Inorg. Chem. **2000,** *39,* 2239−2242 **2239**

Three-Dimensional Oxalate-Bridged Heterometal Supramolecular Complex with a Large Helical Tunnel of 21.191 × 9.294 Å^2

Hao-Yu Shen,[†,‡] Wei-Ming Bu,[§] Dai-Zheng Liao,*[,†] Zong-Hui Jiang,[||] Shi-Ping Yan,[†] and Geng-Lin Wang[†]

Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China, Laboratory of Supramolecular Chemistry and Spectroscopy, Jilin University, Changchun, Jilin Province, 130023, P. R. China, and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210008, P. R. China

Received November 16, 1999

Introduction

Heterometal polynuclear complexes have been the subject of many recent studies with the hope of mimicking the active site of some metal enzymes containing dissimilar metal ions, such as cytochrome oxidase and superoxide dismutase, and elucidating the mechanism of spin coupling between paramagnetic metal ions in view of the electronic structures of the interesting metal ions. With the development of the strategy of "complexes as ligands", the heteropolymetallic systems are arousing a lot of interest among physicists and inorganic chemists in seeking for designing new molecule-based magnetic materials.[1,2]

In the field of molecular-based magnetism, structurally high-dimensional heterometallic oxalate-bridged networks have attracted increasing interest in recent years.[3−10] Some molecule-based magnetism with long-range ferromagnetic orderings was observed at 6−48 K.[10−14] Recently, some materials with spin-glass-like behavior[7,15] and molecular superconductors were also reported.[16] However, a network with a unique large tunnel assembled by a macrocycle complex and oxalate-containing compound is quite scarce.

Table 1. Crystal Data for $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$[a]

empirical formula	$C_{22}H_{32}CrCuKN_4O_{12}$
fw	699.16
T	293(2) K
λ	0.71073 Å
space group	*Cc*
unit cell dimens	$a = 10.3943(9)$ Å, $\alpha = 90°$
	$b = 15.4092(14)$ Å, $\beta = 104.754(10)°$
	$c = 18.205(3)$ Å, $\gamma = 90°$
vol	2819.7(6) Å^3
Z	4
ρ_{obsd}	1.647 g/cm^3
ρ_{calcd}	1.628 g/cm^3
abs coeff	1.355 mm^{-1}
final R indices [$I > 2\sigma(I)$]	R1 = 0.0481, wR2 = 0.0616
R indices (all data)	R1 = 0.0644, wR2 = 0.0756

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

In this work we focus on the use of $K_3Cr(ox)_3$ and $[Cu(trans[14]dien)](ClO_4)_2$ as a building block in designing a novel heterobimetallic supramolecular complex, where (trans[14]dien) is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,-11-diene. The preparation, structural characterization, and magnetic properties of the unique 3D complex $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$ are reported. This compound contains two types of coordination modes of oxalate ligand (monodenate and bis-bidentate fashions) and a macrocycle ligand. Although Kahn et al. reported a $Cr^{III}-Ni^{II}_3$ complex by using $K_3Cr(ox)_3 \cdot 3H_2O$ and $[Ni(Me_6\text{-}[14]ane\text{-}N_4)](ClO_4)_2$ in 1989,[17] the structure of our present compound is unique. The magnetic investigation showed that the oxalate-bridged chromium(III)−copper(II) units were antiferromagnetically coupled ($J = -9.88$ cm^{-1}).

Experimental Section

Synthesis. CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and handled with caution.

$K_3Cr(ox)_3$ and $[Cu(trans[14]dien)](ClO_4)_2$ were prepared according to literature methods.[18,19]

The title compound was synthesized by reacting an ethanol (10 mL) and water (2 mL) mixture of $[Cu(trans[14]dien)](ClO_4)_2$ (0.5 mmol, 108 mg) with 5 mL of a $K_3Cr(ox)_3$ (0.5 mmol, 207.5 mg) aqueous solution. The resulting solution was stirred at 60 °C for 3 h. Any insoluble products were filtered. The resulting dark red solution was undisturbed at room temperature for about 3 months. Then X-ray quality dark-red single crystals were obtained by slow evaporation. The crystals were filtered out, washed with water and ethanol, and air dried. Yield: 68%. Anal. Calcd for $C_{22}H_{32}CrCuKN_4O_{12}$: C, 37.76; H, 4.58; N, 8.01; Cr, 7.44; Cu, 9.08. Found: C, 37.92; H, 4.78; N, 8.45; Cr, 7.32; Cu, 9.28.

X-ray Crystallography. The X-ray single-crystal data were collected on a computer-controlled Siemens P4 diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and a crystal of size 0.3 × 0.23 × 0.18 mm. The crystallographic data,

---

[*] Author to whom correspondence should be addressed.

[†] Nankai University.

[‡] Present address: Sanhuan Lucky New Materials. INC., Tianjin, 300457, P. R. China. Tel: 86-22-25321852. Fax: 86-22-25329459. E-mail: research@teda.tj.cn.

[§] Jilin University.

[||] Nanjing University.

(1) Kahn, O. *Struct. Bonding* **1987**, *68*, 89.
(2) Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.
(3) Decutins, S.; Schmalle, H. W.; Oswald, H. R.; Linden, A.; Ensling, J.; Gutlich, P.; Hauser, A. *Inorg. Chim. Acta* **1994**, *216*, 65.
(4) Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 6974.
(5) Mathoniere, C.; Carling, S. G.; Yusheng, D.; Day, R. *J.Chem. Soc., Chem. Commun.* **1994**, 1551.
(6) Nuttall, C. J.; Bellitto, C.; Day, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1513.
(7) Bhattacharjee, A.; Lijima, S.; Mitzutani, F. *J. Magn. Magn. Mater.* **1996**, *153*, 235.
(8) Mathoniere, C.; Nuttall, C. J.; Carling, S. G.; Day, P. *Inorg. Chem.* **1996**, *35*, 1201.
(9) Carling, S. G.; Mathoniere, C.; Day, P. *J. Chem. Soc., Dalton Trans.* **1996**, 1839.
(10) Larionova, J.; Mombelli, B.; Sanchiz, J.; Kahn, O. *Inorg. Chem.* **1998**, *37*, 679.
(11) Zhong, Z. J.; Matsumoto, H.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 87.
(12) Clemete-Leon, M.; Coronado, E.; Galan-Mascaros, J.; Gomez-Garcia, C. J. *Chem. Commun. (Cambridge)* **1997**, 1727.
(13) Pellaux, R.; Schmalle, H. W.; Huber, R.; Fischer, P.; Hass, T.; Ouladdiaf, B.; Decurtins, S. *Inorg. Chem.* **1997**, *36*, 2301.
(14) Tamaki, H.; Mitsumi, M.; Nakamura, K.; Matsumoto, N.; Kida, S.; Okawa, H.; Iijima, S. *Chem. Lett.* **1992**, 1975.
(15) Bhattacharjee, A.; Iijima, S.; Mizutani, F.; Katsura, T.; Matsumoto, N.; Okawa, H. *Jpn. J. Appl. Phys.* **1995**, *34*, 1521.
(16) Martin, L.; Turner, S. S.; Day, P.; Mabbs, F. E.; McInnes, E. J. L. *Chem. Commun. (Cambridge)* **1997**, 1367.
(17) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100.
(18) Chem. Soc. Jpn., Ed. *Synthesis of Inorganic Compound (III);* Maruzen Inc.: Tokyo, 1976.
(19) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3.

10.1021/ic991325n CCC: $19.00

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) for $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$[a]

Cu−N(3)	1.973(8)	Cr−O(3)	1.982(7)	O(9)−K#2	2.365(8)
Cu−N(1)	1.977(8)	Cr−O(1)	1.987(8)	O(10)−K#2	2.389(9)
Cu−N(4)	2.009(9)	Cr−O(6)	1.984(7)	O(11)−K	2.374(8)
Cu−N(2)	2.017(8)	K−O(8)#3	2.473(9)	O(12)−K	2.387(9)
Cr−O(4)	1.943(8)	K−O(10)#4	2.389(9)	O(7)−K#1	2.333(9)
Cr−O(5)	1.981(8)	K−O(7)#3	2.333(9)	O(8)−K#1	2.473(9)
Cr−O(2)	1.974(7)	K−O(9)#4	2.365(8)		

N(3)−Cu−N(1)	178.6(6)	O(5)−Cr−O(2)	170.7(3)	O(4)−Cr−O(1)	176.0(3)
N(3)−Cu−N(4)	93.9(4)	O(4)−Cr−O(6)	92.0(4)	O(5)−Cr−O(1)	90.3(3)
N(1)−Cu−N(4)	85.2(4)	O(5)−Cr−O(6)	82.3(3)	O(2)−Cr−O(1)	81.7(3)
N(3)−Cu−N(2)	86.0(4)	O(2)−Cr−O(6)	93.1(3)	O(6)−Cr−O(1)	91.8(4)
N(1)−Cu−N(2)	94.7(3)	O(4)−Cr−O(3)	83.3(3)	O(3)−Cr−O(1)	93.1(3)
N(4)−Cu−N(2)	171.0(4)	O(5)−Cr−O(3)	90.6(3)	O(12)−K−O(11)	71.6(3)
O(4)−Cr−O(5)	91.5(3)	O(2)−Cr−O(3)	94.6(3)	O(10)#4−K−O(11)	92.0(3)
O(4)−Cr−O(2)	96.7(3)	O(6)−Cr−O(3)	171.4(3)	O(7)#3−K−O(8)#3	70.8(3)
O(7)#3−K−O(9)#4	99.2(3)	O(9)#4−K−O(10)#4	70.6(3)	O(9)#4−K−O(8)#3	92.0(3)
O(7)#3−K−O(12)	104.6(4)	O(12)−K−O(10)#4	90.4(3)	O(12)−K−O(8)#3	171.5(3)
O(9)#4−K−O(12)	95.8(3)	O(7)#3−K−O(1 1)	100.4(3)	O(10)#4−K−O(8)#3	95.3(3)
O(7)#3−K−O(10)#4	162.9(3)	O(9)#4−K−O(11)	158.9(3)	O(11)−K−O(8)#3	101.9(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $-y$, $z + 1/2$; #2, $x - 1/2$, $y + 1/2$, z; #3, x, $-y$, $z - 1/2$; #4, $x + 1/2$, $y - 1/2$, z.

conditions for the collection of intensity data, and some features of the structure refinements are listed in Table 1. Cell parameters were determined by least-squares calculations based on the setting angles and 46 reflections with θ angles ranging from 4.63° to 14.72° at 293(2) K. A total of 2925 independent reflections were measured ($I \geq 2\sigma(I)$). No absorption correction was made during processing. Hydrogen atoms were added theoretically, refined with riding model position parameters, and fixed with isotropic thermal parameters. The structure was solved by direct methods (SHELX86)[20,21] and refined by the full-matrix least-squares method with use of the SHELXL-93 package of program. The final refinement was by full-matrix least squares on F^2. The final R1 = 0.0481, wR2 = 0.0616 ($I \geq 2\sigma(I)$), R1 = 0.0644, wR2 = 0.0756 (all data), and S = 1.151. The largest peak and hole in the final difference Fourier map had values of 0.546 and −1.142 e Å^{-3}, respectively. Significant bond parameters are given in Table 2.

Magnetic Measurements. The magnetic susceptibilities were measured on polycrystalline samples at fields of 10000 G and at temperatures ranging from 2 to 300 K with use of a vibrating sample magnetometer, model CF-1.

Results and Discussion

Description of the Structure. An ORTEP drawing of $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$ is shown in Figure 1. The Cr^{3+} and K^+ ions in this molecule are alternately linked by three oxalate ligands to three neighboring metal ions. In each $[KCr(ox)_3]^{2-}$ unit, a copper(II) atom is coordinated to an oxygen atom of ox^{2-} in monodentate fashion. Both Cr^{3+} and K^+ ions are located in an octahedral environment with Cr−O distances in the region of 1.943−1.987 Å, and K−O distance in the region of 2.333−2.389 Å. The copper(II) ion assumes a five-coordinated square pyramidal environment, with Cu−N distances in the region of 1.973−2.017 Å and a Cu−O(8) distance of 2.6 Å. Every three alternately connected K^+ and three Cr^+ ions form a hexacyclic ring which further extends to a three-dimensional network. It is interesting to contrast the structure of the present compound with those of some previously reported 3D $[M_2^{II}(ox)_3]^{2-}$ and $\{M^IM^{III}(ox)_3]\}^{2-}$ type networks.[22,23] We found out that the main difference between the present one and the previously reported ones is that the latter ones are composed of octagons and squares in three-dimensional networks, while the present compound is composed of hexagons only. In the present compound, each Cr(III) or K(I) site surrounded by three oxalate groups is chiral and the three-dimensional network is generated by an alternation Cr(III) and K(I) sites. Another interesting phenomenon is that there are helical tunnels with the size of 21.191 × 9.294 Å^2 in the direction of the diagonal line of a and b axes, and the copper(II) units are located in these tunnels, as shown in Figure 2. In comparing to the square meshes, the enlargement of the grids in the tunnels can have some influence on the dimension-controlled properties and may be useful in guest exchange and catalysis.

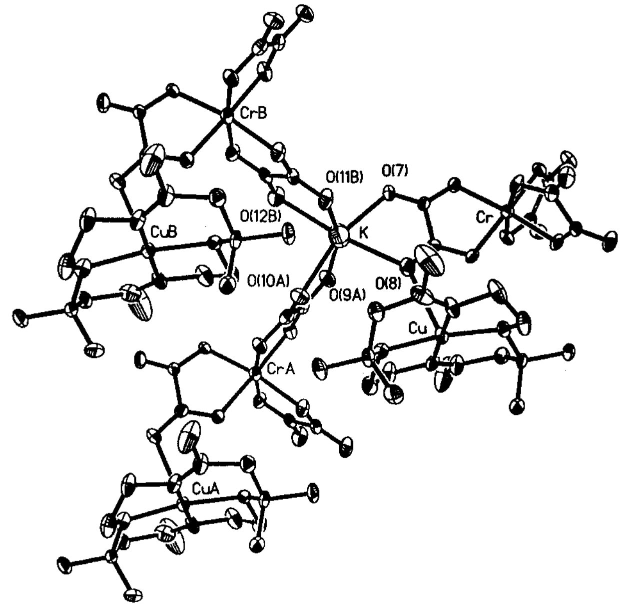


Figure 1. ORTEP drawing of $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$.

The Magnetic Studies. The magnetic behavior of the title compound has been studied and is represented in Figure 3, in the form of χ_mT vs T. The observed χ_mT value is 3.558 cm^3 K mol^{-1} at 292.5 K, which is lower than the spin-only value of 4.24 cm^3 K mol^{-1} for the uncoupled Cu(II)−Cr(III) dimer unit, probably because of the existence of an effective antiferromagnetic coupling at room temperature as the χ_mT product is not a plateau at room temperature. A gradual decrease in χ_mT is observed as the temperature is decreased, indicating the presence of an antiferromagnetic intrachain interaction.

---

(20) *SPD-PLUS*; Enraf-Nonius: Delft, The Netherlands, 1985.
(21) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(22) Kahn, O. *Adv. Inorg. Chem.* **1996**, *43*, 179.
(23) Decurtins, S.; Schmale, H. W.; Schneuwly, P.; Ensling, J.; Gutlich, P. *J. Am. Chem. Soc.* **1994**, *116*, 9521.

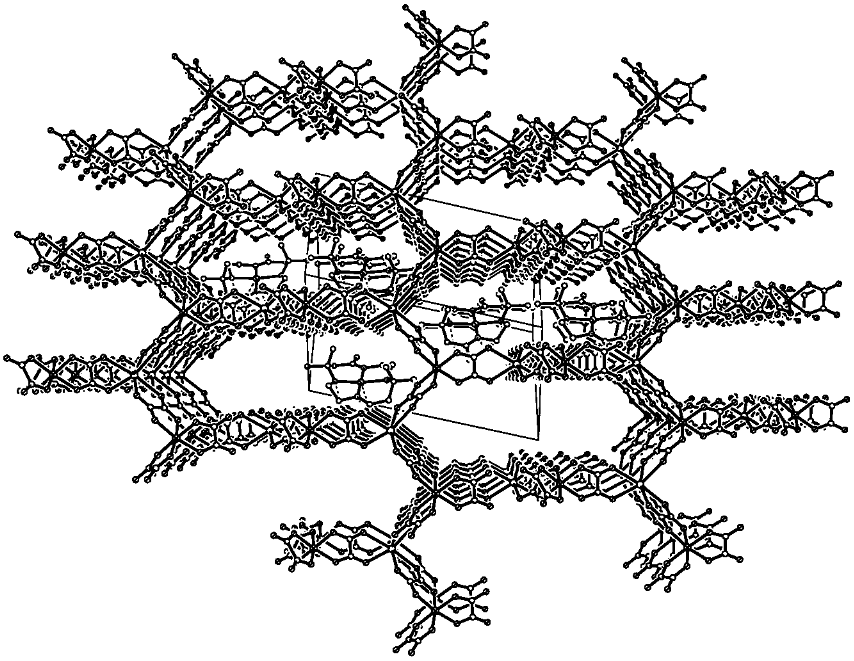


Figure 2. View of the crystal cell of $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$ in the direction of the diagonal line of *a* and *b* axes.

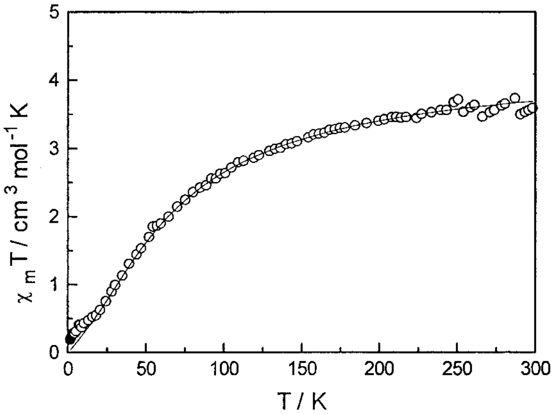
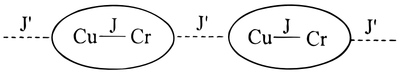


Figure 3. Plots of the products $\chi_m T$ vs temperature for $\{K[Cu(trans\text{-}[l4]dien)]Cr(ox)_3\}_n$. The solid line represents the best fitting (see text for the fitted parameters).

Scheme 1. Relationship of the Magnetic Exchange Coupling of $\{K[Cu(trans[14]dien)]Cr(ox)_3\}_n$



In order to analyze the magnetic data, we used an approximation[24,25] for the system shown in Scheme 1. As indicated in Scheme 1, the title complex can be considered as a uniform chain formed by Cr−OX−Cu binuclear units, for simplicity

$$\cdots S_b \overset{J}{\cdots} S_b \overset{J}{\cdots} S_b \cdots$$

where S_b symbolizes the effective spin of heterobinuclear unit

$$(\mathrm{Cu}^{\mathrm{II}} \overset{J}{-} \mathrm{Cr}^{\mathrm{III}})$$

where *J* is the exchange coupling parameter associated with a $\mathrm{Cu}^{\mathrm{II}}-\mathrm{Cr}^{\mathrm{III}}$ binuclear pair, and J' refers to the interbinuclear magnetic parameter of the $\mathrm{Cu}^{\mathrm{II}}-\mathrm{Cr}^{\mathrm{III}}$ unit. On the assumption of purely isotropic interactions, the susceptibility of binuclear unit ($\mathrm{Cu}^{\mathrm{II}}-\mathrm{Cr}^{\mathrm{III}}$) χ_b is calculated from eq 1. Assuming that S_{eff}

$$\chi_b = \chi_{\mathrm{Cu-Cr}} = (Ng^2\beta^2/kT)\{[10 + 2\exp(-4J/kT)]/[5 + 3\exp(-4J/kT)]\} \quad (1)$$

is treated as a classical spin, $g_{\mathrm{eff}} = 2$, S_{eff} can be calculated from eq 2, and the magnetic susceptibility of the chain can be described by the classical spin model (eq 3) derived by Fisher,[26] with $u = \coth[J'S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1)/kT] - kT/J'S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1)$.

$$S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1) = 3k(\chi_b T)/N{g_{\mathrm{eff}}}^2\beta^2 \quad (2)$$

$$\chi_M = [Ng^2\beta^2 S_{\mathrm{eff}}(S_{\mathrm{eff}} + 1)/3kT](1 + u)/(1 - u) \quad (3)$$

The least-squares fit from eq 3 to the data was found with $J = -9.88$ cm^{-1}, $J' = -2.72$ cm^{-1}, $g = 2.05$. The agreement factor, defined as $F = \sum_i(\chi_i^{\mathrm{obs}} - \chi_i^{\mathrm{calcd}})^2/(\chi_i^{\mathrm{obs}})^2$, was 8.72×10^{-3}, for all of the 92 observations. But the absolute value of the coupling constant J' seems to be slightly larger for the diamagnetic −ox−K−ox− bridge. This may be due to the limitation of the present approximate model. Nevertheless, this result (negative and small *J* and small J' values) indicates that a weak antiferromagnetic intrachain interaction exists between the Cr(III) and Cu(II) ions within the title compound.

In general, Cr(III)−Cu(II) systems show ferromagnetic coupling due to the strict orthogonality of the magnetic orbitals, $\langle t_{2g}|e_g\rangle = 0$, $(t_{2g})^3(\mathrm{Cr})-(e_g)^1(\mathrm{Cu})$. However, the crystallographic data of the title complex has indicated a five-coordinated square-pyramid environment for Cu(II). The axially distorted geometry of Cu(II) is important as it removes the strict orthogonality of the e_g and t_{2g} orbitals on $\mathrm{Cu}^{\mathrm{II}}$ and $\mathrm{Cr}^{\mathrm{III}}$ ions, thus introducing an antiferromagnetic interaction between the $\mathrm{Cr}^{\mathrm{III}}$ and $\mathrm{Cu}^{\mathrm{II}}$ within the complex.[27]

---

(24) Kou, H. Z.; Bu, W. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P. *J. Chem. Soc., Dalton Trans.* **1998**, 4161.

(25) Shen, H.-Y.; Bu, W.-M.; Gao, E.-Q.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P. *Inorg. Chem.* **2000**, *39*, 396.

(26) Hernandez-Molina, M.; Lloret, F.; Ruiz-Perez, C.; Julve, M. *Inorg. Chem.* **1998**, *37*, 4131.

(27) Andruh, M.; Melanson, R.; Stager, C. V.; Rochon, F. D. *Inorg. Chim. Acta* **1996**, *251*, 309.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 59772020, No. 29631040), The Research Fund for the Doctoral Program of Higher Education and Natural Science Foundation of Tianjin (No. 983604611).

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, and perspective view along the three main direction *a*, *b*, *c* axes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991325N