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Characterization of the Chloranilate(•3–) π Radical as a Strong Spin-Coupling Bridging Ligand

Kil Sik Min,[†] Arnold L. Rheingold,[‡] Antonio DiPasquale,[‡] and Joel S. Miller*[,†]

Department of Chemistry, University of Utah, 315 South 1400 East, Room 2124, Salt Lake City, Utah 84112-0850, and Department of Chemistry, University of California, San Diego, La Jolla, California 92093-0358

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Dinuclear $[(TPA)Co^{II}(CA^{2-})Co^{II}(TPA)](BF_4)_2 \cdot 2MeOH$ (**1**) [TPA = tris-(2-pyridylmethyl)amine] and $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)](BF_4) \cdot 2Et_2O$ (**2**) with a bridging chloranilate radical ligand formed by reduction of **1** are crystallographically and magnetically characterized. **1** has shown a weak antiferromagnetic coupling within the Co^{II} dimer [$J/k_B = -0.65$ K (-0.45 cm^{-1})], while **2** has a 2 orders of magnitude stronger antiferromagnetic interaction between the Co^{II} ion and a radical [$J/k_B = -75$ K (52 cm^{-1})].

Molecule-based materials containing organic radicals have attracted considerable interest for the development of organic-based magnets[1] as well as valence tautomerism[2] and mixed-valence materials.[3] Metal complexes with 1,4-dihydroxybenzoquinonediide, chloranilate (CA^{2-}), ligands have been widely studied because they are good building blocks to make extended network structures because they can coordinate in a bis-bidentate manner.[4] However, metal compounds with the CA ligand as a radical, and consequently their spin-coupling ability, have yet to be described, although two dinuclear Co^{III} complexes with the $DHBQ^{\bullet 3-}$ (DHBQ = deprotonated 2,5-dihydroxy-1,4-benzoquinone) radical have recently been reported.[5] Herein, we report the formation of $[(TPA)Co^{II}(CA^{2-})Co^{II}(TPA)](BF_4)_2 \cdot 2MeOH$ (**1**) [TPA = tris(2-pyridylmethyl)amine] and its monoreduced species $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)](BF_4) \cdot 2Et_2O$ (**2**), revealing that the $CA^{\bullet 3-}$ trianion radical strongly spin couples with two high-spin $S = {}^3/_2$ Co^{II} ions.

1 was prepared from the reaction of $Co(BF_4)_2$, TPA, and CA in an inert-atmosphere glovebox.[6] Dark-red **2** was prepared by the one-electron reduction of **1** with $CoCp_2$.[7] Compound **2** can be formulated as either mixed-valent $[(TPA)Co^{I}(CA^{2-})Co^{II}(TPA)]^+$ or $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)]^+$ containing $CA^{\bullet 3-}$. In the cyclic voltammogram, the reduction potential ($E_{1/2}$) from **1** to **2** was at -1.04 V vs Fc/Fc^+ couple; thus, **1** can be reduced to **2** easily by $CoCp_2$ ($CoCp_2/CoCp_2^+$, $E_{1/2} = -1.33$ V).

Red-brown block-shaped crystals of **1** and **2** suitable for X-ray crystal analysis were obtained by allowing the reaction mixture to stand for several days without agitation or via diffusion with diethyl ether. The structures of the cations of **1** and **2** (Figure 1)[8] display a distorted octahedral geometry by coordinating with the four N atoms of TPA and the two O atoms of CA in the cis positions. Both **1** and **2** possess

* To whom correspondence should be addressed. E-mail: jsmiller@chem.utah.edu. Tel: 1 801 5855455. Fax: 1 801 5818433.
[†] University of Utah.
[‡] University of California, San Diego.

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(6) To a MeOH solution (10 mL) of $Co(BF_4)_2 \cdot 6H_2O$ (234 mg, 0.688 mmol) was added a MeOH solution (10 mL) of TPA (200 mg, 0.688 mmol) and a MeOH solution of chloranilic acid (H_2CA; 72 mg, 0.344 mmol) in a wet box (<1 ppm O_2). The color of the mixture resulted in a dark-red and then a dark-red-brown solution. Triethylamine (0.1 mL, 0.688 mmol) was added to the mixture for neutralization, which gives rise to a red-brown solution. Then the solution was heated to reflux for 30 min. The solution was allowed to stand at room temperature overnight, whereupon dark-red-brown crystals formed, which were collected by filtration, washed with MeOH, and dried in vacuo to afford 257 mg (65%) of **1**. Anal. Calcd for $C_{44}H_{44}B_2Cl_2Co_2F_8N_8O_6$: C, 46.22; H, 3.88; N, 9.80. Found: C, 46.25; H, 3.85; N, 9.96. FT-IR (KBr): ν_{CH} 3082 (w), 2919 (w), 1609 (s), ν_{CO} 1526 (vs), 1484 (s), 1438 (s), 1379 (s), 1291 (m), 1060 (m, br), 851 (s), 771 (s) cm^{-1}. Absorption spectrum (CH_2Cl_2): λ_{max}, nm (ϵ_M, L mol^{-1} cm^{-1}): 390 (5.5×10^3), 537 (8.3×10^2).
(7) To an MeCN solution (5 mL) of **1** (50 mg, 0.044 mmol) was added an MeCN solution (5 mL) of $CoCp_2$ (8.3 mg, 0.044 mmol) in a drybox (<1 ppm O_2). The color turned dark red. The solution was stirred for 1 h at room temperature. Red-brown block-shaped crystals of **2** were obtained by solvent diffusion of diethyl ether into the reaction mixture of acetonitrile for 2 or 3 days and then were collected by filtration, washed with MeCN, and dried in vacuo (yield: 40 mg, 80%). FT-IR (KBr): ν_{CH} 3065 (w), 2926 (w), 1604 (s), 1534 (w), 1481 (s), ν_{CO} 1442 (vs), 1264 (m), 1055 (m, br), 832 (s), 773 (s) cm^{-1}. Absorption spectrum (MeCN): λ_{max}, nm (ϵ_M, L mol^{-1} cm^{-1}): 247 (1.8×10^4), 330 (1.2×10^4), 484 (6.8×10^3), 562 (sh, 3.3×10^3), 738 (2.5×10^3). This compound is very sensitive to air.

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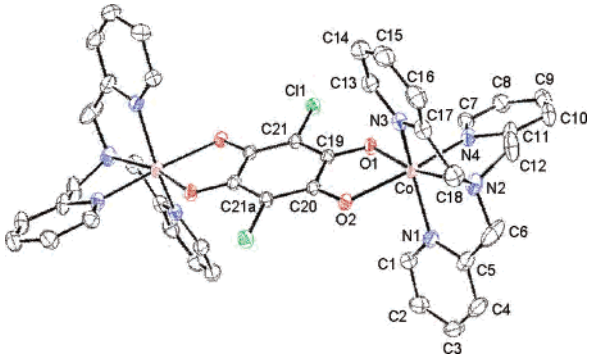

Figure 1. Structure of the monocation $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)]^{+}$ in crystals of **2**. The atoms are represented by 30% probable thermal ellipsoids. That of the dication in crystals of **1** is similar and not shown. H atoms, solvent, and $[BF_4]^{-}$ are omitted for clarity. Relevant distances (Å) and angles (deg): for **1**, Co−O1 2.030(2), Co−O2 2.277(3), Co−N1 2.110(3), Co−N2 2.239(3), Co−N3 2.080(3), Co−N4 2.108(3), C19−O1 1.266(4), C20−O2 1.246(4), C19−C20 1.527(5), C19−C21 1.372(5), C20−C21a 1.409(5), C21−Cl1 1.729(4), O1−Co−O2 74.29(9), N1−Co−N2 76.09(11), N2−Co−N3 77.61(11), N2−Co−N4 75.81(12); for **2**, Co−O1 1.978(2), Co−O2 2.166(2), Co−N1 2.085(2), Co−N2 2.262(2), Co−N3 2.090(2), Co−N4 2.109(2), C19−O1 1.304(3), C20−O2 1.282(2), C19−C20 1.473(3), C19−C21 1.386(3), C20−C21a 1.400(3), C21−Cl1 1.743(2), O1−Co−O2 79.62(7), N1−Co−N2 77.43(9), N2−Co−N3 76.06(8), N2−Co−N4 77.20(9).

crystallographic centers of symmetry, and average Co−O and Co−N bond distances are 2.106(2) and 2.134(2) Å and 2.072(1) and 2.137(1) Å for **1** and **2**, respectively. Interestingly, the average Co−L bond lengths are very similar to each other [$Co-L_{av}$ = 2.122(1) Å for **1** and 2.115(1) Å for **2**] and indicate that the oxidation state of the Co ion in **2** is 2+, as is the Co ion in **1**. Thus, the $[(TPA)Co^{I}(CA^{2-})Co^{II}(TPA)]^{+}$ formulation for **2** can be excluded. Furthermore, the average C−O bond distance [1.256(3) Å] of **1** is shorter than that of **2** [1.293(1) Å], while the C19−C20 bonds of **1** are longer than those of **2** by 0.054 Å. The significant difference is attributed to the reduction of CA^{2-} to $CA^{\bullet 3-}$ by $CoCp_2$. Additionally, the very strong peak at 1526 cm^{-1} for **1** shifts to 1442 cm^{-1} upon reduction, indicating that CA^{2-} in **1** is reduced to $CA^{\bullet 3-}$ in **2**, and a metal-centered reduction does not occur.

The pyridyl groups of TPA ligands in **1** and **2** are involved in offset $\pi-\pi$-stacking interactions[9] between the Co^{II} dimers, in which both complexes give rise to 1-D supramolecular network structures.

While several metal(II/III) dimers with bridged CA^{2-} have been reported,[4,10] however, this is the first example with the radical bridging the two spin-bearing metal sites. Thus, the magnetic properties of the $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)]^{+}$ cation were characterized to ascertain the spin coupling (J) between Co^{II} and $CA^{\bullet 3-}$ as well as for the presence of valence tautomerism and/or spin-crossover behavior(s).

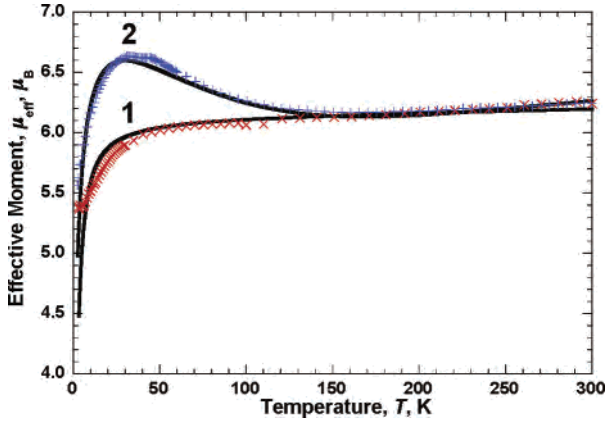

Figure 2. $\mu_{eff}(T)$ for **1** (×) and **2** (+). The solid lines are the best-fit curves to eqs 1 and 2, respectively.

Variable-temperature 2−300 K magnetic susceptibility, χ, measurements on solid samples of **1** and **2** have been performed on a SQUID magnetometer (external field 1000 Oe). For complex **1**, at room temperature, the effective moment, μ_{eff} [$=(8\chi T)^{1/2}$], is 6.26 μ_B/Co_2, and $\mu_{eff}(T)$ decreases monotonically with decreasing temperature to 5.38 μ_B at 3 K (Figure 2), indicating a very weak antiferromagnetic interaction within the $Co^{II}(CA^{2-})Co^{II}$ unit. $\chi(T)$ for **1** was fit to an analytical expression, eq 1 ($H = -2JS_1 \cdot S_2$), for a coupled $S = {}^3/_2$ dimer.[11] The best fit had J/k_B of −0.65 K (−0.45 cm^{-1}), $g = 2.24$, $\theta = -0.1$ K, and the temperature-independent paramagnetism, TIP = 4×10^{-4} emu mol^{-1}.[12] The weak interaction can be attributed to a long distance between the Co^{II} ions (8.089 Å)

$$\chi = [Ng^2\mu_B{}^2/k_B(T-\theta)]F(T) + \mathrm{TIP} \qquad (1)$$

where

$$F(T) = [2\exp(2J/k_BT) + 10\exp(6J/k_BT) + 28\exp(12J/k_BT)]/[1 + 3\exp(2J/k_BT) + 5\exp(6J/k_BT) + 7\exp(12J/k_BT)]$$

Complex **2** has a room temperature μ_{eff} of 6.20 μ_B/Co_2; $\mu_{eff}(T)$ decreases slightly with a decrease in the temperature to 6.17 μ_B at 160 K, then gradually increases to a maximum of 6.63 μ_B at 32 K, and again decreases to 5.56 μ_B at 2 K (Figure 2), indicating a strong antiferromagnetic interaction within the three-spin-site $Co^{II}(CA^{\bullet 3-})Co^{II}$ unit. $\chi(T)$ for **2** was fit to eq 2 [$H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$] for a linear three-spin system with $S_1 = S_3 = {}^3/_2$ and $S_2 = {}^1/_2$.[13] The best fit had J/k_B of −75 K (−52 cm^{-1}), $g = 2.36$, $\theta = -2.6$ K, and TIP

(8) Crystal and structural refinement parameters for **1** and **2**: for **1**, $C_{44}H_{44}B_2Cl_2Co_2F_8N_8O_6$, fw = 1143.25 g mol^{-1}, monoclinic, space group $C2/c$, a = 26.785(3) Å, b = 10.884(1) Å, c = 16.707(2) Å, β = 92.832(2)°, V = 4864.6(9) Å^3, Z = 4, d_{calcd} = 1.561 g cm^{-3}, μ(Mo Kα) = 0.879 mm^{-1}, R1 = 0.0545, wR2 = 0.1399; for **2**, $C_{50}H_{56}BCl_2Co_2F_4N_8O_6$, fw = 1140.60 g mol^{-1}, monoclinic, space group $P2/n$, a = 13.846(7) Å, b = 11.493(6) Å, c = 15.958(8) Å, β = 90.687(9)°, V = 2539(2) Å^3, Z = 2, d_{calcd} = 1.492 g cm^{-3}, μ(Mo Kα) = 0.831 mm^{-1}, R1 = 0.0469, wR2 = 0.1300. Data were collected on a Bruker SMART automatic diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Structures were solved by direct methods (*SIR-2004*) and refined by full-matrix least-squares refinement using the *SHELXL97* program.

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$= 4 \times 10^{-4}$ emu mol^{-1}.[12] The strong antiferromagnetic interaction is attributed to the overlap of the singly occupied molecular π^* orbital of $CA^{\bullet 3-}$ and the t_{2g} orbitals of the Co^{II} ion. This interaction is 2 orders of magnitude stronger than the weak antiferromagnetic interaction (-0.65 K) between the Co^{II} ions

$$\chi = \{Ng^2{\mu_B}^2/k_B(T-\theta)\}F(T) + \mathrm{TIP} \qquad (2)$$

where

$$F(T) = [84 + 35\exp(-J/k_BT) + 10\exp(-2J/k_BT) + \exp(-3J/k_BT) + \exp(-5J/k_BT) + 10\exp(-6J/k_BT) + 35\exp(-7J/k_BT)]/[16 + 12\exp(-J/k_BT) + 8\exp(-2J/k_BT) + 4\exp(-3J/k_BT) + 4\exp(-5J/k_BT) + 8\exp(-6J/k_BT) + 12\exp(-7J/k_BT)]$$

In conclusion, $[(TPA)Co^{II}(CA^{\bullet 3-})Co^{II}(TPA)]^+$ possessing $S = {}^1/_2$ $CA^{\bullet 3-}$ has been characterized, and the presence of $CA^{\bullet 3-}$ enhances the spin coupling between the $S = {}^3/_2$ Co^{II} centers by 2 orders of magnitude. Further studies on the magnetism and fabrication of new molecule-based materials containing different oxidation states exhibiting valence tautomerism and spin crossover are ongoing.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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