

Bistable Molecular System *via* Intramolecular Electron Transfer: the First Cyclodimeric 1,2-Semiquinonato/Catecholacobalt Complex Containing 1,4-Bis(dimethyl-3-pyridylsilyl)benzene

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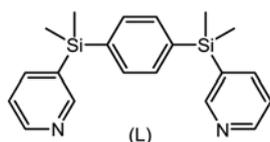
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Metal complexes containing 1,2-semiquinonato (sq^- , $S = 1/2$) and catecholato (cat^{2-} , $S = 0$) ligands have shown a unique bistability *via* the intramolecular electron transfer between the metal and the ligand around room temperature.¹ Different valence states of the bistable complexes have significantly different charge and spin distributions, and consequently, show different optical, electric, and magnetic properties.^{2,3} This has been very prominently elucidated for the cobalt complexes where temperature- and photo-dependent equilibria between the $[\text{Co}^{\text{III}}]$ and $[\text{Co}^{\text{II}}]$ valence tautomeric species have been demonstrated both in solution and in the solid state.^{4,5} Such electronic-labile complexes have been utilized as potential building blocks for molecular electronic devices,⁶⁻⁸ and are very sensitive to environment such as temperature, solvent, state, and photo-energy. Even though some dicobalt valence tautomeric systems were reported,^{9,10} but the corresponding cyclodimeric cobalt complexes remain unexplored. In order to construct new cyclodimeric cobalt complexes, 1,4-bis(dimethyl-3-pyridylsilyl)benzene (L) as a bridged bidentate ligand was provided. Herein we report the synthesis, structure, and physico-chemical properties of unprecedented cyclodimeric valence tautomeric cobalt complex.



The cyclodimeric cobalt complex was smoothly synthesized using a potential horse-shoe type bidentate L instead of simple bidentate coligands according to the procedures described in earlier studies:^{2,11,12} the reaction between $[\text{Co}_2(\text{CO})_8]$ and 3,5-dbbq in the presence of L in diethyl ether at room temperature afforded single crystals suitable for X-ray crystallography. The product was soluble in common solvents such as toluene, benzene, tetrahydrofuran, acetone, dimethyl sulfoxide, and *N,N*-dimethylformamide, indicating that the product is discrete molecule rather than polymeric species. However, the product was easily dissociated in dimethyl sulfoxide, alcohols, and *N,N*-dimethyl-

formamide. Formation of the desirable cyclodimeric complex may be attributed to a subtle combination of 3,5-dbbq ligand and L coligand. For example, 3,6-dbbq (3,6-di-*tert*-butyl-1,2-benzoquinone) was used instead of 3,5-dbbq, the cyclodimeric complex was not formed. Furthermore, in the case of 1,4-bis(dimethyl-4-pyridylsilyl)benzene instead of 1,4-bis(dimethyl-3-pyridylsilyl)benzene such a cyclodimeric structure was not constructed. The cyclodimeric cobalt complex was characterized based on spectral, magnetic, and X-ray crystallography.

Dark blue crystals were obtained as diethyl ether solvates. A view of the molecule is depicted in Figure 1. The ligand is coordinated to two cobalt ions, resulting in formation of a centrosymmetric 26-membered cyclodimeric square. The structural data suggests that the molecule exists as $[\text{Co}^{\text{III}}(3,5\text{-dbbq})(3,5\text{-dbcatal})_2(\text{L})]_2$ in the solid state at 173 K. In the Figure 1, oxygen atoms O(1) and O(2) ($\text{O}(1)\text{-C}(1) = 1.30(1)$ Å; $\text{O}(2)\text{-C}(2) = 1.32(1)$ Å) are associated with the 3,5-di-*tert*-butyl-1,2-semiquinonato (3,5-dbsq⁻, $S = 1/2$), and O(3) and O(4) ($\text{O}(3)\text{-C}(15) = 1.35(1)$ Å; $\text{O}(4)\text{-C}(16) = 1.34(1)$ Å) belong to 3,5-di-*tert*-butylcatecholato (3,5-dbcatal²⁻, $S = 0$). This is apparent from the ligand C-O bond lengths which average to 1.30 Å for the semiquinonato and 1.34 Å for the catecholato ligands.¹³ Furthermore, the bond lengths of CoO (1.870(6)-1.893(6) Å) are also shorter than general Co^{II}-O bonds (≥ 2.00 Å). The radius of low spin $[\text{Co}^{\text{III}}]$ is roughly

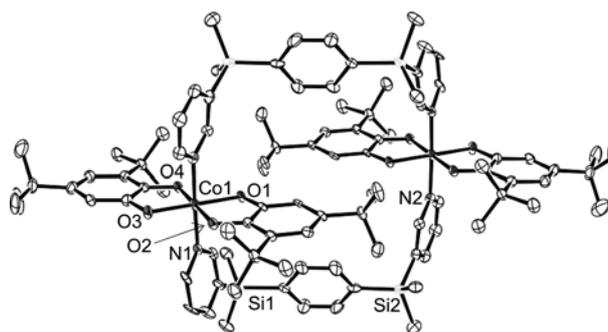


Figure 1. ORTEP drawing of $[\text{Co}^{\text{III}}(3,5\text{-dbsq})(3,5\text{-dbcatal})(\text{L})]_2 \cdot 5\text{C}_4\text{H}_{10}\text{O}$ along with thermal ellipsoids at the 20% level. Hydrogen atoms and solvated molecules were omitted for clarity.

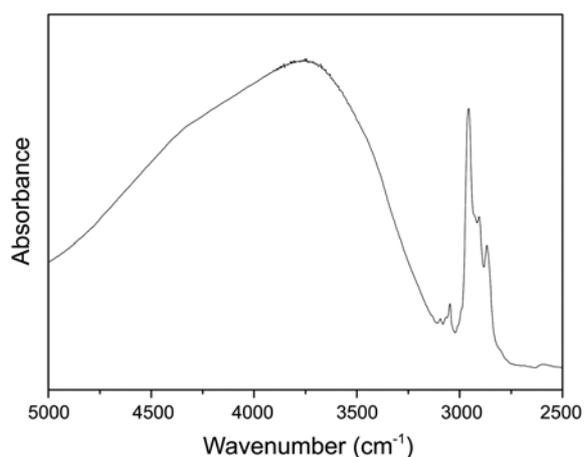


Figure 2. IR spectrum of $[\text{Co}^{\text{III}}(3,5\text{-dbsq})(3,5\text{-dbcac})(\text{L})_2]$.

0.2 Å shorter than the radius of high spin $[\text{Co}^{\text{II}}]$.² Thus, the molecule is clearly a low spin $[\text{Co}^{\text{III}}]$ species with one 3,5-dbcac²⁻ and one 3,5-dbsq⁻ ligand in the solid state at 173 K. The local geometry around the cobalt ion is severely distorted from a typical octahedral arrangement. The low spin $[\text{Co}^{\text{III}}]$ would be expected to be in a rigidly octahedral arrangement¹⁴ in contrast to a few examples of the high spin $[\text{Co}^{\text{II}}]$ trigonal prism.¹⁵

IR spectrum in the region of 5000-2500 cm^{-1} at room temperature is shown in Figure 2. The intensity of a characteristic broad band around 4000 cm^{-1} is dependent on the ratio of $[\text{Co}^{\text{III}}]/[\text{Co}^{\text{II}}]$ tautomers.¹³ The band is relatively weaker than that of $[\text{Co}_2(\text{hmteta})(3,6\text{-dbbq})_4]\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (hmteta = 1,1,4,7,10,10-hexamethyltriethylenetetramine) complex,¹⁰ indicating that, for the complex, the ratio of $[\text{Co}^{\text{III}}]/[\text{Co}^{\text{II}}]$ tautomers is low in the solid state at room temperature. Electronic spectra ($\sim 10^{-4}$ M) in the range of 400-900 nm were measured (Figure 3). There are two bands at 640 nm and 740 nm, which are characteristic of $[\text{Co}^{\text{III}}]$ and $[\text{Co}^{\text{II}}]$ tautomer, respectively.¹³ The electronic spectra are a proof that the compound exists as equilibrium between $[\text{Co}^{\text{III}}]$ and $[\text{Co}^{\text{II}}]$ in solution. The strong band at 740 nm

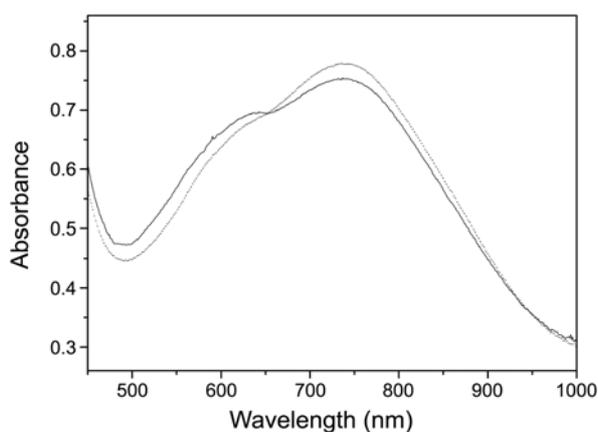


Figure 3. Electronic spectra of $[\text{Co}^{\text{III}}(3,5\text{-dbsq})(3,5\text{-dbcac})(\text{L})_2]$ $[\text{Co}^{\text{II}}(3,5\text{-dbsq})_2(\text{L})_2]$ in toluene (solid line) and diethyl ether (dotted line).

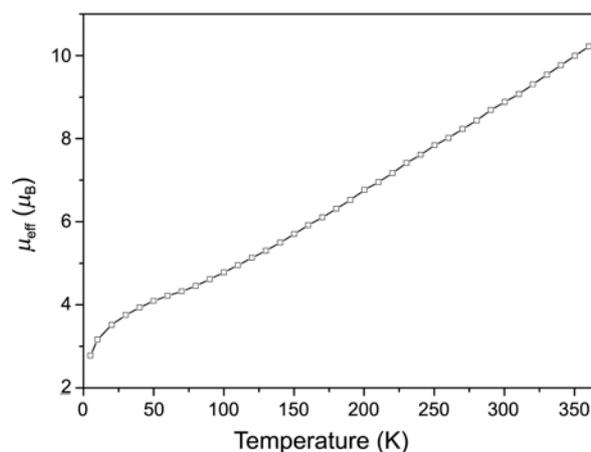


Figure 4. Magnetic measurements for $[\text{Co}^{\text{III}}(3,5\text{-dbsq})(3,5\text{-dbcac})(\text{L})_2]\cdot 5\text{C}_4\text{H}_{10}\text{O}$ in the solid state.

indicates that the high spin $[\text{Co}^{\text{II}}]$ is a major tautomer in solution, which is coincident with IR spectrum in the solid state. According to the solvent-dependent spectra, the ratio of $[\text{Co}^{\text{III}}]/[\text{Co}^{\text{II}}]$ is slightly dependent on solvents.

Magnetic measurements are an effective means of monitoring the equilibrium due to the change in metal spin state as well as the shift in charge distribution.⁷ The temperature-dependent magnetic moments recorded on solid samples are depicted in Figure 4. For the cyclodimeric molecule, the magnetic moments, μ_{eff} retain approximately 2.8 μ_{B} in 5 K, increasing the temperature range 5-360 K, and finally approach 10.2 μ_{B} at 360 K, indicating that the valence tautomerism occurs in the solid state. The spin only value of $[\text{Co}^{\text{III}}(3,5\text{-dbbq})(3,5\text{-dbcac})(\text{L})_2]$ at low temperature should be 3.46 μ_{B} , but 2.8 μ_{B} in 5 K may result from intramolecular weak-magnetic interaction at the temperature. The two $S = 3/2$ Co^{II} center couples with the four $S = 1/2$ radical semiquinonato ligands to give spin state $S = 10/2$ at high temperatures (10.2 μ_{B}). The molecule exists as $[\text{Co}^{\text{III}}(3,5\text{-dbsq})(3,5\text{-dbcac})(\text{L})_2]\cdot 5\text{C}_4\text{H}_{10}\text{O}$ at low temperature, and gradually shifts to $[\text{Co}^{\text{II}}(3,5\text{-dbsq})_2(\text{L})_2]\cdot 5\text{C}_4\text{H}_{10}\text{O}$ at high temperature. As a consequence, temperature-dependent magnetic behavior may be complicated, and the use of magnetic data to give a value for transition temperature is tenuous.

In conclusion, the first centrosymmetric cyclodimeric valence tautomeric cobalt complex was synthesized by a subtle combination of a unique ancillary bidentate ligand as a bridging spacer with 3,5-di-*tert*-butyl-benzoquinone. For the cyclodimer, the two cobalt ions have the same charge distribution, and the valence tautomeric equilibria between $[\text{Co}^{\text{III}}]/[\text{Co}^{\text{II}}]$ are monitored *via* electronic spectra and magnetic susceptibility. Further detailed intracyclodimeric effects on valence tautomerism and application are underway.

Experimental

Materials and Measurements. Dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) and 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-

dbbq) were purchased from Aldrich, and used without further purification. 1,4-Bis(dimethyl-3-pyridylsilyl)benzene (L) was prepared according to the procedures outlined in the literature.¹⁶ Elemental microanalyses (C, H, N) were performed on crystalline samples by the Pusan Center, KBSI, using a Vario-EL III. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. Electronic spectra were obtained on a UV-vis spectrophotometer S-3105. Temperature-dependent magnetic measurements were accomplished using a Quantum Design PPMS-9T SQUID magnetometer at a field of strength 10 kG.

[Co^{III}(3,5-dbsq)(3,5-dbcac)(L)]₂·5C₄H₁₀O. Co₂(CO)₈ (86 mg, 0.25 mmol) and L (174 mg, 0.50 mmol) were combined in 30 mL of diethyl ether. The mixture was stirred for 5 min, and 3,5-dbbq (220 mg, 1.00 mmol) dissolved in 30 mL of diethyl ether was added. The solution was stirred for 1 h at room temperature. The reaction mixture was filtered, and the reaction solution was leaved at -20 °C to obtain dark blue crystals (56% yield) suitable for X-ray single crystallography. Anal. Calcd. for C₁₁₆H₁₇₈N₄O₁₃Si₄Co₂: C, 67.41; H, 8.68; N, 2.71. Found: C, 66.90; H, 8.51; N, 2.70. IR (KBr, cm⁻¹): 3714 (br, s), 2956 (s), 1583 (m), 1400 (m), 1356 (m), 1330 (w), 1252 (m), 1134 (m), 985 (m), 816 (s), 773 (s), 706 (w), 667 (w), 490 (m).

Crystallographic Structure Determinations. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K α radiation (λ = 0.71073 Å) and a CCD detector at 170 K. Thirty-six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method (SADABS). The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).¹⁷ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in

Table 1. Crystallographic data for [Co^{III}(3,5-dbsq)(3,5-dbcac)(L)]₂·5C₄H₁₀O

Formula	C ₁₁₆ H ₁₇₈ N ₄ O ₁₃ Si ₄ Co ₂
<i>M_w</i>	2066.84
Space group	Monoclinic, C2/c
<i>a</i> (Å)	33.663(2)
<i>b</i> (Å)	17.871(1)
<i>c</i> (Å)	25.947(1)
β (°)	129.14(1)
<i>V</i> (Å ³)	12107.3(1)
<i>Z</i>	4
<i>d</i> _{calcd} , (g/cm ⁻³)	1.134
μ (mm ⁻¹)	0.370
<i>R</i> _{int}	0.1089
GoF on <i>F</i> ²	1.188
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0818
<i>wR</i> ₂ (all data) ^b	0.2083

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2)^{1/2}$$

Table 2. Selected bond lengths (Å) and angles (°) for [Co^{III}(3,5-dbsq)(3,5-dbcac)(L)]₂·5C₄H₁₀O

Co(1)–O(1)	1.892(6)
Co(1)–O(2)	1.888(6)
Co(1)–O(3)	1.871(6)
Co(1)–O(4)	1.870(6)
O(1)–C(1)	1.30(1)
O(2)–C(2)	1.32(1)
O(3)–C(15)	1.35(1)
O(4)–C(16)	1.34(1)
Co(1)–N(1)	1.949(8)
Co(1)–N(2)	1.930(8)
O(1)–Co(1)–O(2)	86.6(3)
O(3)–Co(1)–O(4)	87.9(3)
O(1)–Co(1)–O(3)	179.6(3)
O(2)–Co(1)–O(4)	178.4(3)
N(1)–Co(1)–N(2) ^{#1}	177.6(3)

^{#1} -x+1, -y+1, -z+1.

calculated positions and refined using a riding model. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1 and the relevant bond lengths and angles are listed in Table 2.

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Supporting Information. X-ray crystallographic data, in CIF format, for the structure determination of [Co^{III}(3,5-dbsq)(3,5-dbcac)(L)]₂·5C₄H₁₀O is deposited with the Cambridge Crystallographic Data Center, CCDC, under supplementary publication number CCDC-869625. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk.

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