Cyano-Bridged Dimetallic Polynuclear Cu_6Cr, Cu_6Cr_6, Cu_2W, and CuW Arrays: Synthesis, Crystal Structure, and Magnetism

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The synthesis, structure, and properties of the dimetallic complexes $[CuLCr(CN)_6]_6\cdot[\{CuL(H_2O)\}_6Cr(CN)_6](ClO_4)_3\cdot 16H_2O$ (**1**), $[CuLCr(CN)_5(NO)]_6\cdot[\{CuL(H_2O)\}_6Cr(CN)_5(NO)](ClO_4)_3\cdot 16H_2O$ (**2**) and $[CuL]_3[W(CN)_8]_2\cdot 4H_2O$ (**3**) {L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.2]decane} are presented. The structures of **1** and **2** are isomorphous and consist of novel cyano-bridged $[CuL(\mu\text{-}CN)_2Cr(CN)_4]_6$ dodecanuclear units and $[CuL(H_2O)(\mu\text{-}CN)]_6Cr$ heptanuclear moieties. Every cyclic dodecanuclear Cu_6Cr_6 group embeds a ClO_4^- anion. The heptanuclear and the dodecanuclear units are connected through hydrogen bonds to generate a vacant hole, in which another ClO_4^- anion is accommodated. Complex **3** contains cyano-bridged Cu_2W trimers and CuW dimers. Magnetic studies have shown that the three complexes display ferromagnetic coupling across the Cr–CN–Cu or W–CN–Cu linkages. The best fit to the magnetic data gave for complex **1** $J_{CuCr} = +2.40\ cm^{-1}$, $g_{Cr} = 1.99$, $g_{Cu} = 2.09$, and an intermolecular coupling constant $\theta = +0.23$ K while for complex **2** $J_{CuCr} = +12\ cm^{-1}$, $g = 2.13$, and $\theta = -0.49$ K. Ferromagnetic Cu^{II}-W^{V} coupling is operative in complex **3**.

Introduction

The magnetic properties of cyano-bridged dimetallic assemblies have been actively researched.[1−55] Exciting findings include the design and synthesis of cyano-bridged room-temperature molecule-based magnets[1] and magnetically tunable materials.[2−5] In particular, cyano-bridged polynuclear species can be used to elucidate the strength of intermetallic coupling through the bridges and to search for single-molecule magnets.[10−21] Until now, cyano-bridged star-like heptanuclear complexes $\{[ML^1]_6[M'(CN)_6]\}^{n+}$ (M = Cu^{II}, Ni^{II}, or $Mn^{II/III}$; L^1 = organic ligands; M′ = Fe^{III}, Cr^{III}) have been synthesized,[21−29] some of which have been structurally characterized. The magnetism of cyano-bridged tri-, tetra-, penta-, and pentadecanuclear complexes has also been reported.[34−50] These studies show that the coupling constants of Ni^{II}-Fe^{III}, Mn^{II}-Fe^{III}, Ni^{II}-Cr^{III}, Mn^{II}-Cr^{III}, and Cu^{II}-Cr^{III} through the cyano bridges are generally less than 20 cm^{-1} (absolute values). Very recently, a cyano-bridged Mo_6Mn complex has been found to exhibit interesting single-molecule magnet behavior.[20] Our interest in low-dimensional cyano-bridged dimetallic complexes[41,46] has suggested that treating the Cu^{II} building block $[CuL](ClO_4)_2$ {L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.2]decane} with $[Cr(CN)_6]^{3-}$, $[Cr(CN)_5(NO)]^{3-}$ or $[W(CN)_8]^{3-}$ will generate cyano-bridged species since the cyano nitrogen atoms can replace the weakly coordinated ClO_4^- oxygen atoms around the Cu^{II} atom.[56] Three novel polynuclear dimetallic complexes have been obtained and investigated for their magnetic properties. We report our findings here.

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Results and Discussion

Synthesis and Physical Characterization

$[Cr(CN)_6]^{3-}$/$[Cr(CN)_5(NO)]^{3-}$ and $[CuL](ClO_4)_2$ react to form the new complexes **1** and **2** irrespective of the molar ratios of two precursors. Usually, di- or trinuclear and 1D chain complexes are produced by the reactions of hexacyanometallate with Cu^{II} complexes.[30,43−45,47−49] Thus, the formation of cyano-bridged dodecanuclear Cu_6Cr_6 and heptanuclear Cu_6Cr moieties is unexpected. Similarly, an attempt to synthesize Cu_6Fe complexes led to the cocrystallisation of heptanuclear and pentanuclear moieties.[23]

Similar to the reaction of $[Cu(en)_2]^{2+}$ with $[W(CN)_8]^{3-}$, $[CuL]^{2+}$ with $[W(CN)_8]^{3-}$ affords a cyano-bridged polynuclear Cu_3W_2 complex (**3**). Although a cyano-bridged 3D molecular structure is assumed for $Cu(en)_2-W(CN)_8$, it may be best regarded as polynuclear owing to its considerably weak $Cu-N_{cyano}$ coordination bonds.[52]

The three strong IR bands at 2129, 2119, and 2112 cm^{-1} for complex **1**, and 2115, 2110, 2098 cm^{-1} for complex **2** are attributed to C≡N stretching modes. The splitting of $\nu_{C\equiv N}$ indicates the presence of both bridging and nonbridging cyano ligands, which is consistent with the X-ray structural results (vide infra). The strong band centred at 1089 cm^{-1} (ν_{Cl-O}) indicates the existence of ClO_4^- anions. The

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very strong band at 1664 cm^{-1} ($\nu_{O=N}$) shows the presence of NO^+ groups in complex **2**.[55,57,58]

The solution electronic spectrum of complex **1** shows a weak broad band centred at 530 nm due to the d−d transition of Cu^{II}.[56] The d−d transition of Cr^{III} may be masked by that of Cu^{II}.

The powder X-band EPR spectrum of **1** at room temperature shows a broad, nearly isotropic signal that affords a g_{iso} value of 2.02. No half-field transition was observed. The broad isotropic signal differs from that of an axial $S = 1/2$ Cu^{II} complex. With the presence of nearly isolated Cu^{II} moieties in the complex, the EPR spectrum can be tentatively explained as the superimposition of the transitions for $S = 3/2$ (Cr^{III}), $S = 1/2$ (Cu^{II}) and the ferromagnetically coupled ground state $S = 2$ for $Cu^{II}Cr^{III}$ (vide infra).

Crystal Structures

The structures of complexes **1** and **2** are shown in Figures 1, 2, and 3. Figure 4 shows the Cu_6Cr_6 dodecanuclear unit of both complexes. The cell packing plots of three complexes are shown in the Supporting Information. The structure of the polynuclear units for complex **3** is shown in Figure 6. Selected bond lengths and angles are listed in Tables 1 and 2.

Complex **1** is isostructural to complex **2**. The structure of both complexes confirms the cocrystallization of heptanuclear Cu_6Cr^{9+} cations, cyclic $Cu_6Cr_6^{6-}$ anions, and ClO_4^- counter-anions. The molar ratio of the constituents is 1:1:3.

The $Cu_6Cr_6^{6-}$ anion consists of six $[CuL]^{2+}$ moieties and six $[Cr(CN)_6]^{3-}$ (**1**) or $[Cr(CN)_5(NO)]^{3-}$ (**2**), which are alternatively connected by the cyano ligands. The coordination environment of Cu^{II} is distorted octahedral (4 + 1 + 1) with the N_{cyano} atom at the axial position [Cu(1)−N(2) and Cu(1)−N(4A) bond lengths are 2.506(5) and 3.072(6) Å for **1**, and 2.378(5) and 3.082(6) Å for **2**].

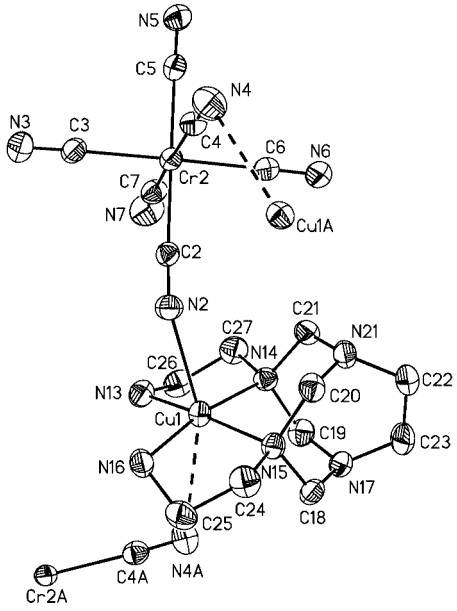

Figure 1. ORTEP diagram of the asymmetric unit of Cu_6Cr_6 for complex **1** with thermal ellipsoids at 30% probability

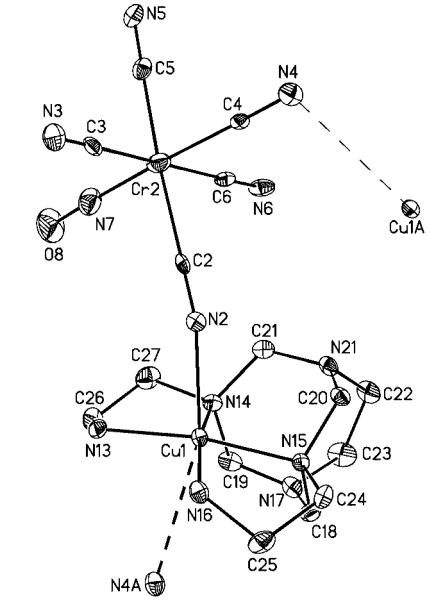

Figure 2. ORTEP diagram of the asymmetric unit of Cu_6Cr_6 for complex **2** with thermal ellipsoids at 30% probability

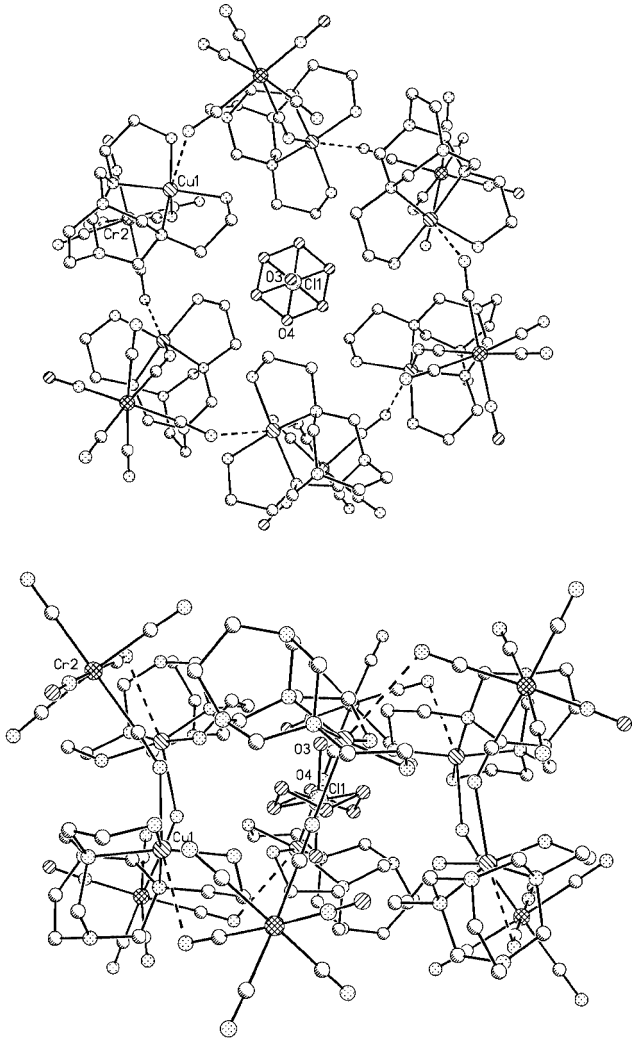

Figure 3. Cyclic Cu_6Cr_6 unit of complexes **1** and **2** showing the encapsulated ClO_4^- anion; (a) top view, (b) side view

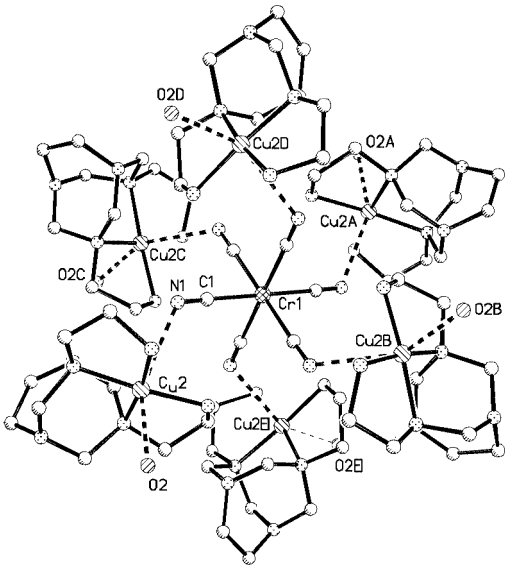

Figure 4. Star-like Cu_6Cr cation of **1**; the Cu_6Cr cation of **2** is similar to that of **1** except that one of the cyanide ligands is replaced by NO^+

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**

1		**2**	
Cu(1)−N(16)	2.000(5)	Cu(1)−N(16)	2.001(5)
Cu(1)−N(13)	2.006(5)	Cu(1)−N(13)	2.034(5)
Cu(1)−N(14)	2.016(4)	Cu(1)−N(14)	2.023(5)
Cu(1)−N(15)	2.029(4)	Cu(1)−N(15)	2.028(5)
Cu(1)−N(2)	2.506(5)	Cu(1)−N(2)	2.378(5)
Cu(1)−N(4)#1[a]	3.072(6)	Cu(1)−N(4)#1	3.082(6)
Cu(2)−N(9)	2.023(5)	Cu(2)−N(9)	2.036(7)
Cu(2)−N(10)	1.997(5)	Cu(2)−N(10)	1.984(7)
Cu(2)−N(11)	2.001(5)	Cu(2)−N(11)	1.985(7)
Cu(2)−O(2)	2.463(5)	Cu(2)−O(2)	2.464(7)
Cu(2)−N(1)	3.021(5)	Cu(2)−N(1)	2.950(7)
Cr(2)−C(7)	2.079(7)	Cr(2)−N(7)	1.886(8)
Cr(2)−C(6)	2.080(6)	Cr(2)−C(6)	2.036(7)
Cr(2)−C(5)	2.073(6)	Cr(2)−C(5)	1.985(8)
Cr(2)−C(4)	2.079(7)	Cr(2)−C(4)	2.016(7)
Cr(2)−C(3)	2.081(6)	Cr(2)−C(3)	2.037(8)
Cr(2)−C(2)	2.101(6)	Cr(2)−C(2)	2.099(7)
Cr(1)−C(1)	2.078(6)	Cr(1)−C(1)/N(30)	1.989(6)
N(1)−C(1)−Cr(1)	174.0(6)	N(1)−C(1)−Cr(1)	173.9(7)
N(2)−C(2)−Cr(2)	176.4(5)	N(2)−C(2)−Cr(2)	176.2(5)
N(3)−C(3)−Cr(2)	178.7(6)	N(3)−C(3)−Cr(2)	178.7(6)
N(4)−C(4)−Cr(2)	176.8(6)	N(4)−C(4)−Cr(2)	175.4(6)
N(5)−C(5)−Cr(2)	179.1(5)	N(5)−C(5)−Cr(2)	179.2(6)
N(6)−C(6)−Cr(2)	177.8(6)	N(6)−C(6)−Cr(2)	177.7(7)
N(7)−C(7)−Cr(2)	177.7(6)	O(8)−N(7)−Cr(2)	177.7(6)
C(2)−N(2)−Cu(1)	142.7(6)	C(2)−N(2)−Cu(1)	144.8(5)
C(1)−N(1)−Cu(2)	129.1(5)	C(1)−N(1)−Cu(2)/ N(30)−O(9)−Cu(2)	129.8(5)

[a] Symmetry operation: #1: $2/3 + x - y$, $1/3 + x$, $1/3 - z$.

The Cu^{II} ion is equatorially coordinated by four nitrogen atoms from the L ligand. The cyano ligand coordinates to the Cu^{II} ion in a bent fashion with Cu−N−C angles of 142.7(6) and 114.1(5)° for **1**, and 144.8(5)° and 112.2(5)° for **2**. In **2**, the bridging cyano ligands are *cis* or *trans* to the NO^+ ligand (Figure 2). The Cr···Cu distances through the cyano bridge are 5.427(1), 5.248(1) Å for **1** and 5.333(1), 5.225(1) Å for **2**. Within the cyclic Cu_6Cr_6 group, a perchlorate anion [Cl(1)] is embedded, which is disordered over two sets of positions (Figure 3).

Table 2. Selected bond lengths [Å] and angles [°] for **3**

W(2)−C(1)	2.154(6)	W(1)−C(40)	2.157(6)
W(2)−C(2)	2.148(6)	W(1)−C(41)	2.171(5)
W(2)−C(3)	2.162(6)	W(1)−C(42)	2.155(6)
W(2)−C(4)	2.143(7)	W(1)−C(43)	2.157(6)
W(2)−C(5)	2.163(7)	W(1)−C(44)	2.158(6)
W(2)−C(6)	2.123(5)	W(1)−C(45)	2.179(5)
W(2)−C(7)	2.190(7)	W(1)−C(46)	2.146(6)
W(2)−C(8)	2.155(7)	W(1)−C(47)	2.160(6)
Cu(1)−N(1)	2.300(5)	Cu(2)−N(6)	2.210(5)
Cu(1)−N(9)	2.003(5)	Cu(2)−N(15)	2.016(6)
Cu(1)−N(10)	2.002(5)	Cu(2)−N(16)	2.004(6)
Cu(1)−N(11)	2.029(5)	Cu(2)−N(18)	1.994(5)
Cu(1)−N(13)	2.011(4)	Cu(2)−N(20)	2.003(6)
Cu(1)−N(9)	2.003(5)	Cu(1)−N(10)	2.002(5)
Cu(1)−N(11)	2.029(5)	Cu(1)−N(13)	2.011(4)
Cu(3)−N(47)	2.368(4)		
C(1)−N(1)−Cu(1)	161.0(5)	C(6)−N(6)−Cu(2)	169.3(8)
C(47)−N(47)−Cu(3)	147.5(4)		

The $[Cr(CN)_6]^{3-}$ anion is nearly octahedral: the *cis*- and *trans*-C−Cr−C angles are close to 90° and 180°, respectively. The Cr−C−N linkages show only a slight deviation from linearity. The $[Cr(CN)_5(NO)]^{3-}$ anion has a distorted octahedral environment (C_{4v} symmetry): the Cr−*N*−O and Cr−C−N linkages are nearly linear, and the N−Cr−C *cis* angles are > 90° due to the greater electronegativity (EN) of the nitrosyl group with respect to the cyanide groups. This agrees with the EN calculations of Huheey ($NO^+ > CN^- > H_2O$).[59] The Cr−C bonds range from 1.985(8) to 2.099(7) Å, while the Cr−N distance is 1.886(8) Å. These data are in good agreement with complexes incorporating $[Cr(CN)_5(NO)]^{3-}$.[55,58]

In the heptanuclear cation (Figure 4), $[Cr(CN)_6]^{3-}$ (**1**) or $[Cr(CN)_5(NO)]^{3-}$ (**2**) is encapsulated by six $[CuL(H_2O)]^{2+}$ units through the weak $Cu-N_{cyano}$ coordination bonds [Cu−N = 3.021(5) Å for **1** and 2.950(7) Å for **2**], forming an almost spherical cluster. The Cu(2) coordination geometry is elongated octahedral with four nitrogen atoms of L at the equatorial plane, and the oxygen atom [O(2)] of one water molecule and one nitrogen atom of the bridging CN^- ligand at the axial positions [Cu(2)−O(2) = 2.463(5) Å for **1** and 2.464(7) Å for **2**]. The disorder of NO^+ over six positions in **2** precludes an accurate determination of the Cu−O(NO^+) bond length. However, the encapsulation of the $[CuL(H_2O)]^{2+}$ group reveals an NO^+ bridge.

The Cu−N≡C angles in the heptanuclear cations [129.1(5)° for **1** and 129.8(5)° for **2**] show a greater deviation from linearity. The axial O(2)−Cu(1)−N(1) angles also deviate from linearity [154.9(2)° for **1** and 155.6(2)° for **2**]. The Cr···Cu distances through the cyano bridge are 5.591(1) Å (**1**) and 5.489(1) Å (**2**).

Cl(1) and Cr(1) lie in special positions, viz. at the $\bar{3}$ rotation axis along the *c* axis, resulting in the disorder of the ClO_4^- anion. Also, the heptanuclear and the dodecanuclear units pack along the *c* axis (Figure 5), and are connected through hydrogen bonds [O(2)···N(3A)] (Figure 6). A ClO_4^- anion is accommodated between the two polynuclear units, and is hydrogen-bonded to the nitrogen atoms [N(8)] of L.

The structure of **3** consists of two cyano-bridged trimeric Cu_2W and dimeric CuW moieties (Figure 6). In the Cu_2W trimer, $[W(CN)_8]^{3-}$ uses two cyano ligands to connect two $[CuL]^{2+}$ groups, giving rise to a "V"-shaped structure. The Cu^{II} ions are five-coordinate with four nitrogen atoms of the L ligand occupying the equatorial plane and one cyano nitrogen atom at the apical position. The $Cu-N_{cyano}$ bond lengths are 2.300(5) Å for Cu(1)−N(1) and 2.210(5) Å for Cu(2)−N(6). The cyano bridging ligands coordinate to the copper ions with bond angles of 161.0(5)° for Cu(1)−N(1)−C(1) and 169.3(8)° for Cu(2)−N(6)−C(6). The CuW dimer differs from the trimer in that it contains only one cyano bridge linking two metal ions. The cyano bridging ligand coordinates to the copper ion [Cu(3)−N(47) = 2.368(4) Å] with a bond angle of 147.5(4)°. Based on the $Cu-N_{cyano}$ bond lengths and the corresponding Cu−N−C bond angles, the shorter the $Cu-N_{cyano}$ bond lengths the larger are the Cu−N−C bond angles. The corresponding metal−metal separations are 5.535 Å for Cu(1)−W(2), 5.458 Å for Cu(2)−W(2) and 5.436 Å for W(1)−Cu(3). In the cell, two polynuclear moieties are linked through weak intermolecular contacts ($Cu-N_{cyano} > 3.16$ Å) giving rise to a 3D network (see Supporting Information). Water molecules within the network are hydrogen-bonded to the primary amine nitrogen atoms and the nonbridging cyano nitrogen atoms.

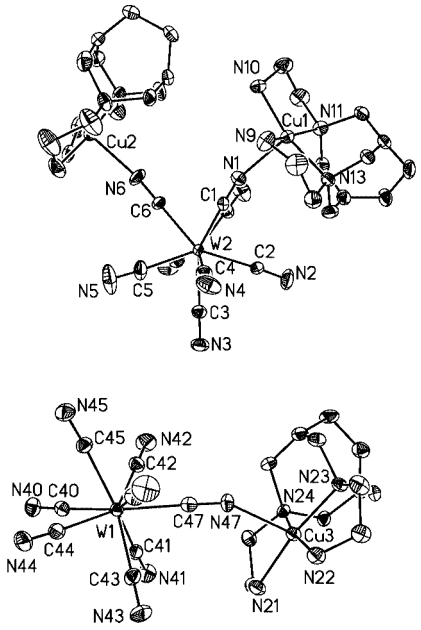

Figure 6. Structure of complex **3**, showing the discrete trimeric and dimeric units

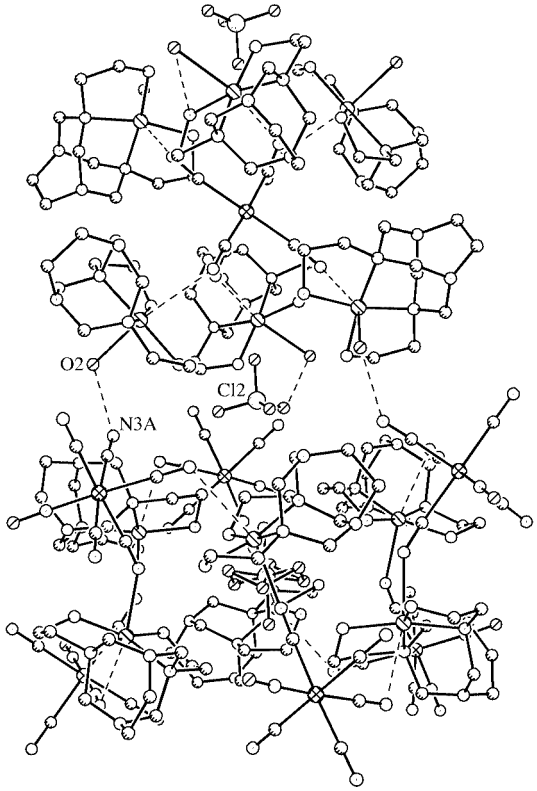

Figure 5. Hydrogen-bonded cyclic Cu_6Cr_6 and spherical Cu_6Cr units of **1** and **2** showing the encapsulation of the ClO_4^- anion (Cl2)

Magnetic Properties

The magnetic susceptibilities of the three complexes have been measured, and plots of $\chi_m T$ vs. T are shown in Figures 7, 8, and 9, where χ_m is the magnetic susceptibility per $Cu_{12}Cr_7$ unit or per Cu_3W_2 unit.

With decreasing temperature, $\chi_m T$ of **1** increases slowly until ca. 30 K and then sharply reaches a maximum of 23.0 emu·K·mol^{-1} at 4 K. The magnetic susceptibilities obey the Curie−Weiss law with a positive Weiss constant of +2.1 K and a Curie constant of 17.9 emu·K·mol^{-1} (calculated

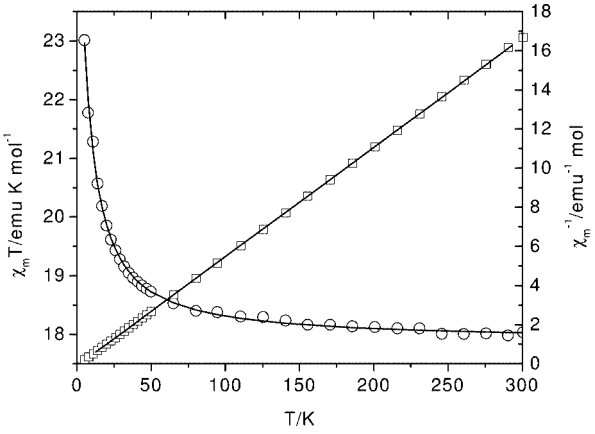

Figure 7. Temperature dependence of $\chi_m T$ and χ_m for **1**; the solid line is the best fit with the parameters in the text

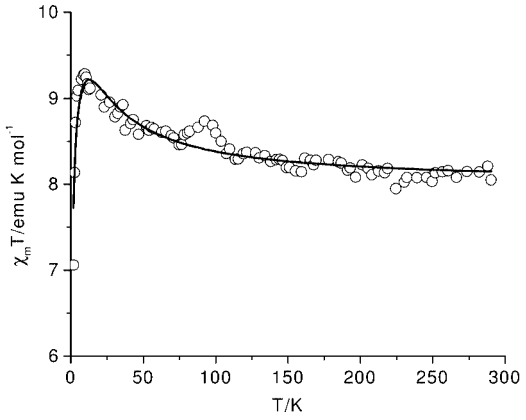

Figure 8. Temperature dependence of $\chi_m T$ for **2**; the solid line is the fit to the Curie−Weiss law

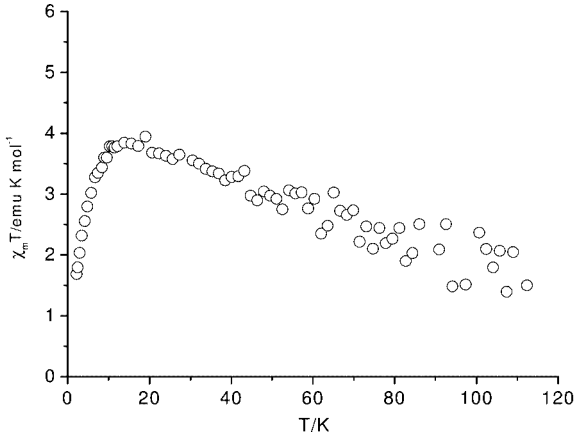

Figure 9. Temperature dependence of $\chi_m T$ for **3**

value is 17.75 emu·K·mol^{-1} assuming $g = 2$). This magnetic behaviour reveals ferromagnetic coupling between the $Cu^{II}-Cr^{III}$ ions through the cyanide bridges. The ferromagnetic interaction between the Cr^{III} and Cu^{II} ions is due to the orthogonality of the magnetic orbitals of Cr^{III} (t_{2g}^3) and Cu^{II} (e_g^3).

From the structural information of **1**, the system can be treated as six strongly interacting CuCr dimers [$Cu-N_{cyano}$ = 2.506(5) Å] between which a weak interaction is present [$Cu-N_{cyano}$ = 3.072(6) Å] and weakly interacting Cu_6Cr clusters [$Cu-N_{cyano}$ = 3.021(6) Å]. The weak interactions are negligibly small and can be included in the intermolecular field term during the fit. Hence, the magnetic susceptibilities can be simulated by Equations (1) and (2) based on the isotropic spin Hamiltonian $\hat{H} = -2J_d S_{Cr} S_{Cu}$ for the strongly interacting $Cu^{II}Cr^{III}$ dimer, where g_1 and g_2 are the g factors for the total spin states of $S_T = 1$ and 2, respectively, and θ accounts for the interdimeric coupling. The g_1 and g_2 factors are related to g_{Cu} and g_{Cr}, viz. $g_1 = 3/4g_{Cr} - 1/4g_{Cu}$ and $g_2 = 3/4g_{Cr} + 1/4g_{Cu}$ according to the literature method.[61−63]

$$\chi_d = \frac{Ng^2\beta^2}{k(T-\theta)} \cdot \frac{2g_1^2 + 10g_2^2 \exp(4J_d/kT)}{3 + 5\exp(4J_d/kT)} \quad (1)$$

$$\chi_m = 6\times\chi_d + 6\times\frac{Ng_{Cu}^2\beta^2}{3kT} S_{Cu}(S_{Cu}+1) + \frac{Ng_{Cr}^2\beta^2}{3kT} S_{Cr}(S_{Cr}+1) \quad (2)$$

The best fit to the magnetization data gives g_{Cu} = 2.09, g_{Cr} = 1.99, J_d = +2.40 cm^{-1} and θ = +0.23 K (Figure 7). To approximate the $Cu^{II}-Cr^{III}$ coupling in the Cu_6Cr moieties we used an identical θ, giving rise to a similar result with g_{Cu} = 2.09, g_{Cr} = 1.99, J_d = +2.37 cm^{-1} and θ = +0.17 K. The positive θ indicates weak intermolecular ferromagnetic interactions. Of course, this θ includes two effects: the $Cu^{II}-Cr^{III}$ magnetic coupling through the weak bridging cyano ligands and the intercluster magnetic exchange. The $Cu^{II}-Cr^{III}$ coupling constant is similar to those reported for the cyano-bridged 1D CuCr complexes $\{[Cu(L^2)][Cu(L^2)Cr(CN)_6]ClO_4\cdot 2H_2O\}_n$ (L^2 = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (J = +4.82 cm^{-1}) and $[Cu(cyclam)]_3[Cr(CN)_6]_2\cdot 4H_2O$ (J = +4.33 cm^{-1}),[64,30] and is lower than that of the cyano-bridged Cu_3Cr complex $[Cu(edma)]_3Cr(CN)_6$ ($edma^-$ = ethylenediaminemonoacetate) (J = +9.16 cm^{-1}).[44]

A Cu^{II} ion in elongated octahedral surroundings has a magnetic orbital built from a $d_{x^2-y^2}$ orbital (x and y axes are taken along the $Cu-N_{equatorial}$ directions) with little contribution from the d_z^2 orbital and localized in the equatorial plane. A weak magnetic interaction is anticipated due to the little delocalization of the magnetic orbital towards the axial position by the bridging cyano atom for complex **1** and $\{[Cu(L^2)][Cu(L^2)Cr(CN)_6]ClO_4\cdot 2H_2O\}_n$.[64] That the strongest Cu···Cr coupling is present in the Cu_3Cr complex is understandable because the bridging cyano atom is situated within the coordination plane (xy plane).

The magnetic behaviour of complex **2** is similar to that of complex **1** (Figure 8); $\chi_m T$ increases smoothly as the temperature is lowered to ca. 9.6 K, reaching a maximum of 9.3 cm^3·K·mol^{-1}, and then decreases. The anomaly at ca. 90 K is due to experimental errors. Such magnetic behaviour is characteristic of an unambiguous local ferromagnetic interaction. The magnetic susceptibility in the range 10−300 K has been fitted by the Curie−Weiss expression that is usually used to describe weakly coupled systems. The positive Weiss constant obtained (+4.0 K) suggests a ferromagnetic interaction. The Curie constant C (8.0 emu·K·mol^{-1}) is consistent with the theoretical value of 8.00 emu·K·mol^{-1} with g = 2.12.

The fit to the magnetic data of **2** with a model similar to complex **1** affords g = 2.13, J_d = +12 cm^{-1}, and θ = −0.49 K. The $Cu^{II}-Cr^{I}$ magnetic coupling constant (J_d) is positive, indicating a ferromagnetic interaction between the metal ions.

Complex **2** is the first example incorporating Cu^{II} and low-spin Cr^{I} ions. Analogously, the ferromagnetic nature of

the $Cu^{II}-Cr^{I}$ coupling can be interpreted by the orthogonality of the magnetic orbitals of the low-spin Cr^{I} [$3d^5$, $(d_{xy})^1$] and Cu^{II} [$3d^9$, $(d_{x^2-y^2})^1$] ions.[55]

The comparatively large Weiss constant and J_d compared to that of complex **1** may be partially due to the shorter Cu(1)−N(2) bond length in complex **2**, which favours a stronger Cu···Cr coupling through the cyano bridge.

The magnetic behavior of complex **3** indicates a ferromagnetic nature (Figure 9), which is consistent with the reported analogous cyano-bridged $Cu^{II}-W^{V}$ complexes, in which ferromagnetic $Cu^{II}-W^{V}$ coupling is always observed.[50,52] The decrease of $\chi_m T$ below 18 K may be due to intermolecular antiferromagnetic interaction through the weak cyano contacts and the field saturation effect.

Conclusion

The self-assembly of the $[CuL]^{2+}$ precursor, and $K_3[Cr(CN)_6]$, $K_3[Cr(CN)_5(NO)]$, or $K_3[W(CN)_8]$ affords a series of cyano-bridged polynuclear complexes. X-ray diffraction analysis shows that they consist of novel polynuclear star-like Cu_6Cr and cyclic Cu_6Cr_6 moieties, and that the CuW complex has a cyano-bridged dinuclear and trinuclear structure. Variable-temperature magnetic susceptibility measurements show that the three complexes exhibit ferromagnetic coupling between neighbouring metal ions.

Experimental Section

General Remarks: Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. Infrared spectroscopy was performed with a Magna-IR 750 spectrophotometer in the 4000−650 cm^{-1} region. The electronic spectrum of **1** was measured with a Perkin−Elmer Hitachi-240 spectrophotometer in water. The room-temperature EPR powder spectrum of **1** was recorded at the X-band with a Bruker ER 200B spectrometer. Variable-temperature magnetic susceptibility measurements of **1** were performed with a Quantum Design MPMS SQUID magnetometer, while those of **2** and **3** were carried out with a MagLab 2000 magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables) and the sample holder (gelatine capsule). All chemicals and solvents used in the synthesis were of reagent grade. $[CuL](ClO_4)_2$, $K_3[Cr(CN)_6]$, $K_3[Cr(CN)_5(NO)]$, and $K_3[W(CN)_8]$ were prepared according to literature methods.[56,57,60,65] ***Caution!*** Perchlorate salts of metal complexes are potentially explosive; only a small amount of material should be prepared, and it should be handled with care.

$[CuLCr(CN)_6]_6[\{CuL(H_2O)\}_6Cr(CN)_6](ClO_4)_3\cdot 16H_2O$ (1): Cubic red single crystals were obtained by slow concentration of an aqueous solution (15 mL) of $[CuL](ClO_4)_2$ (0.1 mmol) and $K_3[Cr(CN)_6]$ (0.1 mmol) in a molar ratio of 1:1. Yield: 23 mg, 40% (based on Cu). IR: $\tilde{\nu}$ = 2129 s, 2119 s, 2112 s ($\nu_{C\equiv N}$); 1086 br (ν_{Cl-O}) cm^{-1}. UV/Vis: λ = 530 nm.

$[CuLCr(CN)_5(NO)]_6\cdot[\{CuL(H_2O)\}_6Cr(CN)_5(NO)](ClO_4)_3\cdot 16H_2O$ (2): Red single crystals of **2** were prepared by a procedure similar to that for **1**, using $K_3[Cr(CN)_5(NO)]$ instead of $K_3[Cr(CN)_6]$. Yield: 24 mg, 50% (based on Cu). IR: 2115 s, 2110 s, 2098 sh ($\nu_{C\equiv N}$); 1664 vs ($\nu_{O=N}$); 1089 vs (ν_{Cl-O}) cm^{-1}.

$[CuL]_3[W(CN)_8]_2\cdot 4H_2O$ (3): Violet single crystals were obtained by slow concentration of an aqueous solution (10 mL) of $[CuL](ClO_4)_2$ (0.1 mmol) and $K_3[W(CN)_8]$ (0.1 mmol) in a molar ratio of 1:1. Yield: 11 mg, 20% (based on Cu). IR: 2142 s, 2105 sh ($\nu_{C\equiv N}$) cm^{-1}.

X-ray Crystallographic Study: The data collections of **1**, **3**, and **2** were made with a Bruker Siemens P4 and a Rigaku R-Axis RIPID IP diffractometer at 293 K, respectively. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares (SHELEXL-97) on F^2.[66] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined by using a riding model. Weighted R factors wR and goodness of fit values (S) are based on F^2, conventional R factors are based on F, with F set to zero for negative F^2. Crystal data are summarized in Table 3. During the solution of the crystal structure of complex **2**, it was found that the atoms (five C and one N) lie from 1.886(8) to 2.099(7) Å away from Cr. Considering that the usual Cr−C bond length is approximately 2.0 Å and that the Cr−N bond length is ca. 1.8 Å,[55,58] the N atom was unambiguously assigned a Cr−N distance of 1.886(8) Å. CCDC-207494 (**1**), -207495 (**2**), -215992 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge

Table 3. Crystallographic data for complexes **1**−**3**

	1	**2**	**3**
Empirical formula	$C_{162}H_{324}Cl_3Cr_7Cu_{12}N_{114}O_{34}$	$C_{155}H_{324}Cl_3Cr_7Cu_{12}N_{114}O_{41}$	$C_{46}H_{79}Cu_3N_{34}O_4W_2$
Formula mass	5646.18	5674.11	1730.75
Space group	$R\bar{3}$	$R\bar{3}$	$P2_12_12_1$
a [Å]	28.866(6)	28.402(4)	11.318(2)
b [Å]	28.866(6)	28.402(4)	15.998(3)
c [Å]	25.145(7)	24.786(5)	36.261(7)
V [Å^3]	18144(7)	17316(5)	6566(2)
Z	3	3	4
μ(Mo-K_a) [mm^{-1}]	1.449	1.521	1.751
Data/restraints/parameters	7181/0/500	12854/0/500	23770/0/802
R_{int} (on F^2)	0.0343	0.0440	0.0607
Goodness of fit on F^2	1.185	1.110	0.964
$R1$ [$I > 2\sigma(I)$]	0.0553	0.0722	0.0461
$wR2$ (all data)	0.1477	0.1556	0.0933

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