380 mV). These changes in the oxidation potentials and the potentials associated with the reversible reduction waves at –1.15, –1.50 mV and –1.00, –1.35 mV, respectively, for II and IV are consistent with a shift of electron density from the $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ bridge to the macrocyclic subunits. The effect of such a charge shift in the redox potentials would be more pronounced in II than in IV.

The Ni(II) complexes I and III are diamagnetic, and their ^{1}H-NMR spectra verify the predicted $[\text{R}_4\text{N}]^+$ to $[\text{NiETC}]^{2-}$ ratios. The cobalt complexes II and IV are paramagnetic as expected for the square-planar low-spin cobalt centers. The Co(II) complexes show Curie paramagnetic behavior from 5 to 300 K and have $\mu_\text{eff}(300\ \text{K}) = 2.36\ \mu_\text{B}$ and $\mu_\text{eff}(300\ \text{K}) = 3.01\ \mu_\text{B}$, respectively, for II and IV, as expected for square-planar low-spin cobalt centers.[20] No evidence for intramolecular magnetic interaction is found for IV.

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Supplementary Material Available: Table S1, containing a summary of crystal data and listings of positional parameters, thermal parameters, and selected distances and angles of I (14 pages). Ordering information is given on any current masthead page.

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(18) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970, The bathochromic shifts in the major electronic absorption of the macrocyclic ligand upon the sequential addition of metal ions (or the $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$ complex) qualitatively resemble the shifts observed for a given macrocyclic complex in solvents with increasing dielectric constant.

(19) The electrochemical measurements have been carried out in DMF using platinum working and auxiliary electrodes with silver wire as the reference electrode. Under the same conditions that the voltammetry of the new complexes was studied, the reduction of the Fe(Cp)_2^+ cation is observed at +735 mV.

(20) Low-spin, square-planar Co(II) complexes show magnetic susceptibilities in the range 1.9–2.5 μ_B.[21]

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