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Solid-State Dinuclear-to-Trinuclear Conversion in an Oxalato-Bridged Chromium(III)−Cobalt(II) Complex as a New Route toward Single-Molecule Magnets

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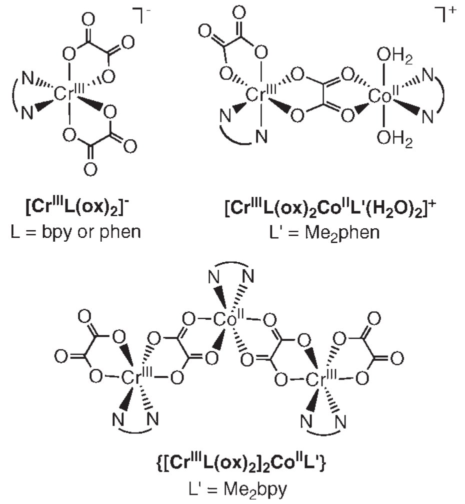
S *Supporting Information*

ABSTRACT: A novel bis(oxalato)chromium(III) salt of a ferromagnetically coupled, oxalato-bridged dinuclear chromium(III)−cobalt(II) complex of formula $[CrL(ox)_2CoL'(H_2O)_2][CrL(ox)_2]\cdot 4H_2O$ (**1**) has been self-assembled in solution using different aromatic α,α′-diimines as blocking ligands, such as 2,2′-bipyridine (L = bpy) and 2,9-dimethyl-1,10-phenanthroline (L′ = Me$_2$phen). Thermal dehydration of **1** leads to an intriguing solid-state reaction between the $S = {}^3/_2$ Cr^{III} anions and the $S = 3$ $Cr^{III}Co^{II}$ cations to give a ferromagnetically coupled, oxalato-bridged trinuclear chromium(III)−cobalt(II) complex of formula $\{[CrL(ox)_2]_2CoL'\}$ (**2**). Complex **2** possesses a moderately anisotropic $S = {}^9/_2$ $Cr^{III}{}_2Co^{II}$ ground state, and it exhibits slow magnetic relaxation behavior at very low temperatures ($T_B < 2.0$ K).

Chart 1



Polynuclear complexes of paramagnetic first-row transition-metal ions have been the subject of a renewed interest in the last years as potential candidates of single-molecule magnets (SMMs) or as precursors of single-chain magnets (SCMs), i.e., molecules with either discrete zero-dimensional (0D) or extended one-dimensional (1D) structures that exhibit slow relaxation of the magnetization below a blocking temperature (T_B).[1,2] Otherwise, the use of small polynuclear complexes as precursors of two- (2D) or three-dimensional (3D) magnets possessing a long-range magnetic ordering below a critical temperature (T_C) was a worthwhile topic in the past.[3] In all cases, however, the polymerization reactions leading to the nD ($n = 1-3$) polymetallic magnetic systems, either in solution[2] or in the solid state,[3] are difficult to control.

The "complex-as-ligand/complex-as-metal" approach represents a rational method toward the preparation of discrete heteropolynuclear species with predetermined structures and spin topologies.[4] In this context, we recently showed that neutral trinuclear chromium(III)−cobalt(II) complexes, $\{[Cr^{III}L(ox)_2]_2Co^{II}L'\}$, can be rationally designed and synthesized from anionic mononuclear bis(oxalato)chromium(III) complexes, $[Cr^{III}L(ox)_2]^-$, acting as bidentate ligands (metalloligands) toward coordinatively unsaturated cationic cobalt(II) complexes, $[Co^{II}L'(H_2O)_4]^{2+}$, where L and L′ are aromatic α,α′-diimine blocking ligands like 2,2′-bipyridine (L = bpy) or 1,10-phenanthroline (L = phen) and their β,β′-dimethyl-substituted derivative 6,6′-dimethyl-2,2′-bipyridine (L′ = Me$_2$bpy) (Chart 1).[5] Surprisingly, when using the 2,9-dimethyl-1,10-phenanthroline (L′ = Me$_2$phen) analogue as a blocking ligand, the cationic dinuclear chromium(III)−cobalt(II) complexes $[Cr^{III}L(ox)_2Co^{II}L']^+$ were isolated as their anionic mononuclear chromium(III) salts. Herein we report the synthesis, crystal structure, thermal behavior, and magnetic properties of such a new complex of formula $[Cr(bpy)(ox)_2Co(Me_2phen)(H_2O)_2][Cr(bpy)(ox)_2]\cdot 4H_2O$ (**1**). Interestingly, **1** exhibits an intriguing solvatomagnetic behavior upon thermal dehydration, which reveals the occurrence of a solid-state reaction to give the corresponding trinuclear chromium(III)−cobalt(II) anhydrous derivative of formula $\{[Cr(bpy)(ox)_2]_2Co(Me_2phen)\}$ (**2**).

The crystal structure of **1** consists of oxalato-bridged heterodinuclear chromium(III)−cobalt(II) cations, $[Cr^{III}(bpy)(ox)_2Co^{II}(Me_2phen)(H_2O)_2]^+$, mononuclear bis(oxalato)chromium(III)

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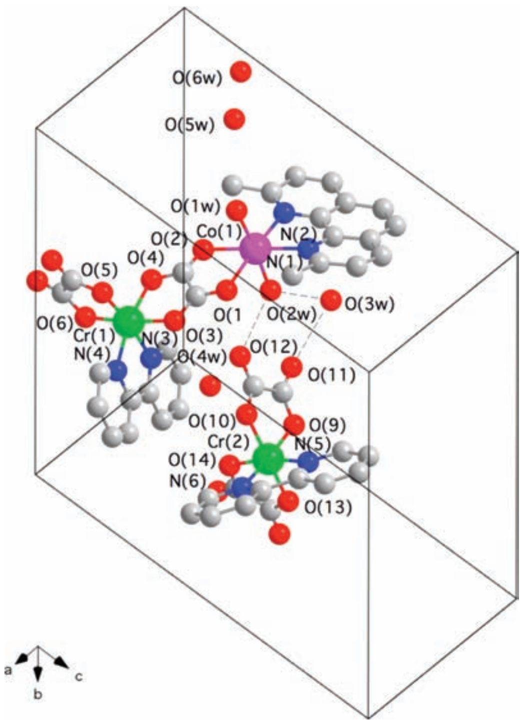

Figure 1. (a) Perspective view of the asymmetric unit of **1** with the atom-numbering scheme for the metal coordination environments and crystallization water molecules. Hydrogen bonds are represented by dashed lines (hydrogen atoms are omitted for clarity). Selected intermetallic distances (Å) with standard deviations in parentheses: Cr(1)−Co(1) =5.423(2), Cr(2)−Co(1) =7.879(2), and Cr(1)−Cr(2) =7.306(4).

anions, $[Cr^{III}(bpy)(ox)_2]^-$, and crystallization water molecules (Figure 1). One of the two $[Cr^{III}(bpy)(ox)_2]^-$ anionic units of **1** coordinates to the trans-diaqua $[Co^{II}(Me_2phen)(H_2O)_2]^{2+}$ moiety in a bidentate manner through one of the two oxalato groups. The other $[Cr^{III}(bpy)(ox)_2]^-$ anionic unit establishes a variety of hydrogen bonds with the resulting $[Cr^{III}(bpy)(ox)_2Co^{II}(Me_2phen)(H_2O)_2]^+$ cationic entity which involve the free carbonyl−oxygen atoms from a terminally bound oxalato group and the coordinated and crystallization water molecules [O···Ow = 2.761(1)−2.876(1) Å]. This situation contrasts with that found in the related oxalato-bridged heterotrinuclear cobalt(II)−chromium(III) complex of formula $\{[Cr(phen)(ox)_2]_2Co(Me_2bpy)_2\}\cdot 1.5H_2O$, whereby the two $[Cr^{III}(phen)(ox)_2]^-$ units coordinate to the $[Co^{II}(Me_2bpy)_2]^{2+}$ unit in a bidentate manner.[5] The greater steric hindrance of the Me_2phen blocking ligand compared to the Me_2bpy one would account for this structural difference. The Cr(1) and Cr(2) atoms of **1** adopt a similar trigonally distorted octahedral geometry [Cr−N = 2.054(3)−2.067(3) Å and Cr−O = 1.938(3)−2.005(3) Å], while the Co(1) atom exhibits an axially compressed octahedral geometry typical of a high-spin Co^{II} ion [Co−N = 2.149(3)−2.151(3) Å, Co−O = 2.152(3)−2.179(2) Å, and Co−Ow = 2.029(3)−2.088(3) Å].

The thermogravimetrogram of **1** under a dry N_2 atmosphere shows a fast weight loss from room temperature to around 165 °C, which is followed by a plateau under further heating to 300 °C just when decomposition occurs (Figure S1, Supporting Information). The value of the mass loss percentage of ca. 10% corresponds to six water molecules per formula unit. This agrees with the release of both the crystallization and coordinated water molecules to give the anhydrous derivative **2**.

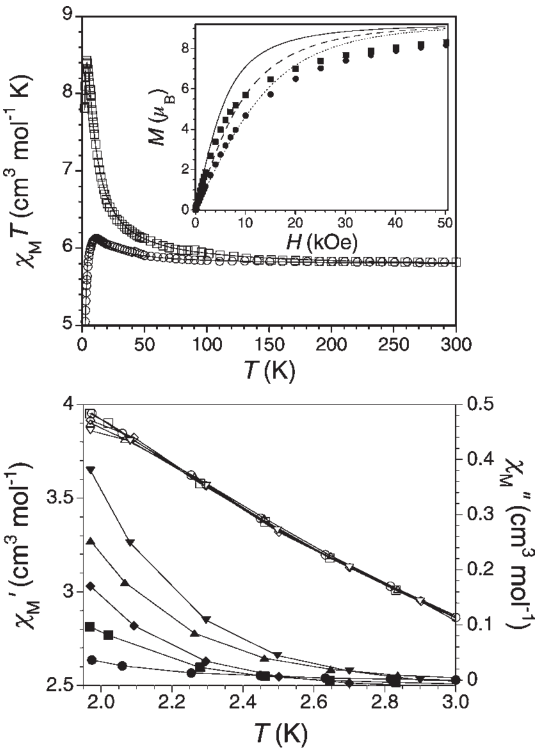

Figure 2. (a) $\chi_M T$ vs T plot for **1** (○) and **2** (□) under dc fields of 10 kOe ($T \geq 25$ K) and 250 Oe ($T < 25$ K). The solid lines are the best-fit curves (see the text). The inset shows the M vs H plots for **1** (●) and **2** (■) at $T = 2.0$ K. The solid, dashed, and dotted lines are the Brillouin curves for one $S = {}^9/_2$, one $S_{Cr} = {}^3/_2$ plus one $S = 3$, and two $S_{Cr} = {}^3/_2$ plus one $S_{Co} = {}^3/_2$ states, respectively (see the text). (b) χ_M' (open symbols) and χ_M'' (closed symbols) vs T plots for **2** at different frequencies of the 4.0 Oe ac field: 10 (○, ●), 100 (□, ■), 333 (◇, ◆), 1000 (△, ▲), and 1400 Hz (▽, ▼). The solid lines are guides for the eye.

The direct-current (dc) magnetic properties of **1** and **2** in the form of χT vs T plots (with χ_M being the molar magnetic susceptibility and T the temperature) show a dramatically different magnetic behavior, which is consistent with their mononuclear plus dinuclear (**1**) and trinuclear (**2**) structures (Figure 2a). At room temperature, the values of $\chi_M T$ are 5.82 (**1**) and 5.80 cm^3 mol^{-1} K (**2**). They are close to that expected for the sum of two d^3 Cr^{III} ($S_{Cr} = {}^3/_2$) ions and one high-spin d^7 Co^{II} ($S_{Co} = {}^3/_2$) ion magnetically isolated [$\chi_M T = 2(N\beta^2 g_{Cr}^2/3k_B)S_{Cr}(S_{Cr} + 1) + (N\beta^2 g_M^2/3k_B)S_{Co}(S_{Co} + 1) = 5.8$ cm^3 mol^{-1} K with $g_{Cr} = 2.0$ and $g_{Co} = 2.1$]. Upon cooling, $\chi_M T$ for **1** slightly increases to reach a maximum of 6.14 cm^3 mol^{-1} K at 14 K, and then it abruptly decreases to 5.05 cm^3 mol^{-1} K at 2.0 K. Instead, $\chi_M T$ for **2** increases abruptly below 50 K to reach a maximum of 8.43 cm^3 mol^{-1} K at 3.5 K, and then it slightly decreases to 7.81 cm^3 mol^{-1} K at 2.0 K. The increase of $\chi_M T$ at high temperatures for **1** and **2** agrees with the occurrence of a moderately weak ferromagnetic intramolecular interaction between the Cr^{III} ($S_{Cr} = {}^3/_2$) and the high-spin Co^{II} ($S_{Co} = {}^3/_2$) ions through the oxalato bridge within the $Cr^{III}Co^{II}$ (**1**) and $Cr^{III}_2Co^{II}$ (**2**) units. The maximum $\chi_M T$ values for **1** and **2** are yet below those expected for magnetically isolated $S_{Cr}={}^3/_2$ Cr^{III} and $S=3$ $Cr^{III}Co^{II}$ units in **1** [$\chi_M T = (N\beta^2 g_{Cr}^2/3k)S_{Cr}(S_{Cr}+1) + (N\beta^2 g^2/3k)S(S + 1) = 8.2$ cm^3 mol^{-1} K with $g_{Cr} = 2.0$ and

$g = (g_{Cr} + g_{Co})/2 = 2.05$] or $S = {}^9/_2$ $Cr^{III}{}_2Co^{II}$ units in **2** [$\chi_M T = (N\beta^2 g^2/3k)S(S + 1) = 12.8$ cm^3 mol^{-1} K with $g = (2g_{Cr} + g_{Co})/3 = 2.033$]. The decrease of $\chi_M T$ at low temperatures for **1** and **2** is most likely due to antiferromagnetic intermolecular interactions and/or zero-field-splitting (ZFS) effects.

In fact, the M vs H plots (with M being the molar magnetization and H the dc field) of **1** and **2** at 2.0 K agree with a solid-state reaction between the $S_{Cr} = {}^3/_2$ Cr^{III} and $S = 3$ $Cr^{III}Co^{II}$ units to give a $S = {}^9/_2$ $Cr^{III}{}_2Co^{II}$ entity (inset of Figure 2a). Thus, the isothermal magnetization curve at low H values for **1** is intermediate between the Brillouin functions of three quartet states ($S_{Cr} = S_{Co} = {}^3/_2$ with $g_{Cr} = 2.0$ and $g_{Co} = 2.1$, respectively) and one quartet ($S_{Cr} = {}^3/_2$ with $g_{Cr} = 2.0$) plus one septet ($S = {}^3/_2$ with $g = 2.05$) states (dotted and dashed lines respectively, in the inset of Figure 2a), while that of **2** is fairly close to the Brillouin function of a decet ($S = {}^9/_2$ with $g = 2.033$) state (solid line in the inset of Figure 2a). Yet, the M values of 8.18 (**1**) and 8.32 μ_B (**2**) at 50 kOe are slightly below the saturation magnetization for the sum of two Cr^{III} ($S_{Cr} = {}^3/_2$) and one high-spin Co^{II} ($S_{Cr} = {}^3/_2$) ions ($M_s = 2g_{Cr}S_{Cr} + g_{Co}S_{Co} = 9.15$ μ_B with $g_{Cr} = 2.0$ and $g_{Co} = 2.1$), supporting thus the presence of a significant single-ion axial magnetic anisotropy of the high-spin Co^{II} ion in a distorted octahedral coordination geometry.

The magnetic susceptibility data of **1** and **2** were analyzed through the appropriate spin Hamiltonian for mononuclear plus dinuclear (**1**) and trinuclear (**2**) models by taking into account both the presence of weak intermolecular interactions within the mean-field approximation and the local axial ZFS of the orbital singlet ^4E_g ground state of the high-spin Co^{II} ion in an axially compressed octahedral geometry (D_{4h} point group) [eqs 1 and 2, with $S_{Cr1} = S_{Cr2} = S_{Co1} = {}^3/_2$],[5] where J and zj are the intra- and intermolecular magnetic coupling parameters, respectively, D is the axial magnetic anisotropy parameter of the Co^{II} ion, and g_{Cr} and g_{Co} are the Landé factors of the Cr^{III} and Co^{II} ions. The least-squares fits of the experimental data by full-matrix diagonalization techniques gave $J = +2.16$ cm^{-1}, $zj = -0.15$ cm^{-1}, $D = -0.61$ cm^{-1}, $g_{Co} = 2.082$, and $g_{Cr} = 2.002$ for **1** and $J = +1.81$ cm^{-1}, $zj = -0.09$ cm^{-1}, $D = -1.27$ cm^{-1}, $g_{Co} = 2.092$, and $g_{Cr} = 1.998$ for **2**. The theoretical curves closely match the experimental data for **1** and **2** (solid lines in Figure 2a). In particular, they reproduce very well the maximum of $\chi_M T$ at low temperatures. The calculated values of J and D for **1** and **2** are close to those previously found in $\{[Cr(phen)(ox)_2]_2Co(Me_2\text{-}bpy)_2\}\cdot 1.5H_2O$ ($J = +2.34$ cm^{-1} and $D = -2.15$ cm^{-1}).[5]

$$\mathbf{H} = -JS_{Cr1}\cdot S_{Co1} + zj\langle S_z\rangle S_z + DS_{Co1z}{}^2 + g_{Cr}(S_{Cr1} + S_{Cr2})\mu_B H + g_{Co}S_{Co1}\mu_B H \quad (1)$$

$$\mathbf{H} = -J(S_{Cr1}\cdot S_{Co1} + S_{Cr2}\cdot S_{Co1}) + zj\langle S_z\rangle S_z + DS_{Co1z}{}^2 + g_{Cr}(S_{Cr1} + S_{Cr2})\mu_B H + g_{Co}S_{Co1}\mu_B H \quad (2)$$

Finally, the alternating-current (ac) magnetic properties of **2** in the form of the χ_M' and χ_M'' vs T plots (with χ_M' and χ_M'' being the in-phase and out-of-phase ac molar magnetic susceptibilities) show evidence of incipient spin-blocking effects, which are characteristic of SMMs (Figure 2b). As the frequency of the ac field increases in the range 10−1400 Hz, χ_M' decreases slightly while χ_M'' becomes different from zero below 3.0 K. However, no maxima of χ_M'' were observed above 2.0 K, even for the highest frequency used ($\nu = 1400$ Hz), indicating thus that $T_B < 2.0$ K for this new example of an oxalato-bridged SMM.[6,7] The preexponential factor (τ_0) and energy barrier (U) to reverse the magnetization can be roughly estimated from the χ_M''/χ_M' vs $1/T$ plots at a given frequency of the ac field by considering a single relaxation time (Figure S2, Supporting Information).[8] The least-squares fits of the experimental data through the expression $\chi_M''/\chi_M' = 2\pi\nu\tau_0 \exp(U/k_BT)$ gave $\tau_0 \approx 2 \times 10^{-9}$ s and $U \approx 13$ cm^{-1} for **2** (solid lines in Figure S2, Supporting Information).

In summary, we have developed a combined solution and solid-state synthetic procedure for the stepwise self-assembly of moderately anisotropic ferromagnetically coupled, oxalato-bridged heteropolynuclear chromium(III)−cobalt(II) complexes, as potential candidates to SMMs. The formation of discrete polynuclear complexes following dehydration reactions in the solid state is rare; more frequently, extended polymers are formed upon vacuum or thermal dehydration in the absence of blocking ligands. The formation of a discrete $S = {}^9/_2$ $Cr^{III}{}_2Co^{II}$ complex upon dehydration of **1** to give **2** is then favored because of the presence of the aromatic α,α′-diimines as blocking ligands. Current efforts are devoted to investigating the magnetic relaxation dynamics of this moderately anisotropic high-spin molecule at very low temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Preparation and characterization of **1** and **2**, X-ray crystallographic data of **1** in CIF format, thermogravimetrogram of **1** (Figure S1), and χ_M''/χ_M' vs $1/T$ plots of **2** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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