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Tristability Arising from Singlet−Triplet and Quartet Spin States for Dimeric Co^{II}Salen

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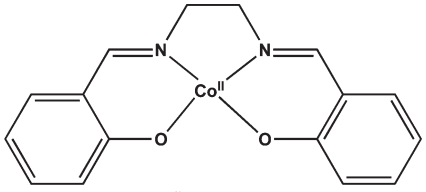
The magnetic behavior of *N*,*N*′-ethylenebis(salicylideniminato) cobalt(II) (Co^{II}Salen, **1**) has been reinvestigated and reveals spin-crossover behavior above 295 K. It has a singlet ground state and a triplet excited state at 30 K (21 cm^{-1}; 60 cal/mol) above the ground state, and at a higher temperature spin crossover to the quartet, a second excited state occurs.

Bistable molecule-based materials that respond to external stimuli are increasingly important as key components in sensors, switches, actuators, and information storage.[1] Technologically important stimuli include electric fields, temperature, pressure, and light. Spin-crossover,[2] valence tautomeric,[3] and photochromic[4] systems are examples of bistable materials. Spin-crossover materials, whereby a stimuli-induced change from a low to high spin state of a metal ion occurs, have been identified as suitable bistable materials.[1b,e] Likewise, valence tautomers exhibit spin-state changes (this results from an intramolecular oxidation−reduction) and have also been explored as bistable materials.

As part of our studies of technologically important magnetic materials, we reinvestigated *N*,*N*′-ethylenebis(salicylideniminato)cobalt(II) (Co^{II}Salen, **1**). **1** has been extensively studied as an oxygen absorber and exists in several structural forms. While **1** is planar (C_{2v}), it dimerizes in the solid state, with each Co^{II} site being square-pyramidal with overall C_i symmetry (Figure 1).[6] Its temperature-dependent susceptibility, $\chi(T)$, indicates that it has a singlet ground state with a triplet excited state above the ground state.[7]



Co^{II}(Salen), **1**

$\chi T(T)$[8] of $\mathbf{1_2}$ is 0.43 emu·K/mol of Co at 200 K, and it decreases with decreasing temperature until it reaches ~0 emu·K/mol of Co at 5 K. Upon warming above 200 K, it gradually increases to 0.45 emu·K/mol of Co at 300 K, before increasing more rapidly to 1.70 emu·K/mol of Co at 550 K (Figure 2). Above 525 K, thermal decomposition occurs. Note that the data below 400 K and above 300 K were taken using different sample holders,[8] and because of different orientations of the polycrystalline sample, different average *g* values occurred; nonetheless, the data are

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(1) For example: (a) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001. (b) Kahn, O.; Launary, J. P. *Chemtronics* **1988**, *3*, 140. (c) Guihery, N.; Durad, G.; Lepetit, M.-B. *Chem. Phys.* **1994**, *183*, 45. (d) Sato, O.; Zhang, Y.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 2152. (e) Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718. (f) Guihery, N.; Durad, G.; Lepetit, M.-B.; Malrieu, J.-P. *Chem. Phys.* **1994**, *183*, 61.

(2) For example: *Spin Crossover in Transition Metal Compounds*; Gütlich, P., Goodwin, H. A., Eds.; Springer: New York, 2004; Vols *1*−*3*.

(3) For example: Shultz, D. A. In *Magnetism—Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. *2*, p 281. Pierpont, G. C.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45. Pierpont, G. C.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.

(4) For example: *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1990; p 64. Organic Photochromic and Thermochromic Compounds. *Main Photochromic Families*; Crano, J. C., Guglielmetti, R., Eds.; Plenum Publishers: New York, 1999; Vol. *1*.

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(7) Carlisle, G. O.; Simpson, G. D.; Hatfield, W. E.; Crawford, V. H.; Drake, R. F. *Inorg. Chem.* **1975**, *14*, 217.

(8) χT was measured in 1 kOe between 5 and 400 K on either a Quantum Design MPMS 5 or 5 XL SQUID magnetometer equipped with a reciprocating sample measurement system as previously described (Brandon, E. J.; Rittenberg, D. K.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* 1998, *37*, 3376). In addition to correcting for the diamagnetic contribution from the sample holder, the core diamagnetic correction of -166×10^{-6} emu/mol of Co was used. The XL magnetometer was equipped with a high-temperature attachment to study the material in the range of 300−600 K. The temperature reproducibility of the high-temperature attachment is ±1%. A home-built brass sample holder (7.9 cm in length with an outer diameter of 0.30 cm) was suspended from the standard transport assembly by a copper wire and was used for the magnetic measurement. The paramagnetic contribution from the sample holder was subtracted from the overall magnetic moment using a point-by-point background subtraction.

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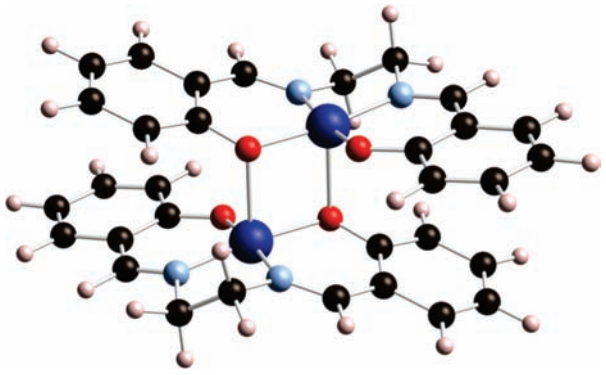

Figure 1. Dimer structure of **1**, $\mathbf{1_2}$ (Co, blue; N, light blue, O, red).[6]

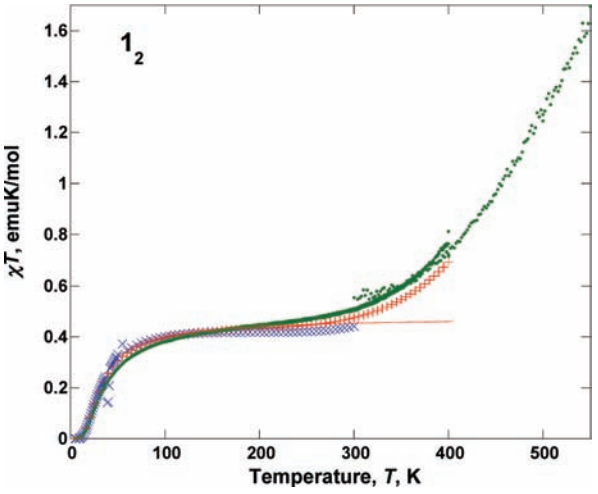

Figure 2. $\chi T(T)$ of $\mathbf{1_2}$ for three samples (×, +, ●); no hysteresis is observed. The solid line is a fit of eq 1 below 250 K.

reproducible (Figure 2). Below 200 K, $\chi T(T)$ can be fit to the Bleaney−Bowers singlet−triplet expression, eq 1 per Co ($H = -2JS_i \cdot S_j$), with $g = 2.26$ and $J/k_B = -30$ K (-21 cm^{-1}; -60 cal/mol) in agreement with earlier work [$g = 2.4$; $J/k_B = -29$ K (-20 cm^{-1}; -58 cal/mol)].[7] The rise in $\chi T(T)$ above 200 K is suggestive of spin-crossover behavior. The dimer model gives a good fit to the data below the onset of the spin-crossover region (~200 K). $\chi T(T)$, however, increases faster than expected from the Boltzmann population of the high-spin state at higher temperature (as is characteristic for spin-crossover materials[2]). Thus, $\chi T(T)$ cannot be mathematically modeled above 200 K. The limiting value for χT for the high-spin $S = {}^3/_2$ state is 2.39 emu·K/mol for $g = 2.26$, and only 71% of this is observed; hence, temperatures greater than the decomposition temperature are needed.

$$\chi T = \frac{N g^2 \mu_B{}^2}{k_B(3 + e^{-2J/k_B T})} \quad (1)$$

The spin-crossover behavior observed for $\mathbf{1_2}$ is associated with a dinuclear site, not a single-ion site, as is well documented.[2] $\chi T(T)$ increases with heating until ~525 K, when thermal decomposition occurs.[9] The singlet ($S = 0$) ground state arises from the antiferromagnetically coupled pair of $\mathbf{1_2}$ Co^{II} ions, each being in the single-ion, low-spin $S = {}^1/_2$ electron configuration, and the triplet ($S = 1$) excited state arises from ferromagnetic coupling of this pair of Co^{II} $S = {}^1/_2$ ions. As the temperature increases, the thermal energy populates both the singlet and triplet states. This leads to $\chi T(T)$ approaching the Curie behavior for two Co^{II} $S = {}^1/_2$ doublets at higher temperature because the exchange coupling, J, is less significant with respect to the thermal energy, $k_B T$. Spin crossover for Co^{II} has been reported for several five-coordinate Co(Salen)L (L = imidazole, pyridine, etc.), as is the situation for [Co(Salen)]$_2$.[10] Likewise, spin crossover of $\mathbf{1_2}$ above room temperature is due to population of the quartet state and depopulation of the doublet state. Both the thermally populated singlet−triplet excitation of the dimer leading to $\chi T(T)$ approaching the Curie limit at ~200 K and spin crossover to the quartet state at higher temperature do not exhibit thermal hysteresis (Figure 2). This temperature dependence has also been reported for dinuclear $Co_2L(NCS)_2$ (L = $C_{18}H_{20}N_8$) with octahedral Co^{II} sites, which has lower J/k_B of -17 K (-12 cm^{-1}; -23 cal/mol), and the crossover onset occurs at ~200 K.[11] Further work targeting spin crossover with hysteresis around room temperature is in progress.

Supporting Information Available: DSC of $\mathbf{1_2}$ showing decomposition. This material is available free of charge via the Internet at http://pubs.acs.org.

(9) A total of 12 reddish-orange crystals turn black irreversibly at ~550 K, and the differential scanning calorimetry (DSC) trace shows a small endotherm, prior to an exotherm similar to melting at ~610 K.

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