Paramagnetic Organocobalt(III) Dithiolate Complex: Crystal Structure and Magnetic Property of [Co(η^5-C_5Me_5)(C_3S_5)Br]

Hiroyuki Mori, Motohiro Nakano, Hatsue Tamura, Gen-etsu Matsubayashi, and Wasuke Mori[†]
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Toyonaka, Osaka 560-0043
[†]Department of Chemistry, Faculty of Science, Kanagawa University, Hiratuka, Kanagawa 259-1205

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The crystal structure of the paramagnetic, title complex revealed one-dimensional molecular interaction through S--S non-bonded contacts. The complex with the one-electron C_3S_5 ligand-centered oxidation exhibited a strong antiferromagnetic interaction in the solid state.

Paramagnetic metal complexes with the sulfur-rich $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate(2-)) ligand attract much attention since their molecular solids with intermolecular S--S interactions exhibit collective electronic properties such as electrical conductivity, superconductivity and magnetism.[1-3] Some C_3S_5-metal complexes containing cyclopentadienyl and pentamethylcyclopentadienyl groups have been studied as electroactive compounds.[4-7] However, their collective electronic properties in the solid state have never been studied. Although they have non-planar geometries, their oxidized species are expected to form new columnar and/or layered structures through S--S interactions in the solid state showing unique electrical and magnetic properties.

In this work, C_3S_5-organocobalt(III) complexes containing η^5-C_5H_5 and η^5-C_5Me_5 groups were oxidized by bromine to afford one-electron oxidized species, of which the title complex was isolated as crystals. The crystal structure of the complex revealed the one-dimensional molecular interaction through S--S contacts and the electrical conductivity was very low, while the magnetism exhibited a strong antiferromagnetic interaction among the oxidized C_3S_5-ligands in the solid state.

To a dichloromethane (15 cm^3) solution of [Co(η^5-C_5Me_5)(C_3S_5)] (**1**)[4] (120 mg, 0.31 mmol) was added with stirring a dichloromethane (4 cm^3) solution of bromine (0.16 mmol). To the solution was added hexane (200 cm^3) to afford dark violet microcrystals of [Co(η^5-C_5Me_5)(C_3S_5)Br] (**2**) (60% yield).[8] Recrystallization from a mixture of dichloromethane and hexane afforded dark violet plates suitable for the X-ray crystal structure analysis.[9] Although [Co(η^5-C_5H_5)(C_3S_5)] was also oxidized by bromine in solution, the one-electron oxidized species was quickly disproportionated to the original species and the further oxidized one in solution.[10]

Complex **2** dissolved in dichloromethane exhibits an ESR signal at g = 2.016. Figure 1 shows the observed and simulated spectra. The isotropic spectrum consists of an octet (^{59}Co, I = 7/2) of quartet (^{79}Br(50.54%) and ^{81}Br(49.46%), I = 3/2) ; ^{59}Co

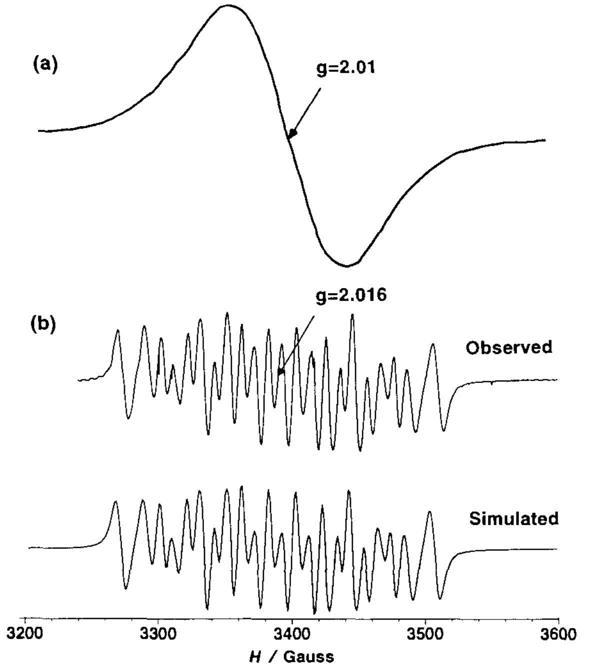

Figure 1. ESR spectra of complex **2** (a) in the solid state and (b) in dichloromethane (observed and simulated).

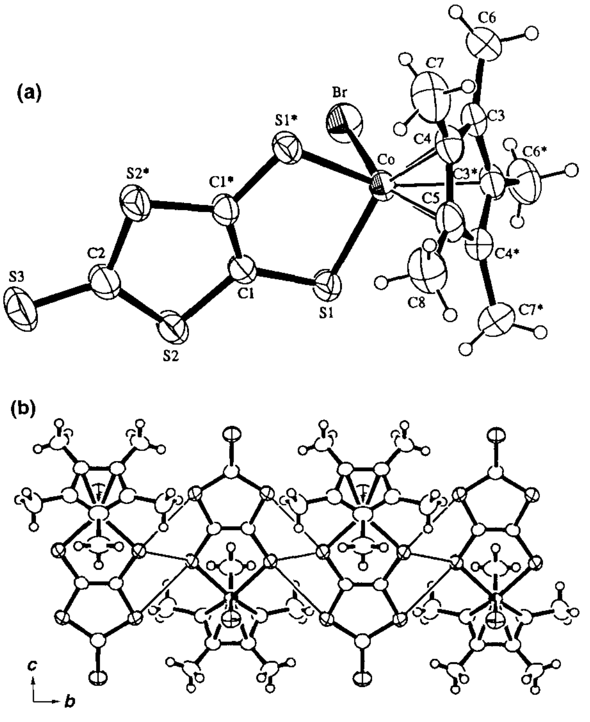

Figure 2. (a) Molecular structure of complex **2** and (b) the packing diagram along the a axis. Fine lines represent S--S non-bonded contacts less than 3.7 Å. Selected bond lengths and non-bonded S--S contacts (Å): Co-Br 2.3951(9), Co-S(1) 2.2173(9), Co-C(3) 2.106(3), Co-C(4) 2.093(3), Co-C(5) 2.053(5), S(1)-S(1') 3.667(1), S(1)-S(2') 3.791(2).

and $^{79/81}$Br hyperfine couplings are 1.9 and 2.8 x 10^{-3} cm^{-1}, respectively. These small values indicate insubstantial spin densities on the Co and Br atoms. In fact, Mulliken spin densities for the complex evaluated by a DFT calculation[11-13] showed the presence of 90% spins on the C_3S_5-ligand; Co, 0.005; Br, 0.058; S(1), S(1*), 0.322; S(2),S(2*); -0.01; S(3), 0.121; C(1),C(1*), 0.084; C(2), -0.016. In the solid state the broad ESR signal was observed at g = 2.01with the peak-to-peak linewidth of 10.7 mT. These findings suggest the C_3S_5-ligand-centered oxidation, as observed for some oxidized C_3S_5-metal complexes.[14-16]

Figure 2 shows (a) the molecular structure of **2** and (b) the molecular packing diagram projected along the a axis. Selected bond distances are given in the caption. The molecule has a mirror containing Co, Br, C(2) and S(3) atoms. The Co(III) complex **1** is oxidized by bromine to form a Co-Br bond [2.3951(9) Å]. The Co-S(1) distance [2.2173(9) Å] is longer than the Co-S distances [2.135(2) and 2.138(2) Å] of **1** and the C(1)-C(1*) distance [1.384(6) Å] also longer than the corresponding bond [1.352(9) Å] of **1**.[7] In accordance with these findings, **2** exhibited a C=C stretching frequency of the C_3S_5 ligand of 1350 cm^{-1}, which is lower by 44 cm^{-1} than that of **1**. Furthermore, **2** showed an XPS band of Co $2p_{1/2}$ electrons at 794.9 eV, which is almost the same as that (795.4 eV) of **1**. These findings reflect the C_3S_5 ligand-centered oxidation of **2**. The molecular packing diagram of **2** shows one-dimensional molecular interaction along the b axis through S--S non-bonded contacts [3.667(1) and 3.791(2) Å]. Such an interaction was not observed for complex **1** [the nearest S--S contact, 3.869(5) Å].[7] The ligand-centered oxidation in **2** seems to enhance intermolecular S--S contacts in the solid state.

Figure 3 shows the temperature dependence of molar paramagnetic susceptibility of complex **2** in the temperature range 4.2 - 300 K, which was measured by a SQUID magnetometer (Quantum Design, MPMS-5S). A shoulder observed around 80 K is due to the Schottky anomaly characteristic of a low-dimensional magnet, which comes from the presence of a remarkable short-range order. The magnetic data were analyzed by the equation (1) based on the one-dimensional antiferromagnetic Heisenberg model,[17] which also takes into account the contribution of paramagnetic impurities:

$$\chi_M = (1 - x)\chi_{1D} + x\,\chi_{para} \qquad (1)$$

where χ_{1D} is the magnetic susceptibility of an antiferromagnetic Heisenberg chain characterized by J_{1D}/k_B = -46.3 K, χ_{para} is the magnetic susceptibility arising from paramagnetic impurities having S = 1/2, and x is a fraction of paramagnetic impurities (15 %). Rather large amounts of paramagnetic impurities are not chemical ones and come from lattice defects and inhomogeneity of the microcrystals due to fragility of molecular crystals. The strong antiferromagnetic interaction in the one-dimensional chain is noteworthy compared with those for neutral organic radicals ($|J_{1D}/k_B|$ = 10^{-1} - 10^{0} K),[18] and suggests a likely spin-Peierls transition at lower temperature than 4.2 K.[19] Such a strong magnetic coupling is attributable to the effective molecular interaction through S--S non-bonded contacts among the C_3S_5-radicals for the present complex.

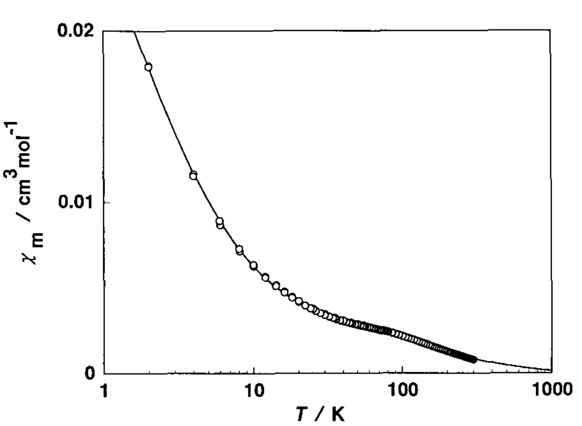

Figure 3. Temperature dependence of molar paramagnetic susceptibility for complex **2**. The solid curve shows the theoretical susceptibility calculated from eq. (1) with J_{1D}/k_B = -46.3 K, and x = 0.15.

The electrical conductivity of **2** measured for a compacted pellet at room temperature was 7.9 x 10^{-8} S cm^{-1}. The present molecular interaction through the S--S contacts in the solid state is not enough to cause an effective electron-conduction.

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