

Binuclear Complexes of Co(III) Containing Extended Conjugated Bis(Catecholate) Ligands

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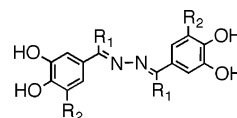
Received February 18, 2005

Binuclear complexes of cobalt(III) have been prepared with 3,3',4,4'-tetrahydroxy-benzaldazine (H₄thB), 3,3',4,4'-tetrahydroxy-5,5'-dimethoxybenzaldazine (H₄thM), and 3,3',4,4'-tetrahydroxydimethylbenzaldazine (H₄thA) as bis(catecholate) ligands that link metal ions separated by 16 Å through a conjugated bridge. In one case, [Co₂(bpy)₄(thM)]²⁺, stereodynamic properties observed in solution by ¹H NMR are associated with valence tautomerism, with formation of a labile hs-Co(II) species by electron transfer from the catecholate regions of the bridge. Electrochemical oxidation of the complexes occurs at the bridges as two closely spaced one-electron couples. Chemical oxidation of [Co₂(bpy)₄(thB)]²⁺ with Ag⁺ is observed to occur as a two-electron process forming [Co₂(bpy)₄(thB^{SQ,SQ})]⁴⁺. Attempted crystallization in the presence of air was observed to result in formation of the [Co(bpy)₂(BACat)]⁺ (H₂BACat, 3,4-dihydroxybenzaldehyde) cation by aerobic oxidation. Structural characterization is provided for the H₄thM ligand and [Co(bpy)₂(BACat)](BF₄).

Introduction

Interests in the coordination chemistry of catecholate and semiquinonate ligands have been extended to studies on complexes containing tethered dioxyethylene groups. Ligands containing saturated attachments linked to a common terminus have been developed for studies on polycatecholate chelates.¹ Direct attachment between dioxylenes has been used in studies on ligands that bridge different metal ions,² and unsaturated connections between dioxyethylene groups may be used to induce electronic and magnetic coupling between bridged complex units.³ The strength of intermetallic coupling for this latter class of bis(dioxyethylene) ligands has been

found to be not only a function of the separation between metals but also dependent upon the electronic structure of the bridge between dioxyethylene rings. In this report, we describe the results of an initial study carried out to investigate the coordination properties of 3,3',4,4'-tetrahydroxybenzaldazine (L1, H₄thB) and related ligands, L2 and L3. These ligands may be conveniently prepared by treating the

(L1) H₄thB R₁; H, R₂; H(L2) H₄thM R₁; H, R₂; OCH₃(L3) H₄thA R₁; CH₃, R₂; H

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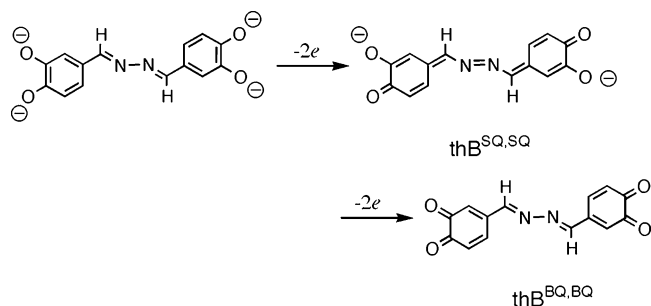
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corresponding 3,5-dihydroxybenzaldehyde with hydrazine.⁴ Coordination of metals at the catecholate oxygens would place them approximately 16 Å apart, with M(Cat) units linked by the conjugated hydrazone bridge. Each of the ligands may undergo oxidation by four electrons to give the bis(benzoquinone) form of the ligand (thB^{SQ,BQ}). However, the bis(semiquinonate—thB^{SQ,SQ}) formed by two-electron

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oxidation will be of greatest interest in studies on the coordination chemistry of the ligand with redox-active transition metal ions. While each SQ may exist as a paramagnetic radical, electronic coupling between SQ regions through the planar bridge should be strong, resulting in a spin singlet ground state. Differences in ligand charge should appear with characteristic C=C, C=O, and C=N bond lengths and spectroscopic properties.

Facile metal–ligand electron transfer has become a unique feature of dioxylyene complexes of redox-active first-row transition metals.⁵ We have referred to the equilibrium between localized $\text{M}^{\text{I}}(\text{SQ})$ and $\text{M}^{\text{II}}(\text{Cat})$ redox isomers as valence tautomerism (VT).⁶ Complexes that exhibit VT characteristically consist of a thermodynamically inert donor/acceptor, in most examples a dioxylyene ligand, and a metal center that undergoes a *tight/floppy* interconversion with electron transfer. This change is primarily responsible for defining the thermodynamic properties and temperature dependence of the equilibrium.⁵ The shift between tight and floppy redox isomers is mainly due to a change in the occupancy of antibonding $d\sigma$ orbitals. The earliest and most widely studied examples of VT are dioxylyene complexes of Co, where the *tight* component is a $ls\text{-Co}^{\text{III}}(\text{Cat})$ species and the *floppy* redox isomer is $hs\text{-Co}^{\text{II}}(\text{SQ})$ formed as the product of intramolecular electron transfer and spin transition. Other metal dioxylyene complexes that have been reported to exhibit VT include complexes of Mn,⁷ Cu,⁸ Ni,⁹ Fe,¹⁰ and Mo.¹¹ The donor atoms of the dioxylyene ligand have been varied with nitrogen and sulfur donors in place of the ring oxygens.¹² The model can be extended to systems other than the dioxylyene complexes. Hashimoto has reported temperature-dependent shifts in the magnetic and electronic proper-

ties of cobalt–iron and manganese–iron Prussian blue compounds, $\text{C}_x[\text{M}_4[\text{Fe}(\text{CN})_6]_y] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Mn}$).¹³ In these systems, the $ls\text{-Fe}^{\text{II/III}}$ center serves as the inert donor/acceptor, the functional equivalent to the Cat/SQ ligands of the dioxylyene complexes.

The choice of a metal for the initial study on the coordination chemistry of the conjugated bis(catecholate) ligands was based on the strong tendency of complexes of cobalt to exhibit VT. This has been emphasized by Dei in recent work on cobalt–dioxylyene complexes that might show the properties of a molecular switch.¹⁴ In this report, we focus on complexes of cobalt that might exhibit unique electrochemical properties associated with electron-transfer reactions with either the metal ions or the bis(catecholate) ligand. Additionally, intramolecular shifts in charge distribution may result in the temperature-dependent formation of redox isomers associated with bimodal, and potentially cooperative, valence tautomerism.

Experimental Section

Materials and Methods. Preparations were performed using Schlenk techniques. All solvents were dried and distilled by standard methods before use. Reagents were obtained from Aldrich Chemical Co. and used without further purification. IR spectra were measured as KBr disks on a Nicolet Avatar 360 FT-IR spectrometer, and ^1H NMR spectra were recorded on a Varian Inova-400 spectrometer. UV–visible spectra were recorded on a Agilent Technologies HP8453 spectrometer, and cyclic voltammetric measurements were made under a flow of nitrogen using a CS-1200 potentiostat from Cypress Systems, Inc. Solutions of the complexes were prepared in DMSO or CH_3CN containing $(\text{NBu}_4)(\text{BF}_4)$ (ca. 0.1 M) as supporting electrolyte. Platinum wire working and counter electrodes were used with a Ag/AgNO₃ reference electrode. The Fc/Fc^+ couple appeared at +0.375 V ($E = 65$ mV) vs SCE with this experimental arrangement, and the ferrocene couple was used as an internal reference. Thermogravimetric analyses were obtained with a TG/DTA-200 from the SEIKO Instrument Co. under nitrogen at a temperature rate of 10 °C/min.

3,3',4,4'-Tetrahydroxybenzaldazine (H_4thB).⁴ Hydrazine dihydrochloride (0.643 g, 6.1 mmol) was placed in a flask with 9 mL of concentrated NH_3 and 40 mL of distilled water under a flow of N_2 . 3,4-Dihydroxybenzaldehyde (1.74 g, 12.6 mmol) dissolved in 45 mL of methanol was added to this solution with stirring. The solution was stirred for 2 h at room temperature as the color changed from light brown to yellow. The solution was then neutralized with concentrated acetic acid to remove excess ammonia and kept at 5 °C for 10 h. During this time, yellow needles of 3,3',4,4'-tetrahydroxybenzaldazine separated from the solution and they were isolated by filtration. The product was recrystallized from methanol– H_2O (1:1) and dried under vacuum. Yield: light yellow needles of 3,3',4,4'-tetrahydroxybenzaldazine (1.09 g, 81%), mp

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(dec) 245–247 °C. IR (KBr, cm^{-1}), 3359m, 3173m, 1614s, 1597s, 1521m, 1458m, 1386m, 1331w, 1293s, 1205w, 1163w, 1108m, 960w, 787w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 6.770–6.790 (2 H, d), 7.058–7.083 (2 H, dd), 7.281–7.285 (2 H, s), 8.433 (2 H, s). Found: C, 54.22; H, 5.49; N, 9.12. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: C, 54.50; H, 5.19; N, 9.90%.

3,3',4,4'-Tetrahydroxy-5,5'-dimethoxybenzaldazine (H_4thM). The same synthetic procedure was carried out as for H_4thB using 3,4-dihydroxy-5-methoxybenzaldehyde as the reagent. Yield: brown needles (96%), mp (dec) 245–247 °C. IR (KBr, cm^{-1}) 3540m, 3195m, 1625m, 1598m, 1516s, 1450m, 1431m, 1343s, 1320s, 1208s, 1151m, 1090s, 945w, 837w, 759w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 3.801 (6 H, s), 6.942–6.984 (4 H, dd), 8.464 (2 H, s). Found: C, 52.30; H, 4.94; N, 7.58. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$: C, 52.17; H, 5.47; N, 7.61%.

3,3',4,4'-Tetrahydroxydimethylbenzaldazine (H_4thA). This synthetic procedure was carried out as that for H_4thB using methyl-3,4-dihydroxyphenyl ketone as the reagent. Yield: light yellow needles (42%), mp (dec) 235–239 °C. IR (KBr, cm^{-1}) 3571w, 3475m, 3357m, 3158m, 1610m, 1580m, 1519m, 1437w, 1377m, 1305s, 1283m, 1255m, 1201w, 1131w, 909w, 864w, 818m, 785w, 633w, 590w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 2.211 (6 H, s), 6.753–6.774 (2 H, d), 7.155–7.181 (2 H, d), 7.408 (2 H, s). Found: C, 55.21; H, 5.70; N, 8.26. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$: C, 55.64; H, 6.13; N, 8.11%.

$[\text{Co}(\text{bpy})_2(\text{CH}_3\text{COO})](\text{PF}_6)$. A solution of cobalt(II) acetate (125 mg, 0.5 mmol) in methanol (25 mL) was added to a solution of 2,2'-bipyridine (156 mg, 1 mmol) under nitrogen. The resulting solution was stirred 1 h and then treated with an aqueous solution KPF_6 . The solution was cooled to 5 °C, and over the period of several hours, yellow crystals of $[\text{Co}(\text{bpy})_2(\text{CH}_3\text{COO})](\text{PF}_6)$ were obtained in 42% yield. IR (KBr, cm^{-1}) 3509w, 3189m, 1615m, 1593s, 1517s, 1445m, 1364m, 1333m, 1299s, 1206m, 1163m, 1115m, 967w, 867w, 804w, 613w. UV–vis (CH_3CN , $\lambda_{\text{max}}(\text{nm})$) 245 ($\epsilon = 5.03 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 297 ($\epsilon = 5.05 \times 10^4$). Found: C, 44.53; H, 3.90; N, 9.26. Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_4\text{O}_2\text{CoPF}_6 \cdot \text{H}_2\text{O}$: C, 44.53; H, 3.57; N, 9.45%.

$[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ (1). A solution of cobalt(II) acetate (125 mg, 0.5 mmol) in methanol (25 mL) was added to a solution of 2,2'-bipyridine (156 mg, 1 mmol) under nitrogen. The resulting solution was stirred for 1 h, and then 10 mL of H_4thB (68 mg, 0.25 mmol) dissolved in methanol was added dropwise. The resulting solution was stirred for 3 h and then treated with an aqueous solution of NaBF_4 . The solution was cooled to 5 °C, and over the period of 8 h, a dark brown powder of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ separated from the solution in 45% yield. IR (KBr, cm^{-1}) 3407m, 3081w, 1609m, 1574m, 1482s, 1441m, 1424m, 1313m, 1261s, 1162w, 1109m, 1063m, 807w, 760m, 726w, 656w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 6.475 (2H, d), 6.624–6.644 (2H, d), 6.896 (2H, s), 7.565–7.597 (8H, m), 7.985–8.018 (4H, t), 8.140 (2H, s), 8.343–8.386 (4H, t), 8.518–8.561 (4H, t), 8.724–8.739 (2H, d), 8.798–8.812 (2H, d), 8.855–8.874 (4H, d), 8.919–8.939 (4H, d). UV–vis (CH_3CN , $\lambda_{\text{max}}(\text{nm})$) 211 ($\epsilon = 1.17 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$), 238 ($\epsilon = 9.82 \times 10^4$), 290 ($\epsilon = 5.64 \times 10^4$), 301 ($\epsilon = 6.14 \times 10^4$), 311 ($\epsilon = 6.32 \times 10^4$), 405 ($\epsilon = 5.68 \times 10^4$), 718(547). Found: C, 52.75; H, 3.55; N, 11.25. Calcd for $\text{C}_{54}\text{H}_{40}\text{N}_{10}\text{O}_4\text{Co}_2\text{B}_2\text{F}_8 \cdot 2 \text{H}_2\text{O}$: C, 53.14; H, 3.63; N, 11.48%.

$[\text{Co}_2(\text{bpy})_4(\text{thM})](\text{PF}_6)_2$ (2). $[\text{Co}(\text{bpy})_2(\text{CH}_3\text{COO})](\text{PF}_6)$ (73 mg, 6 mmol) dissolved in 20 mL of methanol was added to a methanol solution (5 mL) containing H_4thM (21 mg, 6.3 mmol). The mixture was stirred for 1 h, and an aqueous solution of KPF_6 was added to the brown solution. After standing for 2 d at 5 °C, complex 2 separated from solution as a dark brown powder. Yield: 57%. IR

(KBr, cm^{-1}) 3427w, 3086w, 1608m, 1566w, 1477m, 1450m, 1425m, 1344m, 1242w, 1139w, 1109m, 1076m, 844s, 768m, 730w, 652w, 558m. ^1H NMR (400 MHz, d_6 -dmsO, ppm) 3.564 (6H, s), 6.532(2H, s), 6.588 (2H, s), 7.516–7.528 (4H, t), 7.553–7.593 (4H, m), 8.013–8.029 (4H, t), 8.170 (2H, s), 8.356–8.374 (4H, t), 8.539–8.553 (4H, t), 8.622–8.635 (2 H, d), 8.785–8.798 (2 H, d), 8.845–8.936 (8H, m). Found: C, 48.44; H, 3.37; N, 9.66. Calcd for $\text{C}_{56}\text{H}_{44}\text{N}_{10}\text{O}_6\text{Co}_2\text{P}_2\text{F}_{12} \cdot \text{H}_2\text{O}$: C, 48.64; H, 3.64; N, 10.13%.

$[\text{Co}_2(\text{bpy})_4(\text{thA})](\text{ClO}_4)_2$ (3). A solution of cobalt(II) acetate (125 mg, 0.5 mmol) in methanol (25 mL) was added to a solution of 2,2'-bipyridine (156 mg, 1 mmol) under nitrogen. The resulting solution was stirred for 1 h, and then 10 mL of H_4thA (68 mg, 0.25 mmol) dissolved in methanol was added dropwise. The resulting solution was stirred for 3 h and then treated with an aqueous solution of NaClO_4 . The solution was cooled to 5 °C, and over the period of several hours, a dark brown powder of $[\text{Co}_2(\text{bpy})_4(\text{thA})](\text{ClO}_4)_2$ separated from the solution in 63% yield. IR (KBr, cm^{-1}) 3429w, 3084w, 1607m, 1570w, 1548w, 1484s, 1449m, 1424w, 1365w, 1322m, 1296m, 1262s, 1160w, 1095s, 812w, 769m, 729w, 623w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 2.100 (6H, s), 6.413–6.433 (2H, d), 6.766–6.796 (2H, dd), 7.081 (2H, s), 7.551–7.589 (4H, m), 7.975–8.018 (4H, t), 8.340–8.382 (4H, t), 8.514–8.553 (4H, t), 8.744–8.757 (2H, d), 8.802–8.817 (2H, d), 8.851–8.871 (4 H, d), 8.913–8.933 (4H, d). Found: C, 52.72; H, 3.92; N, 10.86. Calcd for $\text{C}_{56}\text{H}_{48}\text{N}_{10}\text{O}_{12}\text{Co}_2\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$: C, 52.63; H, 4.10; N, 10.96%.

$[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$ (4). A solution of cobalt(II) acetate (63 mg, 0.25 mmol) in methanol (25 mL) was added to a solution of 2,2'-bipyridine (78 mg, 0.5 mmol) under nitrogen. The resulting solution was stirred for 1 h, and then 3,4-dihydroxybenzaldehyde (34 mg, 0.25 mmol) dissolved in methanol containing 2 equiv of KOH was added dropwise to this solution. The resulting solution was stirred for 1 h and then treated with an aqueous solution of NaBF_4 . The solution was cooled to 5 °C, and over the period of several hours, dark blue crystals of $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$ separated from the solution in 24% yield. IR (KBr, cm^{-1}) 3431m, 3081w, 1667m, 1606m, 1569m, 1553m, 1483s, 1448m, 1431m, 1292s, 1267s, 1083m, 807w, 767m, 729w, 654w. ^1H NMR (400 MHz, DMSO- d_6 , ppm) 6.560 and 6.581 (1 H, d), 6.856–6.874 (2 H, s and d), 7.571–7.610 (4 H, m), 8.000–8.019 (2 H, m), 8.376 (2 H, t), 8.555 (2 H, t), 8.7 (1 H, d), 8.8 (1 H, d), 8.865 and 8.886 (2 H, d), 8.935 and 8.955 (2 H, d), 9.423 (1 H, s). UV–vis (CH_3CN , $\lambda_{\text{max}}(\text{nm})$) 211 ($\epsilon = 4.32 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 259 ($\epsilon = 3.87 \times 10^4$), 302 ($\epsilon = 2.33 \times 10^4$), 311 ($\epsilon = 2.27 \times 10^4$), 343 ($\epsilon = 1.12 \times 10^4$), 652 ($\epsilon = 184$). Found: C, 53.02; H, 3.61; N, 9.21. Calcd for $\text{C}_{27}\text{H}_{22}\text{N}_4\text{O}_3\text{CoBF}_4 \cdot \text{H}_2\text{O}$: C, 52.79; H, 3.94; N, 9.12%.

Crystallography. Crystal Data for H_4thM . Single crystals of 3,3',4,4'-tetrahydroxy-5,5'-dimethoxybenzaldazine were grown by cooling an acetonitrile/water solution saturated with H_4thM . Once removed from the recrystallization solution, crystals were observed to deteriorate within the period of 1 h due to loss of hydrate solvent. A crystal suitable for crystallographic data collection was coated with an amorphous resin and cooled in the nitrogen stream of a Bruker SMART-CCD diffractometer. A full sphere of intensity data was measured, and the structure was solved using direct methods. The H_4thM molecule was found to be located about an inversion center in the triclinic unit cell. At the conclusion of the refinement on the H_4thM molecule, a water molecule was located and added to the refinement as a solvent of crystallization. Crystallographic data are summarized in Table 1; a CIF file for the structure determination is available as Supporting Information.

Crystal Data for $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$. Brown crystals of $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$ were obtained as the surprising product

Table 1. Crystallographic Data^a for H₄thM and [(bpy)₂Co(BACat)](BF₄)

	H ₄ thM	[(bpy) ₂ Co(BACat)](BF ₄)
formula	C ₁₆ H ₂₀ N ₂ O ₈	C ₂₇ H ₂₀ BN ₄ O ₃ F ₄ Co
fw	368.34	594.21
crystal system	triclinic	triclinic
space group	P1	P1
Z	1	4
a, Å	4.9024(6)	10.8083(7)
b, Å	8.7363(12)	16.3268(11)
c, Å	10.5235(15)	16.3863(10)
α, deg	104.660(3)	62.820(2)
β, deg	103.047(4)	87.714(2)
γ, deg	100.868(5)	79.962(2)
V, Å ³	410.1(1)	2530.3(3)
T, K	293(2)	139(2)
d, g cm ⁻³	1.491	1.782
μ, mm ⁻¹	0.121	0.778
R (Rw) ^b	0.0669 (0.1664)	0.0726 (0.1828)
GOF	0.967	0.921

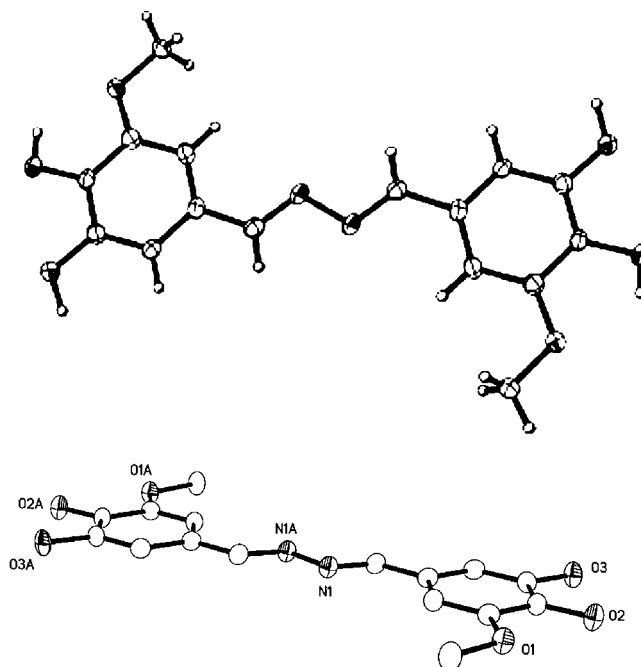
^a Data were collected using Mo Kα radiation with a wavelength of 0.71073 Å. ^b Discrepancy indices are defined as: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

of the oxidation of [Co₂(bpy)₄(thB)](BF₄)₂ with AgBF₄ in acetonitrile/H₂O under an atmosphere of air. Crystals were found to deteriorate within minutes of being separated from solution. A crystal suitable for crystallographic data collection was coated with an amorphous resin and cooled in the nitrogen stream of a Bruker SMART-CCD diffractometer. A full sphere of intensity data was measured, and the structure was solved using a sharpened Patterson map. Crystals form with two independent formula units of complex per asymmetric unit of the triclinic unit cell. Independent complex cations are weakly linked by a stacking interaction between the catechol ring of one cation with one ring of a bipyridine ligand of an adjacent cation. The aldehyde group on the catechol ring of one BACat ligand was found to be disordered over two equivalent locations; the aldehyde group of the second cation was ordered. One BF₄⁻ anion was rotationally disordered about one B–F bond. At the conclusion of the refinement on the complete set of cations and anions, a water molecule of crystallization was located and included in final cycles of refinement. Crystallographic data are summarized in Table 1; a CIF file for the structure determination is available as Supporting Information.

Attempted Structure Determination on [Co₂(bpy)₄(thB)](BF₄)₂. Brown crystals of [Co₂(bpy)₄(thB)](BF₄)₂ could be obtained by cooling a saturated acetonitrile/water solution containing the complex. Crystals formed in this way decomposed immediately upon separation from the recrystallization medium, even upon emersion in oil or an amorphous resin. Consequently, it was not possible to obtain structural characterization on this complex suitable for publication.

Results and Discussion

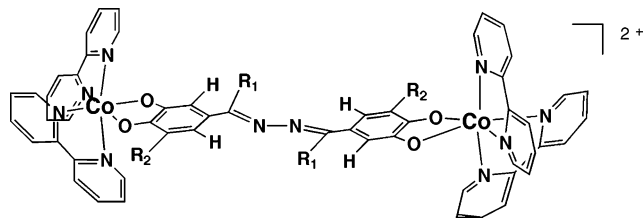
Molecular Structure of H₄thM. The structure of H₄thM was determined to identify features that might be significant in propagating electronic coupling between catechol regions at either end of the benzaldazine bridge and that might promote exchange between metal ions chelated by the catechol groups. The H₄thM molecule is shown in Figure 1; it is located about a site of crystallographically imposed inversion symmetry midway along the N–N bond at the center of the molecule. Atoms of the imine region of the bridge are within error of lying in the least squares plane

**Figure 1.** View of the H₄thM molecule showing planar structure. Thermal ellipsoids are at the 50% probability level.**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for H₄thM and Averaged Values for the [(bpy)₂Co(BACat)]⁺ Cation

H ₄ thM			
N1–C1	1.296(3)	N1–N1'	1.418(4)
O1–C4	1.373(3)	O1–C8	1.452(3)
O2–C5	1.362(3)	O3–C6	1.380(3)
C1–C2	1.453(4)	C2–C3	1.393(4)
C2–C7	1.405(4)	C3–C4	1.381(4)
C4–C5	1.409(4)	C5–C6	1.385(4)
C6–C7	1.381(4)		
C1–N1–N1'	111.9(2)	C4–O1–C8	115.6(6)
N1–C1–C2	123.7(2)	O1–C4–C3	125.6(2)
O1–C4–C5	114.1(2)	O2–C5–C6	118.5(2)
O2–C5–C4	122.2(2)	O3–C6–C7	122.9(2)
O3–C6–C5	116.2(2)		
[(bpy) ₂ Co(BACat)] ⁺			
Co–N1	1.918(3)	Co–N3	1.925(3)
Co–N2	1.931(3)	Co–N4	1.918(3)
Co–O1	1.873(3)	Co–O2	1.877(3)
C–O ^{Cat}	1.341(3)	C ^{Ring} –C ^{Ring}	1.395(3)
O1–Co–O2	88.1(1)	N1–Co–N2	83.4(1)
N3–Co–N4	83.3(1)		

calculated for the ring atoms of the catechol group. With the imposed inversion symmetry, all atoms of both catechol rings and all atoms of the bridge are within error of being coplanar. Bond lengths between carbon atoms within the catechol ring are consistent with values found typically for catechols and catecholate ligands. Lengths within the bridge indicate that delocalization across the N–N bond must play a relatively minor role in stabilizing the planar structure of the molecule. In particular, the N–N length across the center of inversion symmetry is close to a single-bond value with a distance of 1.423(4) Å, and the C=N double bond of the bridge has a localized double-bond value of 1.293(3) Å (Table 2). Consequently, the planar structure of the ligand, while of potential importance in supporting long-range coupling between metal ions chelated at the catecholate sites, is not associated with delocalization across the N–N bond

Scheme 1



of the bridge on a level that can be detected from structural features.

Reactions carried out between H₄thB and bpy and Co(AcO)₂ gave crystals of [Co₂(bpy)₄(thB)](BF₄)₂ as an unusually unstable solvate, and it was disappointing that intensity data obtained gave a structural result unsuitable for publication. However, it was found that the crystals formed in monoclinic space group *P*2₁/*c* with *Z* = 2. This points to a centrosymmetric structure for the [Co₂(bpy)₄(thB)]²⁺ cation, and features of the thB bridge likely have the planar structure of H₄thM with chelated metal ions separated by approximately 16 Å.

IR and UV-Vis Spectra. Infrared spectra obtained on complexes consisting of Co^{III}(bpy)₂ groups coordinated by bridging thB, thM, and thA ligands are consistent with the chelated catecholate structure for the metal ions shown in Scheme 1. Specifically, the complexes show intense peaks at 1607 and 1569 cm⁻¹ due to the -CH=N- group and shifted only slightly from corresponding bands of the free bis(catechol). Additionally, they show strong bands at 1264 (*ν*(C-O)) and at 1480 cm⁻¹ (aromatic ring) that have been associated with catecholate chelation to cobalt(III).¹⁵

Electronic spectra have been reported for [(N₄)Co^{III}(Cat)]⁺ complexes prepared with saturated amine ligands (2 en, trien).¹⁵ They generally show a single absorption in the visible between 550 and 620 nm with a molar extinction coefficient of approximately 170 M⁻¹ cm⁻¹. Brown has assigned this band as the ¹A_{1g} → ¹T_{1g} d-d transition, with intensity enhancement associated with the catecholate ligand.¹⁵ The higher-energy ¹A_{1g} → ¹T_{2g} transition appears overlapped with an intense π → π* transition of the catecholate ligand that appears in the 350 nm region. Substitution of 2,2'-bipyridine for the amine nitrogen donors would be expected to increase the energy of these ligand-field transitions, but the inverse is true, possibly questioning their assignment. The dihydroxybenzaldehyde cation [Co(bpy)₂(BACat)]⁺, obtained under unusual circumstances that will be described below, shows an intense band at 343 nm that is presumably the catecholate π → π* transition and a low-intensity band at 652 nm that can be assigned as a ligand-field transition. The dimeric cations [Co₂(bpy)₄(thB)]²⁺ and [Co₂(bpy)₄(thM)]²⁺ show an intense band in the 400 nm region. This band contains a low-intensity shoulder on the low-energy side and a second low-intensity band that may be a ligand-field transition at 718 nm for [Co₂(bpy)₄(thB)]²⁺ and [Co₂(bpy)₄(thM)]²⁺ (Figure 2). Taken with the spectral data reported earlier by Brown, there seems to be no clear pattern

(15) Wicklund, P. A.; Beckmann, L. S.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 1996.

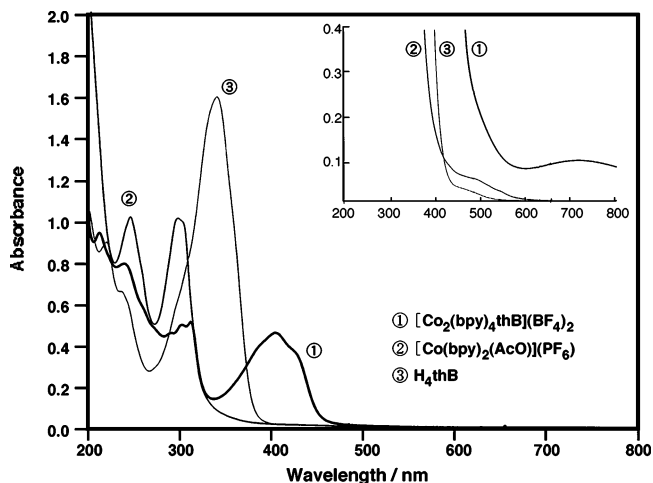


Figure 2. UV-visible spectra of [Co₂(bpy)₄(thB)](BF₄)₂, [Co(bpy)₂(CH₃COO)](PF₆), and H₄thB in CH₃CN.

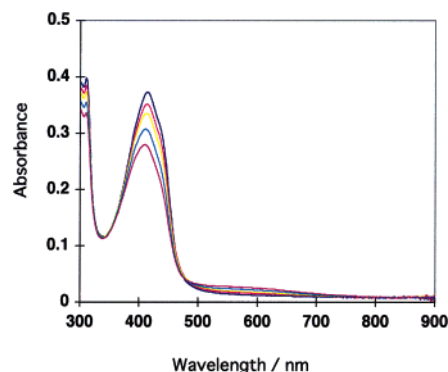


Figure 3. Temperature-dependent changes in the electronic spectrum of [Co₂(bpy)₄(thM)](PF₆)₂ in acetonitrile solution. Spectra were recorded at 10 °C intervals from 25 to 65 °C. Note the decrease in the absorbance at 400 nm with the increase in intensity of the low-intensity band at 600 nm.

for the low-energy low-intensity transitions that would be consistent with a ligand-field interpretation; the band in the 400 nm region for the dimeric complexes is likely associated with the bis(catecholate) ligand. To further complicate the spectral interpretation, the spectrum of [Co₂(bpy)₄(thM)]²⁺ was found to exhibit a temperature dependence in acetonitrile solution (Figure 3). As the solution was increased in temperature from 25 °C, the intensity of the 400 nm transition decreased, the intensity of the band at 620 nm increased, and an isobestic point appeared near 470 nm. This suggested a temperature-dependent shift in electronic structure in solution and the potential formation of a Co^{II}(SQ) species stable in solution at high temperature. The presence of a paramagnetic Co(II) redox isomer should be easily detected by ¹H NMR.

¹H NMR Spectra and Valence Tautomerism. ¹H NMR spectra recorded on [Co₂(bpy)₄(thB)]²⁺ and [Co₂(bpy)₄(thA)]²⁺ at room temperature were clearly resolved. Specific assignments for resonances could be made from spectra obtained on the free H₄thB and H₄thA ligands and for the bipyridine ligands by comparison with *cis*-Ru(bpy)₂Cl₂.¹⁶ The 2D NMR of [Co₂(bpy)₄(thB)]²⁺ is shown in Figure 4, and

(16) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239.

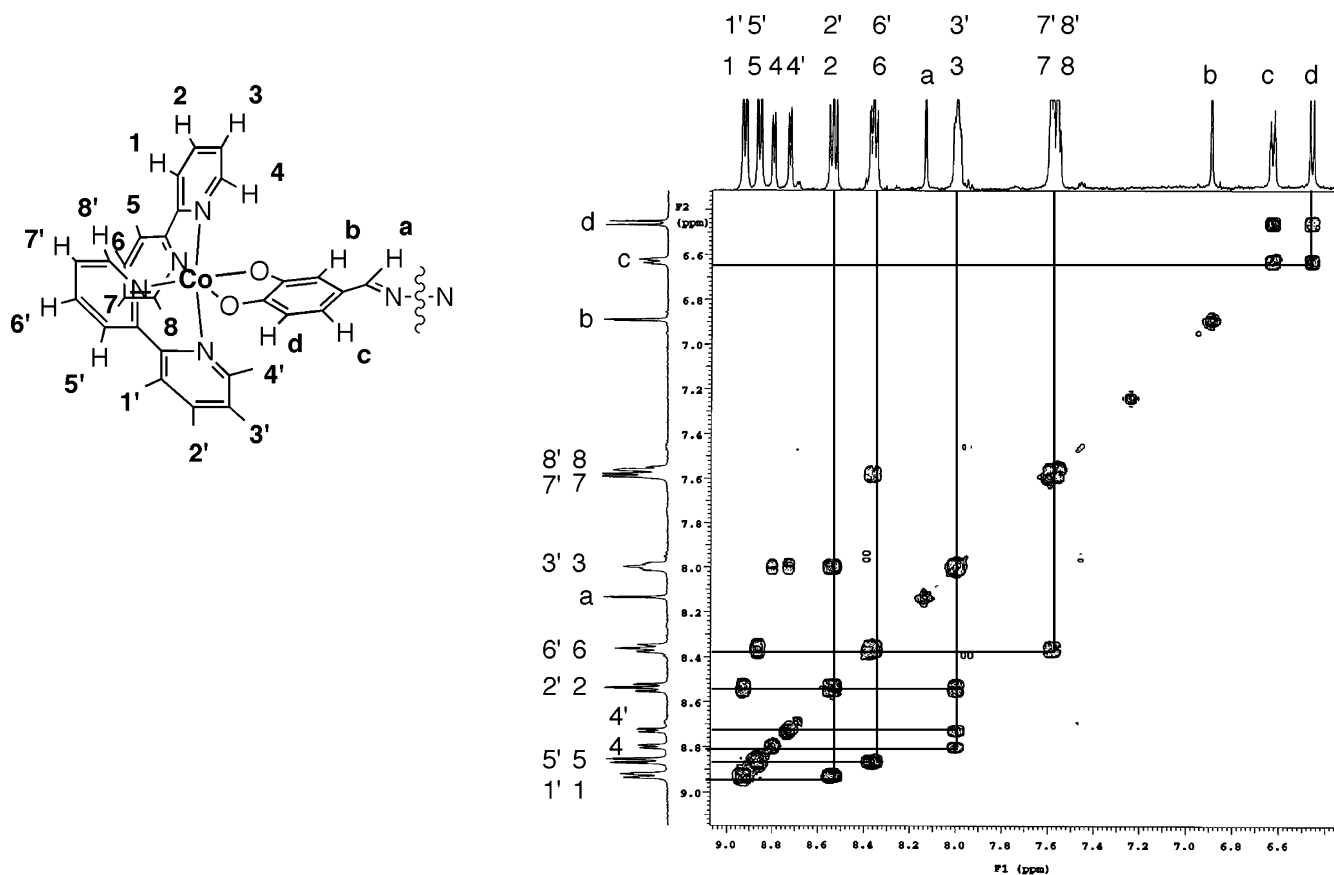


Figure 4. 2D ^1H NMR spectrum of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ using $\text{DMSO}-d_6$ as solvent.

Table 3. ^1H NMR Chemical Shift Assignments (ppm) for $[\text{Co}_2(\text{bpy})_4(\text{thB})]^{2+}$ and H_4ThB in $\text{DMSO}-d_6$ (See Labels in Figure 4)

^1H	$[\text{Co}_2(\text{bpy})_4(\text{thB})]^{2+}$	H_4thB
	thB	
H_a	8.140	8.433
H_b	6.896	7.283
H_c	6.624–6.644	7.058–7.083
H_d	6.475	6.770–6.790
	bpy	
$\text{H}_1, \text{H}_{1'}$	8.919–8.939	
$\text{H}_2, \text{H}_{2'}$	8.518–8.561	
$\text{H}_3, \text{H}_{3'}$	7.985–8.018	
H_4	8.798–8.812	
$\text{H}_{4'}$	8.724–8.739	
$\text{H}_5, \text{H}_{5'}$	8.855–8.874	
$\text{H}_6, \text{H}_{6'}$	8.343–8.386	
$\text{H}_7, \text{H}_{7'}$	7.565–7.597	
$\text{H}_8, \text{H}_{8'}$	7.565–7.597	

assignments for resonances are given in Table 3. In contrast, the resonances in the aromatic region for $[\text{Co}_2(\text{bpy})_4(\text{thM})]^{2+}$ showed evidence of broadening at room temperature but sharpened to give a spectrum similar to those of the other two complexes at 0°C . Spectra recorded at temperatures above 25°C were measured to see if paramagnetic broadening could be observed that might be associated with a shift to a $\text{hs-Co}^{\text{II}}(\text{SQ})$ redox isomer in solution at higher temperatures. Resonances appeared to broaden into the baseline at the higher temperatures but without evidence for a paramagnetic shift in position. Measurements on T1 values for the resonances over the temperature range from 20 to 60°C indicated that they remained constant as the spectrum lost resolution. This is an indication that the collapse of the

spectral resonances is not associated with the formation of a paramagnetic form of the complex. Rather, the loss of resolution is more likely associated with a dynamic process that averages resonance positions, ultimately giving a coalesced time-averaged spectrum at some high temperature. In fact, from the assignments for the specific bipyridine resonances, it is possible to conclude that, not only are the two unique bpy ligands exchanging coordination sites, but also that the two unique halves of the coalesced bpy, with nitrogens trans to either oxygen or nitrogen, coalesce to give four resonances for the ring protons. The temperature-dependence of the spectrum is shown in Figure 5. As temperature is increased to the upper temperature limit of 80°C for acetonitrile, resonances for the 1, 5, 1', and 5' protons coalesce to a single doublet at 8.6 ppm, the 2, 6, 2', and 6' resonances coalesce to a broad singlet at 8.3 ppm, and the 3, 7, 3', and 7' resonances coalesce to a broad resonance at 7.7 ppm. The 7 and 7' resonances that appear at 7.4 ppm and the 4 and 4' resonances at 8.7 and 8.9 ppm at 0°C collapse into the baseline but are too widely separated to give a coalesced resonance within the available temperature range. Resonances for the ring protons of the thM ligand appear as two closely spaced resonances near 6.6 ppm at -40°C . They are observed to move apart as temperature is increased, while resonances for the imine proton and the methoxy methyl group remain essentially fixed in position through the temperature range. The temperature range over which this spectral change takes place is the same as that of the changes observed in the visible region for $[\text{Co}_2(\text{bpy})_4(\text{thM})]^{2+}$.

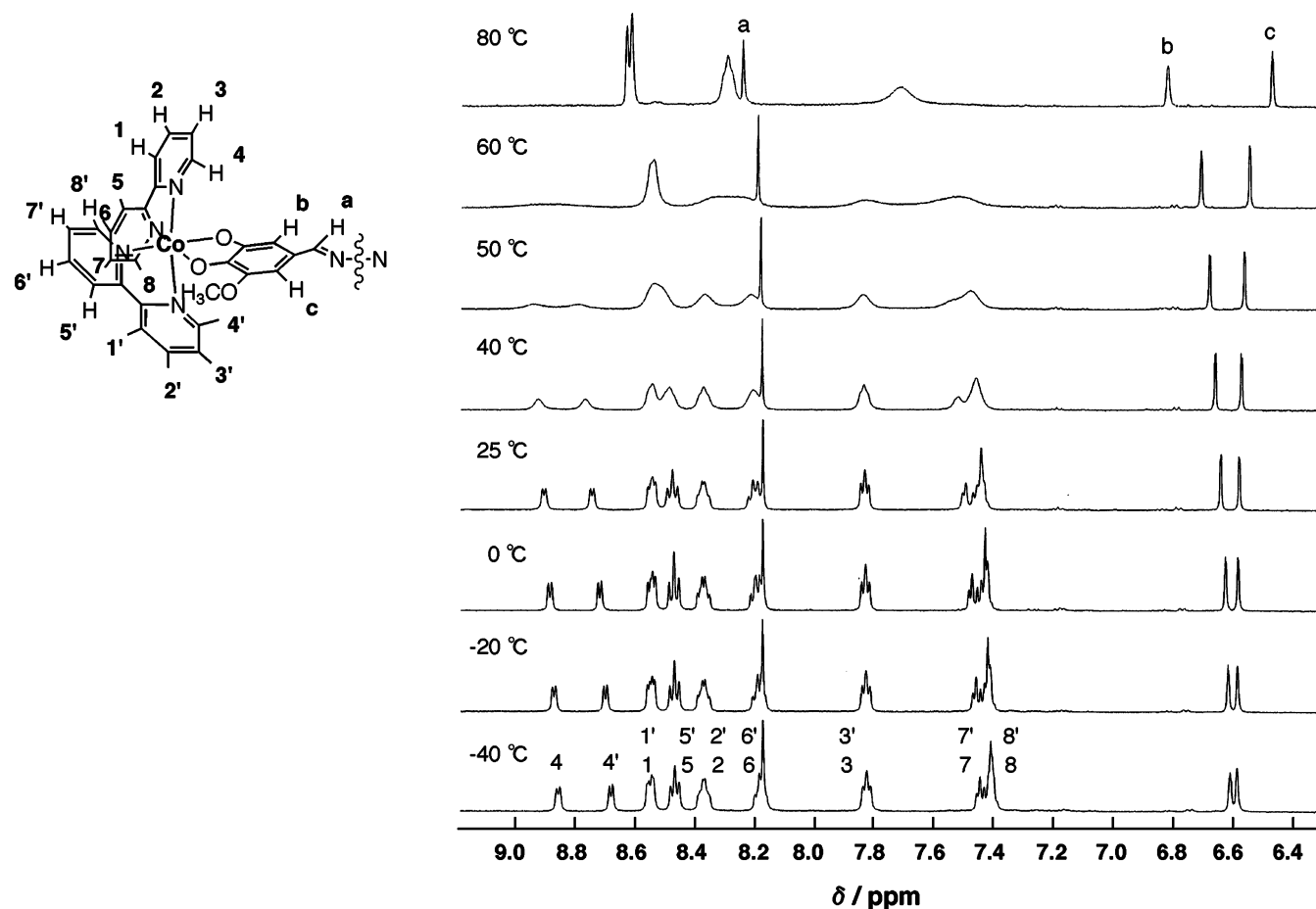


Figure 5. ^1H NMR spectra with various temperature of $[\text{Co}_2(\text{bpy})_4(\text{thM})](\text{PF}_6)_2$ using CD_3CN as solvent.

Differences in the coordination chemistry of the two common ions of cobalt are striking. Octahedral complexes of Co(II) are generally high-spin and both kinetically and stereochemically labile, while corresponding complexes of Co(III) are low-spin, diamagnetic, and inert to ligand exchange and stereodynamic shifts in structure.¹⁷ Optically active complexes of Co(III) may be resolved in solution without evidence for racemization, and this is particularly true for complexes containing diimine ligands such as 2,2'-bipyridine and 1,10-phenanthroline.¹⁷ This is due to the enormous disfavor of the trigonal prismatic intermediate associated with nondissociative racemization and the high energy required for dissociation of a chelating nitrogen or oxygen ligand.¹⁸ With this, it was quite surprising to observe the apparent stereodynamic behavior of the Co(III) centers of $[\text{Co}_2(\text{bpy})_4(\text{thM})]^{2+}$. Further, it is only observed for the complex containing the thM bridge and not for the corresponding complexes prepared with the thA and thB ligands. Therefore, it appears to be associated with an electronic effect associated with the ring methoxide substituent. Electron transfer from one or both catecholate groups to the cobalt center(s) would produce labile Co(II) in a process that

appears to be coupled with the change in electronic spectrum in solution. However, there is no evidence in the NMR for the formation of a hs-Co(II) species that is stable on a time scale that would produce the paramagnetically shifted NMR spectrum that is generally observed for octahedral Co(II).⁶ It is likely that the transition temperature for the equilibrium between $\text{Co}^{\text{III}}(\text{Cat})$ and $\text{Co}^{\text{II}}(\text{SQ})$ redox isomers is well above the temperature range accessible in acetonitrile solution. At the upper experimental temperature range, the equilibrium still favors the $\text{Co}^{\text{III}}(\text{Cat})$ isomer, with $\text{Co}^{\text{II}}(\text{SQ})$ present at low concentration, but sufficiently long-lived to permit equilibration of the bpy ligands in a dynamic process. With the thA and thB ligands, the transition temperature is sufficiently high that even at 80 °C there is no clear evidence for the onset of valence tautomerism.

Electrochemistry. Cyclic voltammograms were recorded on the three binuclear complexes in acetonitrile solution. All three show two closely spaced quasi-reversible oxidations in the potential range between +0.3 and +0.7 V (vs Fc/Fc^+). However, $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ and $[\text{Co}_2(\text{bpy})_4(\text{thA})](\text{ClO}_4)_2$ have low solubility for acetonitrile; these cyclic voltammograms were not obtained a good quality data. Switching to DMSO solvent, the oxidation/reduction waves shown complicated data. Thus, the dissociation of Biscat from the metal may be occurred in this solution. The result of $[\text{Co}_2(\text{bpy})_4(\text{thM})](\text{PF}_6)_2$ in acetonitrile solution is shown in Figure 6. The two oxidations of $[\text{Co}_2(\text{bpy})_4(\text{thM})](\text{PF}_6)_2$

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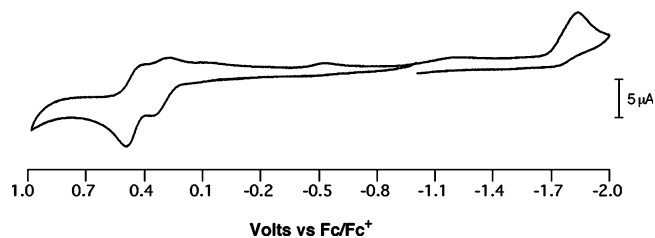


Figure 6. Cyclic voltammogram on $[\text{Co}_2(\text{bpy})_4(\text{thM})](\text{PF}_6)_2$ measured in CH_3CN solution at a scan rate of 50 mV/s.

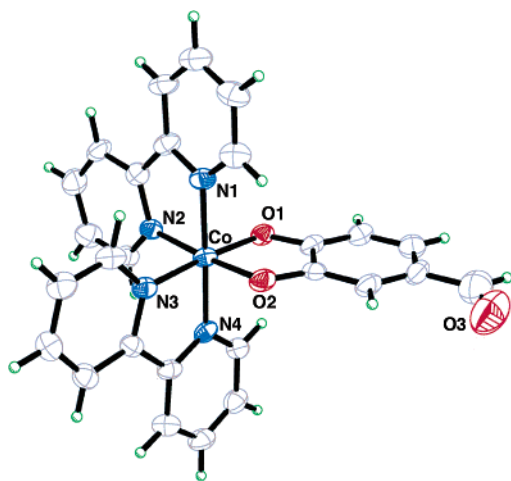


Figure 7. View showing the structure of the $[\text{Co}(\text{bpy})_2(\text{BACat})]^+$ cation obtained by oxidation of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ with $\text{Ag}(\text{BF}_4)$. Thermal ellipsoids are at the 50% probability level.

were shifted negatively by 0.1 V relative to the corresponding oxidations of the other two complexes, an effect associated with the electron-releasing property of the ring methoxide substituents. The two oxidations are separated by approximately 0.25 V, suggesting that they correspond to stepwise Cat-Cat/Cat-SQ and Cat-SQ/SQ-SQ steps of the bridging ligands rather than two-electron Cat-Cat/SQ-SQ and SQ-SQ/BQ-BQ couples. The electronic structure of the bridging ligand of $[(\text{bpy})_2\text{Co}^{\text{III}}(\text{SQ-SQ})\text{Co}^{\text{III}}(\text{bpy})_2]^{2+}$ would have significantly greater carbonyl character at the C–O bond trans to the carbon of the azine bridge. Potential dissociation of this ketonic oxygen from the metal may be significant in contributing to the formation of products responsible for low-current reductions that appear over the range between +0.1 and –1.5 V for solutions prepared with

pure samples of the binuclear complexes. At potentials on the negative side of –1.5 V, irreversible reductions appear that correspond to reduction of the bpy ligands.

Chemical Oxidation of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ and Characterization on $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$. Chemical oxidation reactions were carried out using $\text{Ag}(\text{BF}_4)$ in an effort to isolate oxidized forms of the binuclear complexes containing semiquinonate ligands. A reaction was carried out with $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ dissolved in acetonitrile. Upon addition of 2 equiv of Ag^+ , the brown solution was observed to turn slightly green, and over the period of several days, brown crystals separated from the solution. Crystallographic characterization on the product indicated that it was $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$, where BACat is the deprotonated dianion of 3,4-dihydroxybenzaldehyde. A view of the complex cation is shown in Figure 7; bond lengths and angles listed in Table 2 are in complete accord with a $\text{Co}^{\text{III}}(\text{Cat})$ charge distribution for the cation. Clearly, the azo group has been eliminated from the 3,3',4,4'-tetrahydroxybenzaldazine and replaced by oxygens during the period of time required for crystallization. The UV–vis spectrum of $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$ consists of a ligand-field transition at 652 nm ($184 \text{ M}^{-1} \text{ cm}^{-1}$) and a catecholate $\pi \rightarrow \pi^*$ transition at 343 nm ($1.12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Electrochemical characterization on the complex showed a reversible couple at –0.52 V that may be assigned as a Cat/SQ oxidation and an irreversible oxidation at +0.40 V that corresponds to SQ oxidation to BQ. Oxidation of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ has been followed by monitoring changes in the ^1H NMR spectrum upon oxidation with Ag^+ in a dry DMSO solution. The most dramatic change in the NMR spectrum occurs for the imine proton of the bridge (Figure 8). This proton resonance appears at 8.140 ppm for $[\text{Co}_2(\text{bpy})_4(\text{thB}^{\text{Cat,Cat}})]^{2+}$. Oxidation with Ag^+ occurs as a thB ligand-based two-electron process forming the SQ–SQ tetracation, $[\text{Co}_2(\text{bpy})_4(\text{thB}^{\text{SQ,SQ}})]^{4+}$. The imine proton resonance shifts slightly upon oxidation to 8.285 ppm. No evidence for a paramagnetic Cat,SQ mixed-charge ligand species could be detected during oxidation. During exposure to air for the period of several days, the NMR spectrum of $[\text{Co}(\text{bpy})_2(\text{BACat})]^+$ developed slowly, with a shift in the resonance for the aldehyde (formerly the imine) proton to 9.416 ppm and other changes associated with the ring proton resonances (Figure 9).

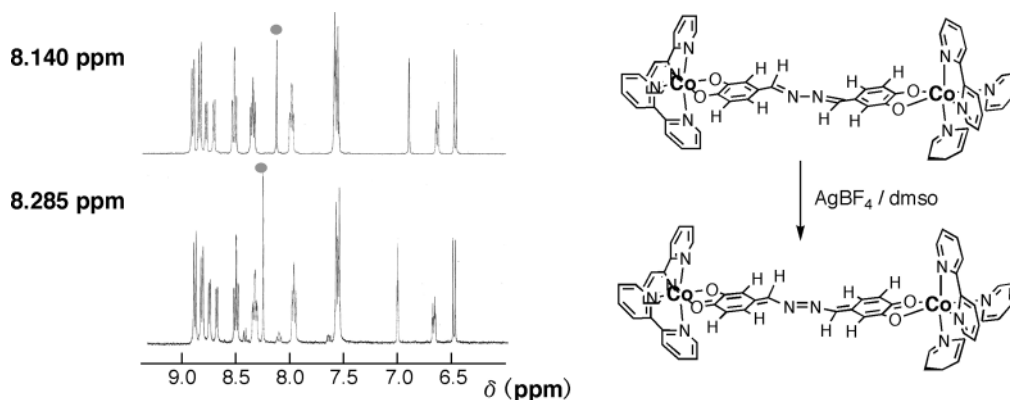


Figure 8. Changes in the ^1H NMR spectrum of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ upon addition of AgBF_4 in $\text{DMSO-}d_6$.

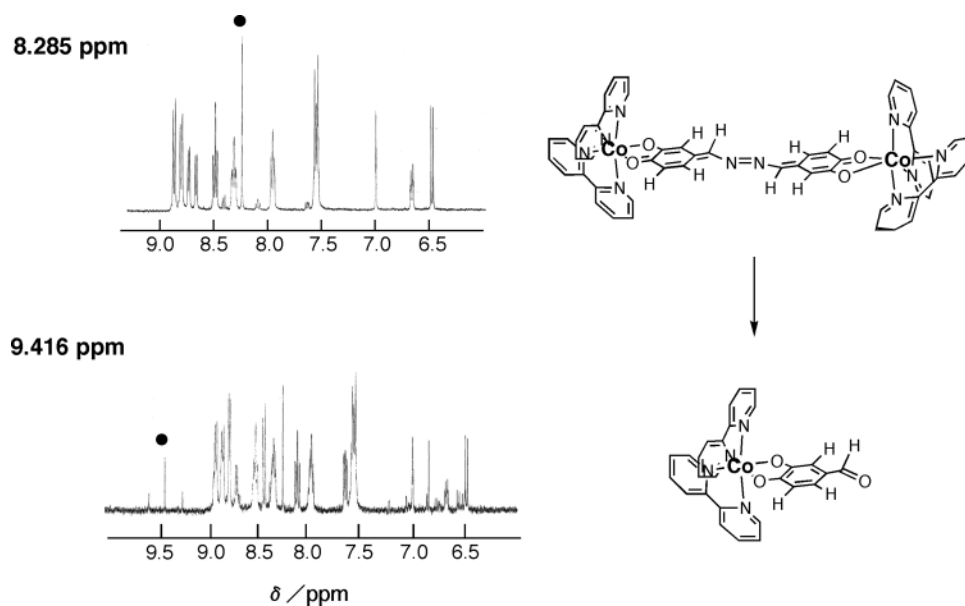


Figure 9. Changes in the ^1H NMR spectrum of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ over the period of 10 days in $\text{DMSO-}d_6/\text{AgBF}_4$ solution with oxidation to $[\text{Co}(\text{bpy})_2(\text{BACat})](\text{BF}_4)$.

Mechanistic details of the oxidation reaction remain unclear, but it is likely that trace quantities of water may be involved.

Summary

Interests in the switching properties of metal–dioxolene complexes that exhibit valence tautomerism have been directed at members of the $\text{L}_n\text{Co}^{\text{III}}(\text{Cat})/\text{L}_n\text{Co}^{\text{II}}(\text{SQ})$ series.¹⁴ Differences in donor strength of the L_n ligands may be used to tune the conditions for electron transfer. The transition from $\text{ls-Co}^{\text{III}}(\text{Cat})$ to $\text{hs-Co}^{\text{II}}(\text{SQ})$ has an accompanying diamagnetic/paramagnetic change in magnetism that may facilitate detection, and properties of ancillary ligands and counterions may contribute to hysteretic effects. The rationale in these investigations draws from studies on spin-transition complexes of Fe(II), with the potential for optically induced shifts in charge distribution and magnetic properties. While there are several $\text{Co}^{\text{III}}(\text{Cat})$ complexes^{15,19} and a few examples of $\text{Co}^{\text{II}}(\text{SQ})$ coordination,²⁰ only the $[\text{Co}(\text{CTH})(\text{Phendio})]^+$ cation has been found to undergo valence tautomerism within a temperature range that may be observed by using variable-temperature magnetic measurements.²¹ It is not unreasonable that the stereodynamic property of $[\text{Co}_2(\text{bpy})_4(\text{thM})]^{2+}$ may be coupled with the onset of a transition to a Co(II) redox isomer. Donation effects of the

bpy ligands place the temperature range of the transition well above room temperature, but the electron-releasing methoxy substituents of the thM Cat rings lowers the transition temperature for $[\text{Co}_2(\text{bpy})_4(\text{thM})]^{2+}$ relative to the related complexes with the thA and thB ligands.

Oxidation of the bis(catecholate) bridges of the complexes appears to occur as two closely spaced one-electron processes, without observation of a paramagnetic mixed-charge Cat-SQ species. Slow aerobic oxidation of the product formed by two-electron oxidation of $[\text{Co}_2(\text{bpy})_4(\text{thB})](\text{BF}_4)_2$ with Ag^+ was observed to give $[\text{Co}(\text{bpy})_2(\text{BACat})]^+$ as a new and structurally characterized example of $\text{Co}^{\text{III}}(\text{Cat})$ coordination.

Acknowledgment. This work was supported by Kinki University and University of Colorado at Boulder. We would like to thank Mike McNevin for assistance with the X-ray measurements and Dr. Richard Shoemaker for help with NMR spectral analyses. Y.S. would like to dedicate this paper to his many friends in Boulder.

Supporting Information Available: Crystallographic information files for the title compounds (cif). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC050250M

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