Inorg. Chem. **2008**, *47*, 9152−9154

Inorganic Chemistry
Communication

$Co(C_2O_4)(HO(CH_2)_3OH)$: An Antiferromagnetic Neutral Zigzag Chain Compound Showing Long-Range Ordering of Spin Canting

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Received August 12, 2008

A centrosymmetric compound consisting of neutral zigzag chains of $[Co(C_2O_4)(HO(CH_2)_3OH)]_n$ displays strong intrachain antiferromagnetic interaction and 3D weak ferromagnetic ordering at 10.6 K.

Oxalate ($C_2O_4^{2-}$, ox) is one of the most commonly used short connectors in the study of molecular-based materials.[1−8] Its versatile abilities in coordinating metal ions and intermediating efficient magnetic coupling among magnetic metal sites have allowed the construction of various molecular materials, including many magnetic metal−ox frameworks of different dimensionalities (1D−3D) showing rich magnetism[1] and dual-functional materials like magnetic conductors/superconductors[2] and magneto-optical compounds.[3] While 2D and even 3D metal−ox frameworks are the majority,[1−3] examples of 1D or chainlike metal−ox systems are still limited, and they are of special interest for low-dimensional magnetism.[4] Small ligands like H_2O or Cl^-, and even the ox anion itself, together with some inorganic and organic cations, could afford such chains.[5,6] Chelating auxiliary ligands such as 2,2′-bipy and phen have been employed.[7] Long ditopic ligands like 4,4′-bipy could also produce metal−ox chains, though they are structurally higher in dimensionality.[8] Within these materials, the interchain magnetic coupling intermediated by dipole−dipole interaction in the (amminonium)$[Fe(C_2O_4)Cl_2]$ series,[5c] the $\pi-\pi$ interaction in $[Fe(C_2O_4)(phen)]_n$,[7b] and the $\pi-d$ interaction in TTF$[Fe(C_2O_4)Cl_2]$ (TTF = tetrathiafulvalene)[6a] could result in magnetic long-range ordering (LRO). In this work, we present a new neutral Co−ox zigzag chainlike compound of $Co(C_2O_4)(HO(CH_2)_3OH)$ in which bisbidentate ox bridges Co^{2+} ions and 1,3-propanediol acts as a chelating auxiliary ligand. Alcohol ligands have been rarely employed in metal−ox systems,[9] and they could provide some new opportunities such as exploring the role of hydrogen bonding in magnetism and further controlling the structures and properties. While the compound is centrosymmetric, it exhibits strong intrachain antiferromagnetic coupling and 3D LRO of weak ferromagnetism (or spin-canted antiferromagnetism) at 10.6 K.

The compound was prepared by a solvothermal method,[10] and the powder X-ray diffraction pattern proved the phase purity (Figure S1 in the Supporting Information, SI). The single-crystal

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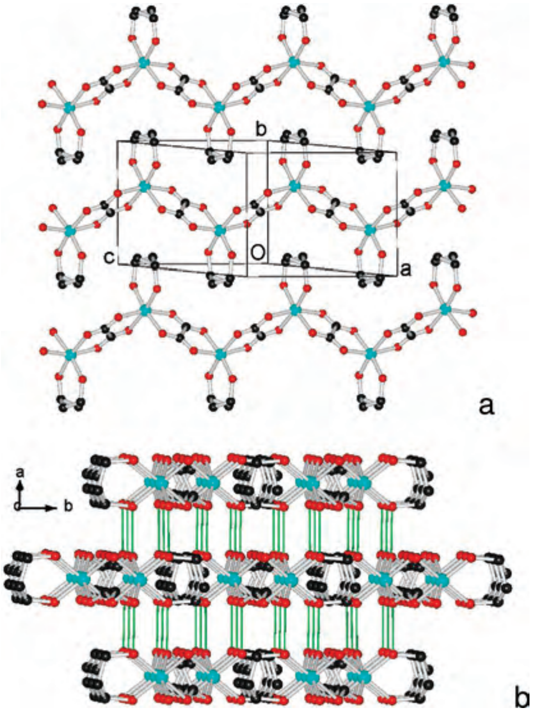

Figure 1. Structure of $Co(C_2O_4)(HO(CH_2)_3OH)$. (a) The zigzag chains of $[Co(C_2O_4)(HO(CH_2)_3OH)]_n$ form a layer parallel to the *bc* plane by the interdigitation of the chains. Atomic scheme: Co, blue; C, black; O, red. The middle CH_2 group of 1,3-propanediol is flipped into two positions. (b) The packing of the layers along the *a* direction, viewed down the *c* axis. Green thin sticks are the interlayer hydrogen bonds between the hydroxyl of 1,3-propanediol and the oxygen of oxalates. Hydrogen atoms are not included.

X-ray structure determination[11] revealed that the structure consists of neutral zigzag chains of $[Co(C_2O_4)(HO(CH_2)_3OH)]_n$ (Figure 1). Within the chain, the Co^{2+} ions are bridged by bisbidentate ox anions. Each unique Co^{2+} is coordinated by two ox ligands in *cis* style and further chelated by one 1,3-propanediol via the two alcohol oxygen atoms (Figure 1a). The distorted CoO_6 octahedron has Co−O distances of 2.060−2.131 Å and *cis* O−Co−O angles of 78.8−99.9° and *trans* ones of 161.6−170.7°, being comparable to those observed in the related Co−ox compounds such as $[Co(C_2O_4)(3\text{-aminopyridine})\cdot 1.5H_2O]_n$,[5b] $[Co(bpy)_3][Co_2(C_2O_4)_3]ClO_4$,[3a] and $K_2[Co(C_2O_4)_2]$.[5e] The zigzag chain is centrosymmetric with the inversion center located at the middle point of the ox bridge; thus, the metal sites have ΔΛΔΛ configurations along the chain. The dihedral angle between the molecular planes of the two ox bridges around one Co^{2+} ion is 77.9°, and the intrachain Co···Co distance is 5.493 Å. In the lattice, the zigzag chains propagate along the *c* axis. They interdigitate to form layers parallel to the *bc* plane (Figure 1a), and the layer is similar to the layer of $[Fe(C_2O_4)(phen)]_n$ chains.[7b] Finally, the layers stack along the *a* axis to give the 3D structure (Figure 1b). The interchain interactions are mainly C−H···O contacts[12] (C···O 3.44−3.65 Å) between the CH_2 groups of 1,3-propanediol and neighboring oxygen atoms within the layer, while these are more significant between the layers, being hydrogen bonds from the hydroxyl groups of 1,3-propanediol to ox (O3−H···O2 2.708 Å/157°; green thin sticks in Figure 1b), together with C−H···O contacts (C···O 3.20−3.72 Å). It is also noted that the middle CH_2 group of 1,3-propanediol might flip between two positions. The shortest interchain Co···Co distances are 6.901 Å within the layer, but between the layers, it is 5.244 Å and spanned by the O3−H···O2 hydrogen bond.

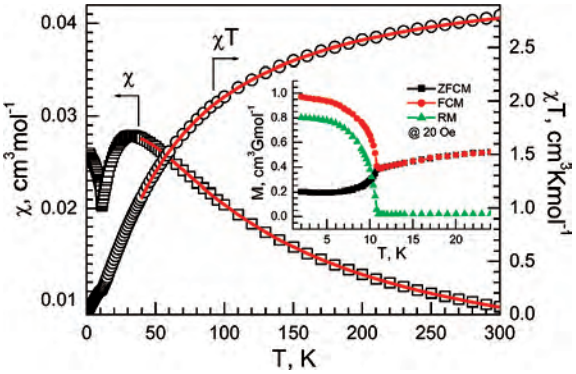

Figure 2. χT vs T and χ vs T plots of $Co(C_2O_4)(HO(CH_2)_3OH)$ under an applied field of 100 Oe. The red lines represent theoretical fits in the high-temperature region (see the text). Inset: ZFCM/FCM/RM plots under 20 Oe in the low-temperature region.

Given the feature of the structure of Co−ox chains linked by O−H···O hydrogen bonds and C−H···O contacts, it is expected that the material could exhibit low-dimensional magnetism. Indeed, under an applied field of 100 Oe, the temperature dependence of χ displayed a broad maximum around 33 K, a minimum at 11 K, and further a quick rise below 11 K (Figure 2). The broad maximum at 33 K corresponded to the strong intrachain antiferromagnetic coupling via the bisbidentate ox bridge for the Co−ox chain, while the rise in the low-temperature region indicated a 3D LRO of spin-canted antiferromagnetism or weak ferromagnetism within the material. At 300 K, the χT value was 2.80 $cm^3\ K\ mol^{-1}$, significantly larger than the expected value[13] (1.875 $cm^3\ K\ mol^{-1}$) for the isolated, spin-only ion with $S = {}^3/_2$ and $g = 2.00$. This is expected for the Co^{2+} ion owing to the significant orbital contribution of Co^{2+} ion with strong spin−orbit coupling in an octahedral environment.[14] The χT values decreased continuously upon temperature lowering and showed a kink point at 11 K, corresponding to the quick rise below 11 K in the χ vs T plot. The susceptibility data above 90 K fitted the Curie−Weiss law well (Figure S2 in the SI), giving Curie and Weiss constants of $C = 3.42$ $cm^3\ K\ mol^{-1}$ and $\theta = -66$ K. The large, negative

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(10) *Preparation*: A mixture of 1.0 mmol of $CoCl_2\cdot 6H_2O$, 1.0 mmol of $H_2C_2O_4\cdot 2H_2O$ and 8 mL of 1,3-propanediol was sealed in a Teflon-lined stainless steel vessel (25 mL), heated at 160 °C for 36 h under autogenous pressure, and then cooled to room temperature. Block purple crystals were harvested in a yield of 40%. Elem anal. Calcd: C, 26.92; H, 3.62. Found: C, 26.94; H, 3.76. IR (KBr pellet, cm^{-1}): 3300−3100s, br, O−H; 2968m, 2902m, C−H; 1670s, 1624s, 1361m, COO; 1311m, O−H; 1232w, 1213w, 1053s, C−O; 931s, C−H.

(11) *Crystallographic data*: $C_5H_8CoO_6$, $M_r = 223.05$, monoclinic, space group $C2/c$, $a = 13.1809(6)$ Å, $b = 7.8494(5)$ Å, $c = 9.4366(5)$ Å, $\beta = 129.352(4)°$, $V = 754.96(7)$ Å^3, $Z = 4$, $D_c = 1.962$ g cm^{-3}, $\mu = 2.261$ mm^{-1}, 6432 measured data, 861 unique, $R_{int} = 0.0444$. R1 = 0.0322 for 697 observations of $I \geq 2\sigma(I)$, wR2 = 0.0923 for all data, GOF = 1.082. CCDC 694325. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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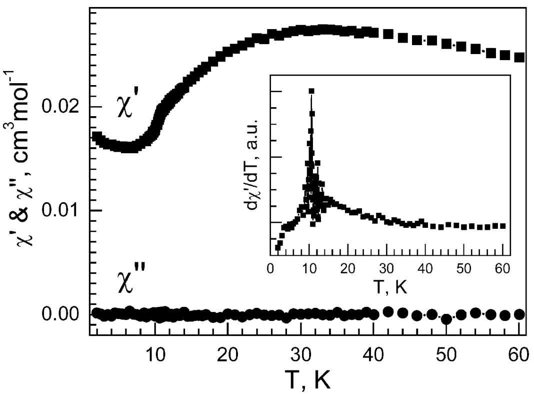

Figure 3. Temperature dependence of ac susceptibility measured with an ac of 2 Oe amplitude and 1 Hz oscillating frequency in a zero dc field for $Co(C_2O_4)(HO(CH_2)_3OH)$. Inset: derivative $d\chi'/dT$.

Weiss temperature indicated the antiferromagnetic interaction between the Co^{2+} ions. Zero-field-cooled and field-cooled magnetizations (ZFCM/FCM) (Figure 2, inset) under a 20 Oe field showed irreversibility below 11 K, and the FCMs were small (0.95−0.97 cm^3 G mol^{-1}) around 2 K. Remanent magnetization (RM; Figure 2, inset) clearly indicated the spontaneous magnetization, though it was very small. The Néel temperature, determined by the negative peak position of the derivative *d*FCM/*d*T or *d*RM/*d*T, was 10.6 K. The isothermal magnetizations at 2 K displayed nearly a linear increase with the increased field and reached 0.143 Nβ at 50 kOe (Figure S3 in the SI). In a very low field region (Figure S3, inset, in the SI), the magnetizations showed a very thin hysteresis loop, but it was observed that when the field scanned from positive (or negative) to negative (or positive), the magnetizations became small negative (positive) when the field was still small positive (negative). This behavior deserves further investigation under extremely low and accurately controlled fields. These results confirmed that the spin-canted antiferromagnetic LRO occurred within the material with a very small coercive field.

In the high-temperature region, the Co−ox chain could be considered as an isotropic Heisenberg chain with $S = {}^3/_2$.[15] The Fisher 1D chain model[16] scaled to $S = {}^3/_2$ was applied to simulate the susceptibility data above 40 K (Figure 2), and the best fitting afforded the intrachain coupling $J = -6.55(1)$ cm^{-1} and $g = 2.632(1)$ with $R = 5.5 \times 10^{-5}$ ($R = \sum(\chi_o - \chi_c)^2/\sum\chi_o^2$). The J value is comparable to those in $K_2[Co(C_2O_4)_2]$ (6.78 cm^{-1})[5e] and other related ox-bridged complexes (∼10 cm^{-1}).[17]

The antiferromagnetic LRO occurring at 10.6 K was further confirmed by alternating current (ac) susceptibility (Figures 3 S4 in the SI) and specific heat measurements in a zero dc field (Figure S5 in the SI). ac responses were weak, and no peaks were found for both χ' and χ'' data because the ac amplitude applied was on the order of the coercive field. However, a kink was observed at 10.6 K in the χ' vs T plot, and this was more clear in the $d\chi'/d$T plot (Figure 3, inset). The ac measurements at 1, 10, 100, and 1000 Hz showed essentially no frequency dependence (Figure S4 in the SI). In the primary specific heat measurement (Figure S5 in the SI), a λ-shaped peak was observed at 10.7 K. These clearly revealed the occurrence of magnetic LRO and agreed with the previous magnetic studies, though detailed information of the magnetic entropy could not be derived yet from the current specific heat data, with the lattice contribution unknown.

It is clear that the interchain O−H···O hydrogen bonds and C−H···O contacts contribute to the antiferromagnetic LRO in the material. Especially, the O−H···O hydrogen bond, being a three-atom bridge in this compound, could intermediate coupling effectively.[18] However, the origin of the spin-canted antiferromagnetic LRO is not clear given the centrosymmetric structure and, especially, the ox bridge lying at the inversion center. The spin canting could have arisen by the acentrosymmetric O−H···O hydrogen bonds, and/or the local acentrosymmetry resulted from the 1,3-propanediol ligand if its flipped CH_2 group was frozen at low temperature, thus satisfying the requirement for the Dzyaloshinski−Moriya interaction.[19] In addition, magnetic anisotropy of the Co^{2+} ion could also give further contribution.[19b] The very low spontaneous magnetization of LRO seemingly supported this argument and also suggested possible a hidden character of the spin canting.[20]

In conclusion, a new neutral Co−ox chain compound of $Co(C_2O_4)(HO(CH_2)_3OH)$ has been synthesized by a solvothermal method. Within the structure, the Co^{2+} ions are bridged by bisbidentate ox ligands and chelated by 1,3-propanediol into zigzag chains, and the chains are glued by interchain O−H···O hydrogen bonds and C−H···O contacts. The material displayed a strong intrachain antiferromagnetic interaction and reached LRO of antiferromagnetism at 10.6 K with small spin canting observed, and this should be caused by interchain hydrogen bonds or local acentrosymmetry. Further work on the preparation and magnetism of such chain compounds of other spin carriers and/or other diol ligands and their spin structures is in progress.

Acknowledgment. The authors thank Prof. Zheming Wang and Prof. Song Gao of College of Chemistry and Molecular Engineering, Peking University, for their kind help in X-ray experiment and magnetic measurements and valuable discussion. This work was supported by NSFC (Nos. 20673120 and 20873154) and MOST 2006CB601001 and 2006CB932102 of China.

Supporting Information Available: X-ray crystallographic file in CIF format for $Co(C_2O_4)(HO(CH_2)_3OH)$, Figures S1−S5, and additional information about physical characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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