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Multifunctional Macrocyclic Ligands. Synthesis and Characterization of Nickel(II) and Cobalt(II) Macrocyclic-Catechol Complexes and Their Dimeric, Antiferromagnetically Coupled, Semiquinone Derivatives

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Interest in the design and synthesis of supramolecules, to a large extent, can be attributed to expectations that the proper organization of metal-complex subunits within a supramolecular assembly may lead to molecular devices with unique function and unusual electronic properties. Included among the various functions or properties that may be associated with such devices are (a) the specific orientation and/or activation of substrate molecules prior to particular reactions,[1] (b) the ability to undergo photoinduced electron transfer and charge separation important in such processes as light energy conversion or photoswitching,[2,3] and (c) the display of particular intramolecular or intermolecular magnetic interactions.[4] Our approach toward the synthesis of supramolecules, using metal complexes as ligands, is based on concepts and procedures developed in our laboratory earlier for the metal dithiooxalate complexes and derivatives[5] and employs modified macrocyclic complexes that contain appended catechol as functional groups. The metallocatecholate complexes readily serve as ligands for other metal ions or coordinatively unsaturated metal complexes[6] to give supramolecules with intramolecular M–M distances in excess of 10 Å (Figure 1). In this communication we report the synthesis of the functionalized N_4-tetraazacyclotetradeca-7,12-diene macrocyclic ligands and the structures of the Ni(II) and Co(II) complexes in the catechol and the Ni(II) complex in the semiquinone forms.

The 2,3-ethylene-5,6:13,14-di(5′-RBzo)-9,10-(4′,5′-$(OH)_2$Bzo)-[14]-1,4,8,11-$[N_4]$-7,12-dienes (R = H, Me), **I** (Figure 1A), are obtained by demethylation of the corresponding methoxy-protected macrocyclic precursors, 2,3-ethylene-5,6:13,14-di(5′-RBzo)-9,10-(4′,5′-$(OMe)_2$Bzo)-[14]-1,4,8,11-$[N_4]$-7,12-dienes, **II**, by a procedure reported previously.[7] The syntheses of **II** are accomplished by Schiff base condensation between the 2,2′-(ethane-1,2-diyldiimino)bis(5′-R-benzaldehyde), **III**, and 1,2-diamino-4,5-dimethoxybenzene (**IV**). The synthesis of **III** (R = H) has been reported,[8] and the synthesis of **III** (R = Me) can be accomplished by an analogous procedure. The synthesis of **IV** by the palladium-catalyzed, hydrogen reduction[7b] of 1,2-dimethoxy-4,5-dinitrobenzene[9] has been described previously. The metal complexes of **II** can be prepared in DMF solution, either by the direct reaction of metal acetates with **II** or by the use of metal acetates in a template reaction between **III** and **IV**. The metal complexes of **II** are demethylated under basic conditions[7] to give the free catechol of the metalated macrocycle (Figure 1).

The diamagnetic Ni^{2+}, **V**, and the paramagnetic (low spin, $\mu_{eff}^{cor} = 2.05\ \mu_B$) Co^{2+}, **VI**, complexes (Figure 1) are planar, neutral molecules.[10] In these complexes the four-coordinate metal ions occupy the deprotonated tetraaza cavity. Crystals of **V**·2THF were obtained by diffusion of hexane into a THF/Et_2O solution of the complex. The structure of **V**·2THF was determined[12] and shows **V** very close to being planar[13] with two THF molecules hydrogen bonded to the catechol hydroxy groups (Figure 2A). One of the OH groups of the complex (O(1)) is strongly hydrogen bonded to one of the THF molecules with a H–O(4) distance of 1.62(9) Å. The hydrogen atom on O(2) is equidistant from O(1) and the THF, O(3), atom at 2.22(10) Å. The Ni–N bonds at 1.860(5) Å are unexceptional. The catecholate C–O bonds at 1.363(6) and 1.373(8) Å and the (HO)C–C(OH) bond at 1.402(9) Å are indistinguishable from the corresponding mean C–O and C–C bonds obtained from 16 simple catecholate structures[14] of 1.350(4) and 1.390(6) Å, respectively. The structure of **VI** has been determined[15] and is nearly identical to that of **V**.

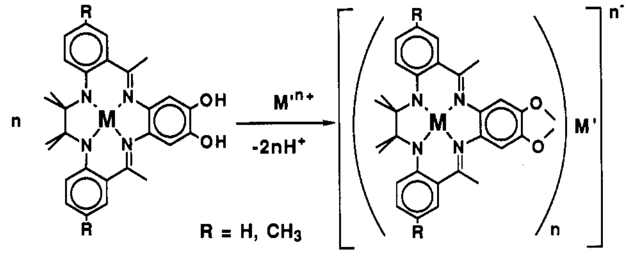

Figure 1. Metallomacrocyclic catechols.

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[10] Anal. Calcd for $C_{24}H_{22}N_4O_2Ni{\cdot}C_4H_8O$, **V**: C, 63.55; H, 5.67; N, 10.59. Found: C, 63.51; H, 5.75; N, 10.85.C. Calcd for $C_{24}H_{22}N_4O_2Co{\cdot}C_3H_7NO$, **VI**: C, 61.14; H, 5.47; N, 13.21. Found: C, 60.94; H, 5.55; N, 13.06. The complexes **V** and **VI**, obtained by demethylation of the corresponding –OMe compexes in DMF solution, initially are isolated with one DMF molecule of solvation. Recrystallization of these solvates from THF leads to new solvates with THF of solvation instead of DMF. From dilute THF solutions the compounds are obtained in crystalline form with two THF molecules of solvation. From concentrated THF solutions the same macrocyclic complexes of Ni^{2+} and Co^{2+} are obtained in a different crystalline modification with only one THF molecule of solvation. A structure determination of the Co complex in this second modification[11] shows a hydrogen-bonded dimeric structure, with the THF molecules also hydrogen bonded to the catecholate O atoms. Electronic spectra in DMF solution [nm ($\epsilon \times 10^{-3}\ M^{-1}\ cm^{-1}$)]: For **V** ($7 \times 10^{-4}$ M), 640 (7.8), 560 (7.5), 428 (29.9), 404 (26.1), 298 (44.9), 270 (38.0). Infrared spectra (CsI): 3454 (s), 1625 (s), 1583 (s), 1517 (s), 1479 (vs), 1458 (s), 1358 (s), 1297 (vs), 1224 (vs) 1174 (s). Electronic spectra for **VI** (6.6×10^{-4} M): 584 (3.5), 424 (24.6), 310 (20.9), 291 (21.9). Infrared spectra (CsI): 3454 (s), 1625 (s), 1597 (m), 1517 (s), 1477 (s), 1455 (m), 1386 (m), 1359 (s), 1291 (vs), 1226 (s), 1184 (s). ^1H-NMR spectra in DMSO-d_6 solution (δ, ppm): For **V**, 2.20 (s, $-CH_3$; 6H), 3.46 (s, $-CH_2CH_2-$; 4H), 6.93 (d, 2H), 7.05 (dxd, 2H), 7.39 (s, 2H), 7.48 (s, 2H), 8.56 (s, 2H), 9.7 (broad, OH).

[11] Jonasdottir, S.; Kim, C. G.; Coucouvanis, D. Work in progress.

[12] Crystal and refinement data: Black crystals of **V**·2THF are triclinic, space group $P1$, with $a = 10.908(1)$ Å, $b = 11.391(3)$ Å, $c = 12.727(3)$ Å, $\alpha = 84.56(2)°$, $\beta = 80.28(2)°$, $\gamma = 73.39(2)°$, and $Z = 2$. Single-crystal X-ray diffraction data for **V**·2THF were collected on a Syntex $P2_1m/v$ diffractometer using Mo Kα radiation. The solution of the structure was carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques using SHELXTL-PLUS. The refinement of the structure by full-matrix least-squares methods was based on 3749 unique reflections ($2\theta_{max} = 50°$; $I > 3\sigma(I)$). Anisotropic temperature factors were used for all non-hydrogen atoms. The refinement of 378 parameters with all atoms present in the asymmetric units has converged to R and R_w of 0.067 and 0.069, respectively.

[13] The largest deviations from the best plane containing all non-hydrogen atoms of the complex **V** are found with C(19) and C(21) at 0.24(1) and 0.38(1) Å, respectively.

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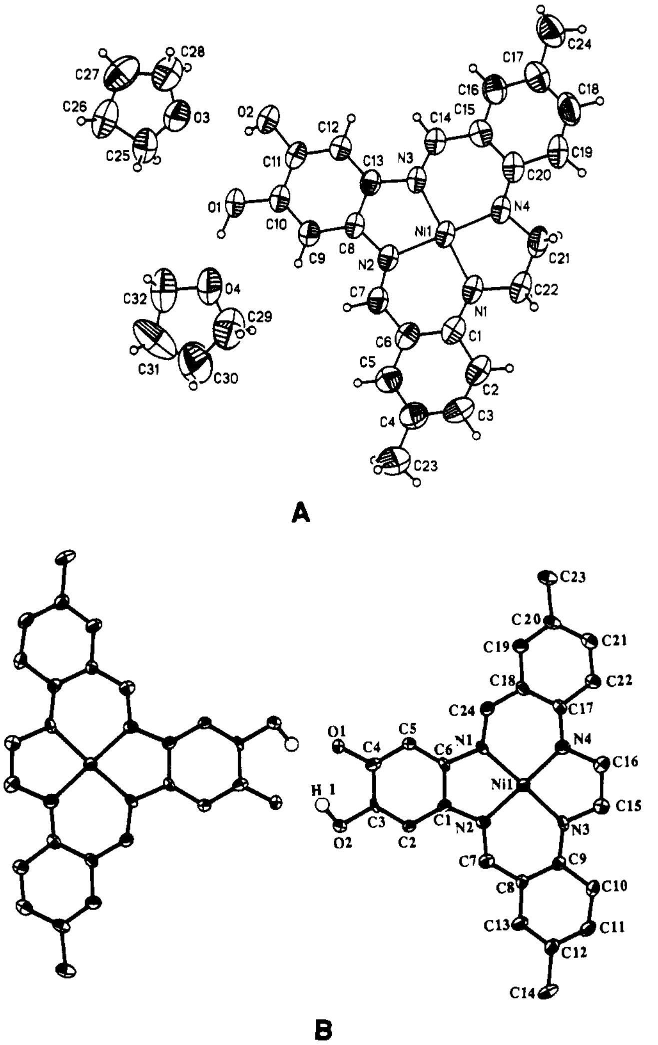

Figure 2. Structures of (A) Ni{2,3-ethylene-5,6:13,14-di(5′-CH_3Bzo)-9,10-(4′,5′-$OH)_2$Bzo)-[14]-1,4,8,11-[N_4]-7,12-diene}·2THF, **V**, and (B) [Ni{2,3-ethylene-5,6:13,14-di(5′-CH_3Bzo)-9,10-(4′,5′-(OH)(O)(Bzo)-[14]-1,4,8,11-[N_4]-7,12-diene}]$_2$, **VII**, showing the atom-labeling schemes and 40% probability elipsoids, drawn by ORTEP.

The oxidation of either **V** or **VI** by $Fe(Cp)_2^+$ in a 1:1 ratio in DMF solution occurs readily and in the presence of base (Et_3N); the oxidized **V** or **VI** complexes undergo deprotonation to give the neutral semiquinone complexes **VII** and **VIII**, respectively.[16] The dimeric structure of the Ni semiquinone complex,[17] **VII**, was determined and shows two planar neutral, semiquinone molecules interacting strongly across a center of symmetry via intermolecular hydrogen bonding (Figure 2B). The bridging hydrogen atom shows two O–H distances of 0.83(9) and 2.075(10) Å. The Ni–N bond in **VII** at 1.860(12) Å is nearly identical to that in **V**. The C–O bonds at 1.354(10) and 1.362(9) Å are only slightly shorter than those in **V** and considerably longer than the mean bonds in the structures of eight simple semiquinone metal complexes[14] (1.291(6) Å). The C–C bond at 1.39(1) Å is shorter than the mean value found in semiquinone metal complexes[14] (1.435(4) Å). The similar C–O and C–C bond lengths in the macrocyclic catecholate and semiquinone complexes very likely are the result of extensive electron delocalization.

In the solid state, at 300 K, **VII** shows a magnetic moment, μ_{eff}^{corr}, of 2.08 μ_B/dimer and shows a strong EPR signal (g = 2.003) with a width at half-height of 15 G. Measurements of the magnetic susceptibility as a function of temperature reveal antiferromagnetic behavior. In DMF solution **VII** does not show an EPR spectrum between 300 and 15 K and appears diamagnetic as evidenced by sharp resonances in the ^{1}H-NMR spectrum in either DMF or DMSO solutions (310 K). A measurement of the molecular weight of **VII** by cryoscopy in DMSO solution is consistent with a dimeric structure and suggests that the compound may retain a hydrogen-bonded structure in solution. A dimeric hydrogen-bonded structure also is supported by a broad resonance in the ^{1}H-NMR spectrum of **VII**, at 9.33 ppm, in DMSO-d_6 solution that we attribute to the bridging OH proton. The diamagnetic nature of **VII** in solution could be the consequence of an electron–proton exchange between the two subunits that results in the formation of a diamagnetic quinone–catechol pair. This contention is supported (a) by the observation that an equimolar mixture of **V** and the *ortho*-quinone derivative of **V**[18] (obtained by Ph_2SeO oxidation[19] of **V**) shows virtually the same electronic spectrum (by wavelength and extinction coefficient criteria) as the one recorded for **VII** with the same concentration of chromophores and (b) by the ^{1}H-NMR spectrum of **VII**, which is best described as a superposition of the independently recorded ^{1}H-NMR spectra of pure **V** and the isolated *ortho*-quinone derivative of **V** in 1:1 ratio. The location and well-behaved isotropic refinement of the OH hydrogen atom in the structure of **VII** (with a reasonable temperature factor of 6.7 Å^2) show that in the solid state the molecule can be described as a dimer of weakly antiferromagnetically coupled semiquinone molecules rather than a diamagnetic catechol–quinone pair, positionally disordered across the center of symmetry. The reactions of **V**–**VIII** with metal ions and metal complexes presently are under investigation.[6]

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Supplementary Material Available: Tables S1 and S2 containing crystal and structure determination details, positional parameters, thermal parameters, and selected distances and angles and best plane calculations for **V** and **VII** (20 pages). Ordering information is given on any current masthead page.

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(15) The structure of **VI** has been determined using marginal, insufficient, data obtained from the best available, yet poorly diffracting, crystal. This determination, albeit of low quality, establishes unequivocally that **VI** is a monomeric planar molecule, essentially isostructural to **V**.

(16) Anal. Calcd for $[C_{24}H_{21}N_4O_2Ni]_2 \cdot 2HCON(CH_3)_2$, **VII**: C, 61.17; H, 5.47; N, 13.22. Found: C, 60.68; H, 5.42; N, 12.82. Calcd for $[C_{24}H_{21}N_4O_2Co]_2 \cdot 2HCON(CH_3)_2$, **VIII**: C, 61.25; H, 5.33; N, 13.23. Found: C, 60.75; H, 5.36; N, 12.09. Electronic spectra in DMF solution [nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})]: For **VII** (2.0×10^{-4} M), 650 (7.2), 544 (19.3), 510 (18.6), 478 (sh), 426 (29.6), 402 (27.1), 376 (sh), 360 (44.4), 346 (sh), 298 (46.7). Infrared spectra (CsI): 3454 (s), 1625 (s), 1583 (s), 1517 (s), 1479 (vs), 1458 (s), 1358 (s), 1297 (vs), 1224 (vs), 1174 (s); for **VIII** (2.4×10^{-4} M), 670 (sh), 580 (sh), 470 (sh), 421 (42.2), 376 (sh), 346 (39.1), 311.5 (45.2), 295 (43.2). Infrared spectra (CsI): For **VII**, 3414 (m), 1664 (m), 1627 (m), 1606 (m), 1584 (s), 1520 (m), 1467 (vs), 1440 (m), 1386 (m), 1360 (s), 1298 (vs), 1227 (s), 1178 (vs), 1172 (s); for **VIII**, 3414 (m), 1659 (m), 1622 (m), 1601 (m), 1519 (m), 1479 (s), 1360 (vs), 1295 (m), 1226 (m), 1184 (m). ^{1}H-NMR spectra of **VII** in DMSO-d_6 solution: 2.12 (s $-CH_3$; 6H), 2.20 (s, $-CH_3$; 6H), 3.48 (s, $-CH_2CH_2-$; 4H), 6.40 (d, 2H), 6.95 (d, 2H), 7.05 (d, 2H), 7.16 (d, 2H.), 7.40 (s, 2H), 7.47 (s, 2H), 8.04 (s, 2H), 8.57 (s, 2H), 9.33 (broad, OH).

(17) Red crystals of **VII**·DMF are monoclinic, space group $P2_1/c$, with a = 9.046(8) Å, b = 7.874(2) Å, c = 33.97(4) Å, β = 95.83(3)°, and Z = 4. Single-crystal X-ray diffraction data were collected on a Nicolet R3m diffractometer using Mo Kα radiation. The solution of the structure was carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 2226 unique reflections ($2\theta_{max} = 40°$, $I > 3\sigma$). Anisotropic temperature factors were used for all non-hydrogen atoms, and an isotropic temperature factor was used for the OH proton. Refinement on 325 parameterswith all atoms present in the asymmetric unitshas converged to R and R_w of 0.062 and 0.064, respectively.

(18) Anal. Calcd for $[C_{24}H_{20}N_4O_2Ni]H_2O$: C, 60.93; H, 4.65; H, 11.85. Found: C, 60.23; H, 4.59; N, 11.17. Electronic spectrum in DMF solution [nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})]: 542 (9.7), 511 (10.1), 484 (sh), 424 (10.0), 404 (sh), 362 (22.5), 354 (sh), 316 (sh), 283 (15), 263 (16.9). Infrared spectra (CsI): 1669 (m), 1615 (m), 1605 (m), 1542 (m), 1482 (vs), 1435 (vs), 1298 (vs) 1250 (s), 1222 (s), 1205 (vs), 1167 (s), 1140 (s), 1090 (m), 1042 (m). ^{1}H-NMR spectrum in DMSO-d_6 solution: 2.12 (s, 6H), 3.49 (s, 4H), 6.39 (s, 2H), 6.93 (d, 2H), 7.04 (s, 2H), 7.17 (d, 2H), 8.03 (s, 2H).

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