Crystal Structure and Magnetic Properties of an Infinite Chainlike and a Tetranuclear Bimetallic Copper(II)−Chromium(III) Complex with Bridging Cyanide Ions

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The crystal structures of two CN^- bridged bimetallic copper(II)−chromiun(III) complexes, $[\{(Cu(dien))_2Cr(CN)_6\}_n][Cu(dien)(H_2O)Cr(CN)_6]_n\cdot4nH_2O$ (**1**) and $[(Cu(edma))_3Cr(CN)_6]$ (**2**) (where dien and edma are diethylenetriamine and ethylenediaminemonoacetate respectively), have been determined. Complex **1** ($C_{24}H_{49}N_{21}O_5Cr_2Cu_3$) crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 20.509(2)$ Å, $b = 14.376(3)$ Å, $c = 15.040(4)$ Å, $\beta = 96.03(2),°$ and $Z = 4$. In the crystal structure, complex **1** has two distinct ionic units: one is a cationic polymeric chain formed by $[(Cu(dien))_2Cr(CN)_6]^+$ and the other is a CN^--bridged binuclear anion $[(Cu(dien)(H_2O)Cr(CN)_6]^-$. Complex **2** crystallizes in the trigonal system, space group R_{3C}, with $a = 24.446(2)$ Å, $b = 14.446(2)$ Å, $c = 22.685(1)$ Å, and $Z = 6$. Complex **2** consists of discrete tetranuclear molecule $[(Cu(edma))_3Cr(CN)_6]^-$. In both complexes, the Cr atoms all have an octahedral configuration with six coordinated CN^- ions and connect to the copper atoms via the CN^- ions. At higher temperature, the χT of both complexes increases with decreased temperature showing the ferromagnetic behavior which is due to the ferromagnetic exchange interaction between Cu and Cr atoms through the bridging CN^- ions. However at lower temperature, χT decreases with decreased temperature; this can be attributed to the occurrence of the antiferromagnetic intramolecular interaction (zJ'). The fitting to the experimental magnetic susceptibilities gives $g = 2.10$, $J^a = 7.24$ cm^{-1}, $J^c = 6.41$ cm^{-1}, and $zJ' = -0.16$ cm^{-1} for **1** and $g = 2.09$, $J = 9.16$ cm^{-1}, and $zJ' = -0.09$ cm^{-1} for **2**.

Introduction

In the past few years, molecular-based magnetic materials have attracted intensive interest from chemists.[1] So far, at least three molecular-based systems exhibiting a ferromagnetic transition have been well characterized from both structural and magnetic viewpoints. One such system is organometallic ferromagnets such as $[Fe(C_5Me_3)_2]^{\bullet+}(TCNE)^{\bullet-}\cdot MeCN$.[2] The other two systems are constructed by assembling ferrimagnetic chains in the crystal lattice with a ferromagnetic interaction between these chains. These two systems are distinguished from each other by the composition of the ferrimagnetic chains. For example, the chains of one system consist of two different metal ions, e.g. $[MnCu(pbaOH)(H_2O)_2]$ (pbaOH = 2-hydroxy-1,3-propanediylbis(oxamato),[3] and the chains of another system consist of metal ions and radicals, e.g. $[Mn(hfac)_2NiT\text{-}iPr]$.[4] However, most members of these three systems perform a magnetic ordering at low temperature (4−30 K). In recent years, Verdaguer et al. has reported a CN^- bridging complex formulated as $CsNi[Cr(CN)_6]\cdot2H_2O$, which exhibits a spontaneous magnetization at $T_c = 90$ K.[5a] In the latter, a few high-temperature molecular magnets based on cyanide building blocks were reported by Girolami,[5b] and Verdaguer[5c] et al. with T_c at 230, 190, and 240 K, respectively. These works show that transition metal cyanides are good candidates for a system of molecule-based magnetic materials.[5] However, at this time there are only a few papers on the magnetic exchange interaction through a bridging CN^- ligand, which may be due to a difficulty in growing crystals of cyanide-containing complexes.[6] In this paper, we present the synthesis, crystal structure, and magnetic properties of two new cyanide bridged bimetalic complexes: one has a chainlike structure, $[\{(Cu(dien))_2Cr(CN)_6\}_n][Cu(dien)(H_2O)Cr(CN)_6]_n\cdot4nH_2O$ (**1**), and the other is a tetranuclear complex, $[(Cu(edma))_3Cr(CN)_6]$ (**2**), where dien is diethylenetriamine and edma is ethylenediaminemonoacetate.

Experimental Section

Materials. The complex $[Cu(dien)Cl_2]$ and the ligand Hedma·2HCl were synthesized by literature procedures.[7] $K_3[Cr(CN)_6]$ was an AR reagent and used without further purfication.

$[\{(Cu(dien))_2Cr(CN)_6\}_n][Cu(dien)(H_2O)Cr(CN)_6]_n\cdot4nH_2O$ (1). To an aqueous solution of $[Cu(dien)Cl_2]$ (3 mmol, 30 mL) was added a

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Table 1. Crystallographic Data for Complex **1** and **2**

	1	**2**
formula	$C_{24}H_{49}N_{21}O_5Cr_2Cu_3$	$C_{18}H_{27}N_{12}O_6CrCu_3$
fw	1006.41	750.11
space group	$P2_1/c$	R_{3C}
a (Å)	20.509(2)	14.446(2)
b (Å)	14.376(3)	14.446(2)
c (Å)	15.040(4)	22.685(5)
β (deg)	96.03(2)	90.00(2)
V (Å^3)	4410.1(4)	4099.82(9)
temp (°C)	20 ± 2	20 ± 2
λ (radiation Mo Kα (Å)	0.710 73	0.710 73
Z	4	6
ρ_{obsd} (g/cm^3)	1.52	1.83
ρ_{calcd} (g/cm^3)	1.516	1.82
μ(Mo Kα) (cm^{-1})	19.5	27.4
R (R_w)[a]	0.073 (0.083)	0.032 (0.038)

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

20 mL solution of 2 mmol of $K_3[Cr(CN)_6]$ with stirring for a few seconds. After this solution was allowed to stand at room temperature for 2 days, single crystals suitable for the X-ray diffraction study were collected, washed with water, and dried under vacuum. Anal. Calcd for **1**, $C_{42}H_{49}N_{21}O_5Cu_3Cr_2$: C, 28.48, H, 4.92, N, 29.65, Cu, 18.43, Cr, 10.59. Found: C, 28.64, H, 4.89, N, 29.24, Cu, 18.95, Cr, 10.34.

[(Cu(edma))$_3$Cr(CN)$_6$] 2. A 10 mmol sample of KOH was added to a 10 mL solution of 3 mmol Hedma·2HCl. This solution was mixed with a 10 mL solution of 3 mmol $Cu(NO_3)_2 \cdot 6H_2O$. After this was allowed to stand at room temperature for 12 h, the resulting solution was added to a 30 mL aqueous solution of 1 mmol $K_3[Cr(CN)_6]$. A precipitate formed immediately and was removed by filtration. The filtrate which was allowed to stand for 3 days, giving blue crystals suitable for the X-ray diffraction study were collected, washed with water, and dried under vacuum. Anal. Calcd for **2**, $C_{18}H_{27}N_{12}O_6Cu_3$-Cr: C, 28.39, H, 3.83, N, 22.26, Cu, 25.17, Cr, 6.99; Found: C, 28.48, H, 3.69, N, 22.15, Cu, 25.12, Cr, 6.86.

X-ray Data Collection and Structure Refinement. The suitable single crystals were sealed on glass fibers and aligned on an Enraf-Nonius CAD-4 diffractometer for data collection. Unit cell parameters were determined on the basis of 25 reflections with 10.2° $< 2\theta <$ 13.8° for **1** and 9.8° $< 2\theta <$ 13.4° for **2**. Intensity measurements employed graphite-monochromated Mo Kα radiation and the $\omega - 2\theta$ scan mode in the range 0° $< 2\theta <$ 50° at room temperature. During data collection, the intensity of three standard reflections monitored at every 3600 s of X-ray exposure time showed no significant decay. After taking into account Lorentz and polarization effects, an empirical absorption correction with minimum 72.42% and maximum 99.99% transmission was engaged for **1** which based on seven Ψ scans, and no absorption correction was engaged for **2**. The crystal data are provided in Table 1.

The structure solution by MULTAN 82 and the Patterson method revealed the metal atom coordinates and subsequently difference Fourier methods yielded positions of all remaining non-H atoms and most hydrogen atoms, while the other hydrogen atoms were riding on the related carbon atoms. All non-H atoms were refined anisotropically by unit-weighted full-matrix least-squares methods, while H-atoms were refined isotropically. Refinment converaged at $R = 0.073$ and $R_w = 0.083$ for 4591 observed reflections with $I > 3\sigma(I)$ of 6914 unique ones for **1** and $R = 0.032$ and $R_w = 0.038$ for 730 observed reflections for **2**. The R values for complex **1** are somewhat high. We think this might be that four water molecules in this complex are in disorder-(their temperature factors are high). A final difference Fourier map exhibited no significant peaks greater than 0.18e/Å^3 for **1** and 0.19 e/Å^3 for **2**. Scattering factors were taken from ref 13. All computations were performed on a micro VAX-II computer with SDP-Plus programs.

Magnetic Measurement. The magnetic measurement was carried out on the powdered samples with a CF-1 type extracting sample magnetometer which was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine), in the temperature range 5−300 K. The applied magnetic field was 50 kOe, and the data were corrected for diamagnetism using Pascal's constant.[8]

Table 2. Positional and Thermal Parameters for the Atoms of **1**

atom	x	y	Z	B_{eq}[a] (Å^2)
Cu1	0.38609(6)	0.76923(7)	0.05693(7)	2.23(2)
Cu2	0.35622(6)	0.25636(7)	0.09868(7)	2.26(2)
Cu3	0.03212(7)	0.74926(9)	0.01686(8)	3.47(3)
Cr1	0.46446(7)	0.52440(9)	0.28952(9)	1.88(3)
Cr2	0.13355(8)	0.4974(1)	−0.1626(1)	2.41(3)
Ow1	0.1375(6)	0.5564(8)	0.3557(7)	8.4(3)
Ow2	0.2181(7)	0.340(1)	0.1344(9)	10.5(4)
Ow3	0.218(1)	0.624(2)	0.141(2)	9.9(7)
Ow4	0.244(1)	0.492(1)	0.275(1)	16.1(6)
Ow5	0.1033(4)	0.8835(6)	0.0209(6)	5.4(2)
N11	0.4686(4)	0.7051(5)	0.0286(5)	2.8(2)
N14	0.3429(4)	0.6911(5)	−0.0446(5)	2.8(2)
N17	0.3006(4)	0.8421(6)	0.0407(5)	3.0(2)
N21	0.3316(4)	0.1721(6)	0.1977(5)	3.3(2)
N24	0.3047(4)	0.1628(5)	0.0192(5)	2.7(2)
N27	0.3460(4)	0.3380(6)	−0.0101(5)	3.7(2)
N31	−0.0336(5)	0.8098(6)	−0.0763(6)	3.9(2)
N34	−0.0154(5)	0.8229(7)	0.1024(6)	4.1(2)
N37	0.0752(6)	0.6810(8)	0.1270(6)	5.0(2)
N411	0.3946(5)	0.3578(6)	0.1757(5)	3.5(2)
N421	0.5466(4)	0.6785(5)	0.4077(5)	2.8(2)
N431	0.3582(5)	0.5018(6)	0.4291(6)	4.1(2)
N441	0.3735(5)	0.6730(6)	0.1753(6)	3.6(2)
N451	0.5651(4)	0.5767(6)	0.1475(5)	3.2(2)
N461	0.5629(5)	0.3698(6)	0.3783(6)	3.5(2)
N511	−0.0009(5)	0.4797(7)	−0.2897(7)	4.9(2)
N521	0.2013(5)	0.6081(8)	−0.3156(7)	5.4(3)
N531	0.1778(5)	0.3069(6)	−0.2511(6)	4.5(2)
N541	0.0720(7)	0.3779(8)	−0.0130(8)	7.3(3)
N551	0.0775(5)	0.6723(7)	−0.0675(6)	3.9(2)
N561	0.2650(5)	0.5141(7)	−0.0291(7)	4.9(2)
C12	0.4518(6)	0.6265(7)	−0.0357(7)	3.8(2)
C13	0.3943(6)	0.6581(9)	−0.0983(7)	4.6(3)
C15	0.2910(5)	0.7479(8)	−0.0919(7)	4.2(2)
C16	0.2527(5)	0.7918(9)	−0.0240(9)	4.6(3)
C22	0.3091(5)	0.0833(7)	0.1595(7)	3.5(2)
C23	0.2641(5)	0.1069(7)	0.0735(8)	3.7(2)
C25	0.2672(6)	0.2185(9)	−0.0547(7)	4.7(3)
C26	0.3137(6)	0.2861(9)	−0.0863(6)	4.3(3)
C32	−0.0731(6)	0.8793(9)	−0.0316(9)	5.2(3)
C33	−0.0795(6)	0.8463(9)	0.0634(9)	5.0(3)
C35	−0.0088(7)	0.7715(9)	0.1910(8)	5.1(3)
C36	0.0570(6)	0.7339(9)	0.2066(7)	5.1(3)
C41	0.4191(5)	0.4191(5)	0.2132(6)	2.3(2)
C42	0.5134(5)	0.6242(6)	0.3682(6)	2.2(2)
C43	0.3972(5)	0.5078(6)	0.3803(6)	2.7(2)
C44	0.4041(5)	0.6206(6)	0.2190(6)	2.4(2)
C45	0.5300(5)	0.5535(6)	0.1969(6)	2.3(2)
C46	0.5275(5)	0.4256(6)	0.3489(6)	2.4(2)
C51	0.0472(5)	0.4866(7)	−0.2446(7)	3.3(2)
C52	0.1775(5)	0.5704(8)	−0.2604(7)	3.5(2)
C53	0.1632(5)	0.3756(7)	−0.2185(7)	3.3(2)
C54	0.0930(5)	0.4216(8)	−0.0652(7)	3.8(2)
C55	0.1001(5)	0.6150(6)	−0.1054(6)	2.4(2)
C56	0.2197(5)	0.5069(7)	−0.0776(7)	3.1(2)

[a] $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Results and Discussion

Description of the Structure. ORTEP views of **1** and **2** are given in Figures 1 and 2 respectively. The non-hydrogen atom coordinates, selected bond lengths and angles are listed in Tables 2 and 3, respectively, for **1** and in Tables 4 and 5, respectively, for **2**.

As shown in Figures 1 and 2, both compounds have end-to-end bridging CN^- ions to form bimetalic complexes. The structure of complex **1** consists of two distinct ionic units. One is a cationic polymeric chain formed by the $[(Cu(dien))_2Cr(CN)_6]^+$, the other is a binuclear anion $[Cu(dien)(H_2O)Cr(CN)_6]^-$.

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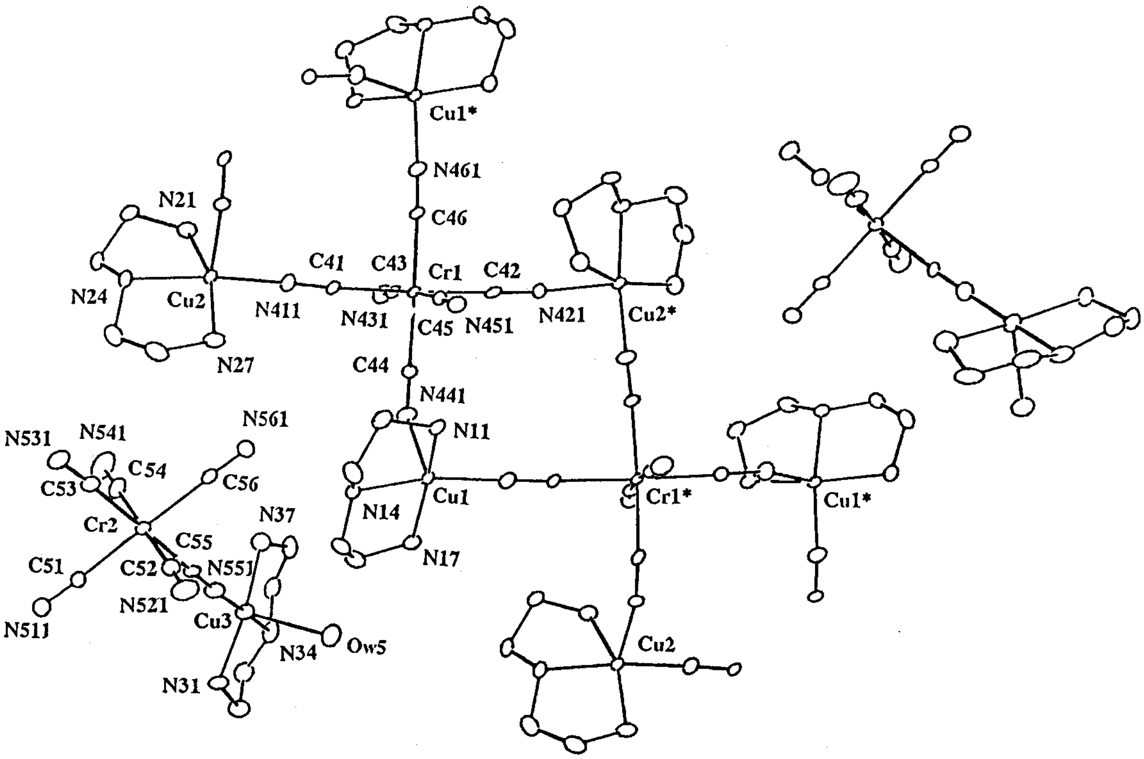


Figure 1. ORTEP diagram of **1**, [{(Cu(dien))$_2$Cr(CN)$_6$}$_n$][Cu(H$_2$O) (dien)Cr(CN)$_6$]$_n$·4nH$_2$O, with thermal ellipsoids at 20% probability. Atoms marked with an asterisk: symmetry operator $1 - x, y + {}^1/_2, -z + {}^1/_2$. All of the H atoms and the C atoms of dien are omited for clarity.

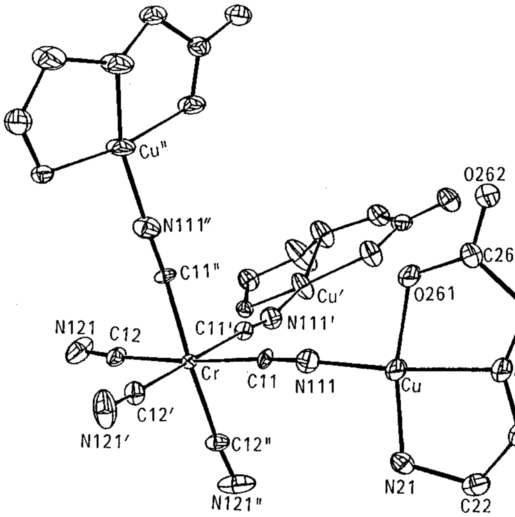


Figure 2. ORTEP diagram of **2** [(Cu(edma))$_3$Cr(CN)$_6$] with thermal ellipsoids at 50% probability. Symmetry operator: (′) $-y, x - y, z$; (″) $- x + y, -x, z$.

In unit cell of **1**, the cationic chains run along the 2_1 screw axes. The Cr atoms have an octahedron configuration with six coordinated CN$^-$ ions. The angles of ∠Cr−C−N are close to 180°. The bond lengths of Cr—C are in the range 2.05−2.08 Å with a mean length of 2.063 Å, the bond lengths of C≡N are in the range 1.13−1.16 Å. Of the six CN$^-$ ions around Cr atom, two (namely C43≡N431 and C45≡N451, trans to each other) are monodentate ligands, while the other four are bidentate ligands as bridging groups. Thus each Cr atom has connected to four Cu atoms of the nearest [Cu(dien)]$^{2+}$ units: Cu1, Cu1* (the asterisk denotes the symmetry operations $1 - x, -{}^1/_2 + y, {}^1/_2 - z$) and Cu2, Cu2*. The two independent copper atoms (Cu1, Cu2) acquired square-based pyramidal configurations. The equatorial was plane was defined by three nitrogens of dien and one nitrogen of a [Cr(CN)$_6$]$^{3-}$ group and the axial coordination completed by the nitrogen of another [Cr(CN)$_6$]$^{3-}$ group. So each Cu atom links two Cr atoms through the axial and the equatorial cyanide ions, respectively, to form an infinite alterating chain as shown in Figure 1. Two different bridging modes exist among the copper atoms, cyanide ions, and chromium atoms: of four bridging CN$^-$ ions in each [Cr(CN)$_6$]$^{3-}$ group, two labeled C41≡N411 and C46≡N461 are respectively connected to the two nearst copper atoms Cu2 and Cu1* through the equatorial planes of copper atoms and form almost linear Cr—C≡N—Cu links (∠C−N−Cu, average 172°). The other two CN$^-$ ions, labeled C44≡N441 and C42≡N421, respectively coordinate to the two nearest copper atoms Cu1 and Cu2* through the axial directions and give nonlinear Cr—C≡N—Cu sequences with ∠C−N−Cu = 139°. The bond length of Cu−N(CN$^-$) in the equarotial plane of copper atom is 1.98 Å, and the corresponding value in the axial direcion is 2.3 Å.

The other structural unit of complex **1** is a binuclear anion, [Cu(dien)(H$_2$O)Cr(CN)$_6$]$^-$, formed by linking [Cu(dien)]$^{2+}$ and [Cr(CN)$_6$]$^{3-}$ ions through one CN$^-$ ion(C55≡N551) which is within the equatorial plane of the Cu atom. The angle ∠C−N−Cu is equal to 167°. The Cu atom in this unit has a pyramidal configuration with four nitrogens in the equatorial plane and an oxygen atom of water in the apical position. The bonding length of Cu(3)−O5 is 2.416(9) Å.

Different from complex **1**, complex **2** is a discrete tetranuclear molecule containing one Cr atom and three Cu atoms. As shown in Figure 2, this molecule has a near C_3 symmetry, the Cr atom lies on the three rotation, axis and three Cu atoms (x, y, z), $(-y, x - y, z)$ and $(-x + y, -x, z)$ are symmetry related. In this molecule, the Cr atom has an octahedral configuration with six coordinated CN$^-$ ions, and the ∠Cr−C−N angles are close to 180°. The six CN$^-$ ions also can be divided into two kinds: monocoordinated terminal cyanide ions and bidentate bridged cyanide ions. In the former, the bond lengths Cr—C and C≡N are 2.061 and 1.13 Å, respectively. In the later, the coresponding values are 2.051 and 1.14 Å. Because the coordination of the nitrogen of the cyanide ion to

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

Bond Distances

Cr1−C41	2.063(9)	Cr1−C42	2.054(9)	Cr1−C43	2.05(2)
Cr1−C44	2.072(9)	Cr1−C45	2.08(1)	Cr1−C46	2.06(1)
Cr2−C51	2.05(2)	Cr2−C52	2.09(1)	Cr2−C53	2.06(2)
Cr2−C54	2.07(1)	Cr2−C55	2.049(9)	Cr2−C56	2.07(1)
Cu1−N441	2.290(9)	Cu1−N461	1.981(8)	Cu1−N11	2.011(9)
Cu1−N14	2.025(8)	Cu1−N17	2.034(9)	Cu2−N411	1.975(8)
Cu2−N421	2.297(8)	Cu2−N21	2.025(8)	Cu2−N24	2.022(7)
Cu2−N27	2.006(8)	Cu3−N31	2.036(9)	Cu3−N34	1.997(9)
Cu3−N37	2.004(1)	Cu3−N551	1.99(1)	Cu3−Ow5	2.416(9)

Bond Angles

C41−Cr1−C42	176.9(4)	C41−Cr1−C43	89.5(4)
C41−Cr1−C44	89.7(3)	C41−Cr1−C45	93.4(4)
C41−Cr1−C46	87.7(3)	C42−Cr1−C43	91.1(4)
C42−Cr1−C44	93.3(3)	42−Cr1−C45	96.2(4)
C42−Cr1−C46	89.2(3)	C43−Cr1−C44	90.6(4)
C43−Cr1−C45	174.9(4)	C43−Cr1−C46	93.8(4)
C44−Cr1−C45	85.2(4)	C44−Cr1−C46	174.9(4)
C45−Cr1−C46	90.5(4)	C51−Cr2−C52	91.4(5)
C51−Cr2−C53	87.9(5)	C51−Cr2−C54	90.0(4)
C51−Cr2−C55	90.5(4)	C51−Cr2−C56	178.7(4)
C52−Cr2−C53	88.4(4)	C52−Cr2−C54	177.8(4)
C52−Cr2−C55	94.0(5)	C52−Cr2−C56	90.0(5)
C53−Cr2−C54	90.0(4)	C53−Cr2−C55	177.2(5)
C53−Cr2−C56	92.2(4)	C54−Cr2−C55	87.7(5)
C54−Cr2−C56	88.7(5)	C55−Cr2−C56	89.2(4)
N441−Cu1−N461	99.0(3)	N441−Cu1−N11	93.1(3)
N441−Cu1−N14	100.1(4)	N441−Cu1−N17	103.8(3)
N461−Cu1−N11	91.5(3)	N461−Cu1−N14	160.7(3)
N461−Cu1−N17	95.0(3)	N11−Cu1−N14	84.2(3)
N11−Cu1−N17	160.7(3)	N14−Cu1−N17	83.8(3)
N411−Cu2−N421	95.2(3)	N411−Cu2−N21	97.2(3)
N411−Cu2−N24	171.7(4)	N411−Cu2−N27	92.7(3)
N421−Cu2−N21	91.4(3)	N421−Cu2−N24	93.0(3)
N421−Cu2−N27	105.5(3)	N21−Cu2−N24	83.2(3)
N21−Cu2−N27	159.6(4)	N24−Cu2−N27	84.5(3)
N31−Cu3−N34	83.4(4)	N31−Cu2−N37	164.1(4)
N31−Cu3−N551	96.9(4)	N31−Cu3−Ow5	91.7(3)
N34−Cu3−N37	86.0(4)	N34−Cu3−N551	178.1(4)
N34−Cu3−Ow5	83.9(4)	N37−Cu3−N551	93.4(4)
N37−Cu3−Ow5	98.9(4)	N551−Cu3−Ow5	98.00(4)

Table 4. Positional and Thermal Parameters for the Atoms of **2**

atom	*x*	*y*	*z*	$B_{eq}{}^{a}$ (Å^2)
Cr	0.000	0.000	0.498	1.45(3)
C11	−0.1168(6)	−0.1160(6)	0.5497(4)	2.1(2)
N111	−0.1864(6)	−.1832(6)	0.5750(3)	3.7(2)
C12	0.1185(6)	0.1249(6)	0.4508(4)	2.8(2)
N121	0.1864(7)	0.1976(6)	0.4286(4)	5.5(2)
Cu	−0.2838(1)	−0.30916(9)	0.61990(1)	3.93(3)
N21	−0.3110(5)	−0.4149(5)	0.5586(3)	2.6(2)
C22	−0.3585(8)	−0.5230(7)	0.5845(4)	3.9(2)
C23	−0.402(1)	−0.5234(8)	0.6435(5)	6.9(4)
N24	−0.3390(7)	−0.4320(6)	0.6768(4)	4.6(2)
C25	−0.3705(8)	−0.4040(6)	0.7310(4)	3.4(2)
C26	−0.3183(6)	−0.2833(6)	0.7375(4)	2.8(2)
O261	−0.2739(5)	−0.2288(4)	0.6916(3)	3.7(2)
O262	−0.32126(6)	−0.2439(5)	0.7849(3)	3.7(2)

[a] $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for the Complex **2**[a]

Bond Distances

Cr−C11	2.051(6)	Cu−O261	1.962(7)
Cr−C12	2.061(7)	Cu−N111	1.941(7)
Cu−N24	2.010(8)	Cu−N21	1.955(8)

Bond Angles

C11−Cr−C11′	90.6(3)	C11−Cr−C12	175.6(3)
C11−Cr−C12′	85.2(4)	C11−Cr−C12″	88.8(4)
C12−Cr−C12′	95.4(4)	N111−Cu−N21	97.3(4)
N111−Cu−N24	161.3(5)	N111−Cu−O261	94.4(3)
N21−Cu−N24	86.0(4)	N21−Cu−O261	168.2(2)
N24−Cu−O261	82.5(4)		

[a] Symmetry operation: (′) −*y*, *x*−*y*, *z*; (″) −*x* + *y*, −*x*, *z*.

the second metal atom should reduce the electron density of cyanide ion, this is beneficial to the forming of M−C π-back-bonding (where M represents metal atom and C is carbon atom of CN$^-$).[9] Therefore, when cyanide ion acts as a bridging ligand, the π-back-bonding in M—C is enhanced. As a results, the bonding length of M—C will decrease and that of C≡N will increase. But the change in bond length of the CN$^-$ ions of the bidentate end-to-end bridging type in complexes **1** and **2** is not satisfactorally signifcant. The failure of X-ray crystallographic measurements to detect changes in M—C and C—N bonding in both compounds is not surprising, because, on one hand, the increase of C≡N bond length due to an increase in M—C π-back-bonding is offset partially by the decrease of the C≡N bond length due to the bonding in M′—N(CN$^-$) and, on the other hand, the bond length for a strong bond is generally insensitive to subtle changes in bond order.

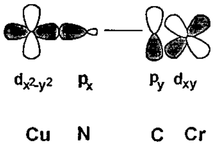
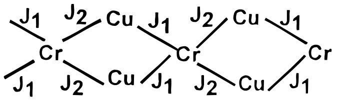


Figure 3. Orthogonality between $t_{2g}(xy)$ Cr^{III} and $e_g(x^2 - y^2)$ Cu^{II} magnetic orbitals in **1** and **2**.

In complex **2**, three Cu atoms have a tetragonal configuration. The coordinating atoms include two nitrogens and one oxygen of edma$^-$ and one nitrogen of the bridging CN$^-$ ion. The angles of the copper atom with the CN$^-$ group (∠Cu−N−C) are equal to168°; thus, the cyanide ion bridge the Cu and Cr atoms in bending fashion such as that seen in the binuclear anion of complex **1**.

Magnetic Properties. It is known that cyanide ions can transmit the magnetic exchange interaction between transition metal ions ferromagnetically or antiferromagnetically, depending on the symmetry of the magnetic orbitals.[10] For compounds **1** and **2**, there exist two kinds of Cu−CN−Cr linkage, one is nearly linear and one is bent. In the former, a ferromagnetic exchange interaction is expected from the orthogonality of the t_{2g} orbitals of Cr^{III} and the e_g orbitals of Cu^{II} (see Figure 3). In the latter, this ferromagnetic exchange interaction may be reduced and may even vary in sign. Actually, the two complexes both exhibit overall ferromagnetic behavior at higher temperature as shown in Figure 4: χT slowly increased with decreasing temperature. However, the decreasing at lower temperature also shows a occurrence of weak antiferromagnetic interaction between magnetic units in these crystals.

As shown in Figure 1, the exchange interaction in cationic chain of complex **1** can be indicated as follows:



J_1 is the exchange constant between Cr and Cu atoms which have a linear Cr—C≡N—Cu linkage, and J_2 is the exchange

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(9) (a) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press: London, 1976. (b) Fee, J. A. *Struct. Bonding* **1975**, *23*, 1. (c) Ryan, R. R.; Swanson, B. I. *Inorg. Chem.* **1974**, *13*, 1681.

(10) (a) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. (b) Kahn, O. *Struct. Bonding* **1987**, *68*, 89.

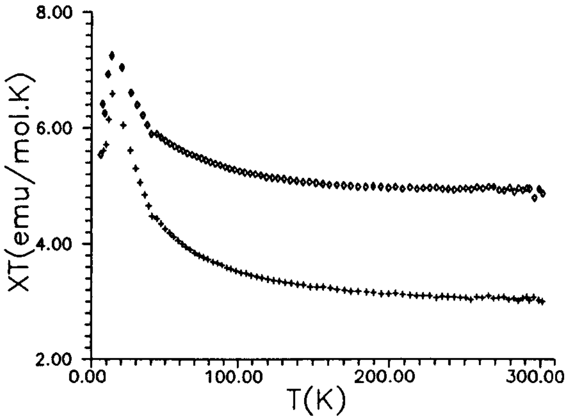

Figure 4. Plot of χT vs T of complexes **1** (◇) and **2** (+).

constant between Cr and Cu atoms which have a nonlinear Cr—C≡N—Cu linkage. The exact formula of the magnetic susceptibility for this kind of alternating chain is difficult to derive from its Hamiltonian as yet. However, in the nonlinear Cr—C≡N—Cu bridges, the CN^- ion is in the axial direction of the copper configuration. Considering that the exchange interaction through this axial cyanide ion is very small because the cyanide ion has a near zero overlap with the magnetic orbital of copper d_{xy} which lies in the equatorial plane, we can assume that the exchange interaction through the axial cyanide ion can be neglected (set $J_2 \approx 0$). So the molar susceptibility for complex **1** can be described as

$$\chi = \chi^a + \chi^c$$

χ^a is the susceptibility of the binuclear anion $[Cu(dien)(H_2O)Cr(CN)_6]^-$ per mole. It can be derived from the exchange Hamiltonian $H = -2J^aS_{Cu}S_{Cr}$ and written as

$$\chi^a = \frac{Ng^2\beta^2}{kT} \times \frac{10 + 2\exp(-4J^a/kT)}{5 + 3\exp(-4J^a/kT)} \tag{1}$$

χ^c is the susceptibility of the trinuclear cation $[(Cu(dien))_2Cr(CN)_6]^+$ per mole. It can be deduced from the exchange Hamiltonian $H = -2J^cS_{Cr}(S_{Cu1} + S_{Cu2})$ and written as

$$\chi^c = \frac{Ng^2\beta^2}{4kT} \times \frac{A}{B} \tag{2}$$

$A = 35 + 10\exp(-5J^c/kT) + \exp(-8J^c/kT) + 10\exp(-3J^c/kT)$, and $B = 3 + 2\exp(-5J^c/kT) + \exp(-8J^c/kT) + 2\exp(-3J^c/kT)$.

In eqs 1 and 2, J^c is same as J_1 in the cationic chain and J^a is the exchange interaction in the binuclear anion $[Cu(dien)(H_2O)]Cr(CN)_6]^-$. The other symbols have their usual meanings.

Considering the further interaction between the magnetic units, the formula of the factual susceptibility can be modified by the molecular field theory as follows:[11]

$$\chi' = \frac{\chi}{1 - (2zJ/Ng^2\beta^2)\chi} \tag{3}$$

In order to reduce the number of fitting parameters, assuming the g values for all spin states of the complex being approximately equal, we can use an unique parameter g in eqs 1−3. Finally, the fitting to the experimental data gives $g = 2.10$, $J^a = 7.24$ cm^{-1}, $J^c = 6.41$ cm^{-1}, $zJ' = -0.16$ cm^{-1} and $R = 2.6 \times 10^{-3}$ ($R = (\chi_e - \chi_c)^2/\chi_e^2$) (see the solid line in Figure 5).

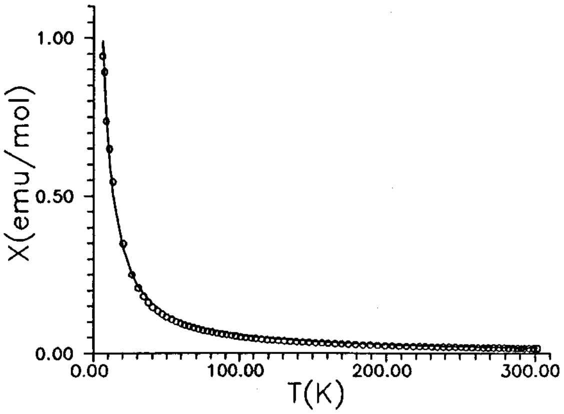

Figure 5. Plot of $\chi - T$ for complex **1**.

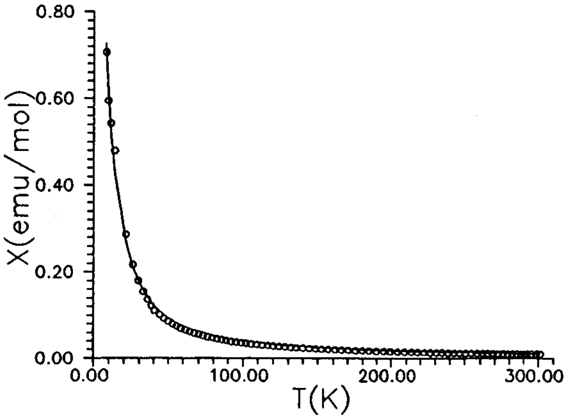

Figure 6. Plot of $\chi - T$ for complex **2**.

The complex $[(Cu(edma))_3Cr(CN)_6]$ (**2**) is a tetranuclear molecule. The exchange Hamiltonian can be written as

$$H = -2JS_{Cr}(S_{Cu1} + S_{Cu2} + S_{Cu3})$$

and the formula of susceptibility per mole is

$$\chi = \frac{Ng^2\beta^2}{kT} \times \frac{A}{B} \tag{4}$$

$A = 28 + 20\exp(-3J/kT) + 10\exp(-6J/kT) + 4\exp(-7J/kT) + 2\exp(-10J/kT)$, and $B = 7 + 10\exp(-3J/kT) + 5\exp(-6J/kT) + 6\exp(-7J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT)$. We also assume that the g values for all spin states of the complex are approximately equal. Similar to complex **1**, the factual susceptibility was also modified by the molecular field theory as in eq 3, and the fitting to the experimental data gives $g = 2.09$, $J = 9.16$ cm^{-1}, $zJ' = -0.09$ cm^{-1}, and $R = 3.5 \times 10^{-3}$ ($R = (\chi_e - \chi_c)^2/\chi_e^2$) (see the solid line in Figure 6).

Conclusion. In the crystal of $M^A{}_K[M^B(CN)_6]_J \cdot xH_2O$, CN^- ions bridge metal ions to form a 3D linkage. Although the magnetization in these complexes has been investigated by several authors,[5,6,12] the detail of the exchange interaction through the CN^- ion has not been explored. This may be due to the 3D structure complexity of these complexes. However, the 3D structure may be broken down when we replace M^A ions with a unsaturated coordinating M^AL groups. Indeed,

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[11] Myers, B. E.; Berger, L.; Friedberg, S. A. *J. Appl. Phys.* **1969**, *40*, 1149.

[12] Klenze, R.; Kanellakopulos; Trageser, G.; Eysel, H. H. *J. Chem. Phys.* **1980**, *72*, 5819.

[13] International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974.

anticipated low dimensional structures are obtained in complexes **1** and **2**. The experimental and theoretical susceptibilities now can be compared. As described above, the *J* values in the two complexes are close to each other and show that the magnetic exchange interaction between Cr and Cu through CN^- is not strong and is maybe about 5−10 cm^{-1}.

Supporting Information Available: Listings of crystallographic data for **1** (Table S1), atomic coordinates for **1** (Table S2), anisotropic thermal parameters for **1** (Table S3), bond lengths for **1** (Table S4), bond angles for **1** (Table S5), crystallographic data for **2** (Table S6), atomic coordinates for **2** (Table S7), anisotropic thermal parameters for **2** (Table S8), bond lengths for **2** (Table S9) and bond angles for **2** (Table S10), experimental and calculated susceptibilities for **1** (Table S11) and for **2** (Table S12), and least-squares planes and deviations therefrom for **1** and **2** and unit cell and packing diagrams for **1** and **2** (19 pages). Ordering information is given on any current masthead page.

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