Synthesis, Crystal Structure, and Magnetic Properties of a Three-Dimensional Cyano-Bridged Bimetallic Coordination Polymer with an Aromatic Amine Capping Ligand: [Cu(2,2'-dpa)]3 [...

6 AUTHORS, INCLUDING:

Cai-Ming Liu
Chinese Academy of Sciences
154 PUBLICATIONS **3,063** CITATIONS

Song Gao
Peking University
490 PUBLICATIONS **16,349** CITATIONS

Hao-Ling Sun
Beijing Normal University
72 PUBLICATIONS **3,198** CITATIONS

Synthesis, Crystal Structure, and Magnetic Properties of a Three-Dimensional Cyano-Bridged Bimetallic Coordination Polymer with an Aromatic Amine Capping Ligand: [Cu(2,2′-dpa)]₃[Cr(CN)₆]₂·3H₂O (2,2′-dpa = 2,2′-Dipicolylamine)

Cai-Ming Liu,*,† Song Gao,‡ Hui-Zhong Kou,§ De-Qing Zhang,*,† Hao-Ling Sun,‡ and Dao-Ben Zhu*,†

Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China, State Key Laboratory of Rare Earth Materials and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China, and Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

ABSTRACT: A three-dimensional (3D) Cu(II)-containing Prussian Blue analogue with two types of [Cr(CN)₆]³⁻ units, [Cu(2,2′-dpa)]₃[Cr(CN)₆]₂·3H₂O (2,2′-dpa = 2,2′-dipicolylamine), was synthesized and characterized. One type of [Cr(CN)₆]³⁻ unit in this complex coordinates to six copper(II) atoms to form the heptanuclear [CrCu₆] unit, which connects with other [CrCu₆] units through the other type of [Cr(CN)₆]³⁻ unit acting as bidentate spacer link only. Magnetic investigations of this complex revealed that long-range ferromagnetic ordering occurs below the Curie temperature of 3 K. It is the first example of 3D complex-based Prussian Blue analogues containing aromatic amine capping ligands.

Introduction

There has been considerable interest in molecule-based magnetic materials showing spontaneous magnetization in the past decades.[1] Particularly interesting are the cyano-bridged magnetic coordination polymers. Hexacyanometalate ions [M(CN)₆]$^{n-}$, which act as good building blocks, have played an important role in realizing bimetallic assemblies of magnetic materials. They can connect with a simple metal ion to form the Prussian Blue family, which often exhibits spontaneous magnetization, and some examples in this family even have high magnetic ordering temperatures, T_c.[2] On the other hand, a more creative strategy for design of cyano-bridged magnetic coordination polymers is utilizing metal complexes containing complementary capping ligands instead of simple metal ions.[3] Many ligands, including NH₃ and organic amines, have found application in the construction of numerous one- (1D),[3a,4] two-(2D),[5] and three-dimensional (3D)[6] molecular magnets based on hexacyanometalate building blocks. The capping ligands not only play an important role in stabilizing structures but also impose a specific topology through their coordination binding modes and geometries. For example, large aromatic amines are generally used as capping ligands to construct 0D cluster-[4d,7] and low-dimensional (1D[4d,4e] and 2D[5b,5d,5j,5k]) complex-based Prussian Blue analogues, while smaller bis-, tri-, or tetradentate aliphatic amines even can be utilized to construct 3D complex-based Prussian Blue analogues.[6] However, to our knowledge, there are still no 3D complex-based Prussian Blue analogues containing aromatic amine capping ligands being explored to date. It is important and interesting to know whether metal complexes with aromatic amine ligands can be also utilized to construct 3D complex-based Prussian Blue analogues. We have now found that by using a copper(II) complex containing a tridentate aromatic amine ligand, 2,2′-dipicolylamine, [Cu(2,2′-

dpa)(N₃)](ClO₄) (2,2′-dpa = 2,2′-dipicolylamine), as one of starting materials,[8] we can obtain a novel dimetallic coordination polymer [Cu(2,2′-dpa)]₃[Cr(CN)₆]₂·3H₂O, **1** (Scheme 1), which possesses a 3D tunnel network structure extended by the Cr−C≡N−Cu−C≡N−Cr−C≡N−Cu−C≡N long linkages and shows magnetic ordering at $T_c = 3$ K.

Experimental Procedures

Materials and Methods. All reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed on a Heraeus CHN-Rapid elemental analyzer. The infrared spectra were recorded on a Perkin-Elmer 2000 spectrophotometer with pressed KBr pellets. The magnetic susceptibility measurements for **1** were carried out on polycrystalline sample (12.9 mg) using a MagLab System 2000 magnetometer. Diamagnetic corrections were estimated from Pascal's constants.[1a]

Preparation of [Cu(2,2′-dpa)]₃[Cr(CN)₆]₂·3H₂O (1). Single crystals were grown in a long test tube. Solid [Cu(2,2′-dpa)(N₃)](ClO₄) (0.2 mmol) was dissolved in 15 mL of water and 5 mL of ethanol, and to this solution was layered carefully a solution of K₃[Cr(CN)₆] in DMF (10 mL). The test tube was then allowed to stand undisturbed at room temperature in the dark for 1 week, yielding deep blue block crystals of **1** on the tube wall. They were collected, washed with water and ethanol, and dried in vacuo. Yield: 40%. All the operations for the synthesis were carried out in the dark to avoid decomposition of the K₃[Cr(CN)₆]. Elemental analysis Calcd for C₄₈H₄₅Cr₂Cu₃N₂₁O₃: C, 45.80; H, 3.60; N, 23.37. Found: C, 45.71; H, 3.68; N, 23.29. IR (KBr pellet, cm⁻¹): 3442 (vs, br), 2921 (w), 2175 (w), 2129 (w), 1610 (s), 1573 (w), 1484 (w), 1448 (m), 1350 (w), 1285 (w), 1252 (w), 1159 (w), 1103 (w), 1055 (w), 1029 (w), 771 (s), 729 (w), 652 (w).

Caution: *Perchlorate salts and azido salts are potentially explosive and should be handled in small quantities and with care!*

X-ray Crystallography. A single crystal of **1** with dimensions 0.39 × 0.38 × 0.30 mm³ was selected, mounted, and flame-sealed in a Lindmann capillary; this crystal was maintained in contact with mother liquor to prevent being effloresced during data collection. The intensity data were collected on a Rigaku RAXIS RAPID IP imaging plate system with Mo Kα radiation (λ = 0.710 73 Å) at 293(2) K in the range 1.66° < θ < 27.62°. An empirical absorption correction from Ψ scan was applied. A total of 21 994 reflections were collected (0 ≤ h ≤ 23, 0 ≤ k ≤ 30, −30 ≤ l ≤ 30), of which 6003 with I > 2σ(I) were used in the refinement. The structure was solved by the direct

* To whom correspondence should be addressed. E-mail addresses: cmliu@iccas.ac.cn; dqzhang@iccas.ac.cn; zhudb@iccas.ac.cn.
† Institute of Chemistry.
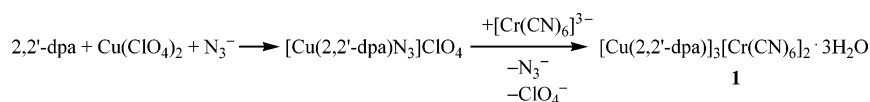‡ Peking University.
§ Tsinghua University.

Scheme 1

$$2,2\text{'-dpa} + \text{Cu(ClO}_4)_2 + \text{N}_3^- \longrightarrow [\text{Cu(2,2'-dpa)N}_3]\text{ClO}_4 \xrightarrow[\substack{-\text{N}_3^- \\ -\text{ClO}_4^-}]{+[\text{Cr(CN)}_6]^{3-}} [\text{Cu(2,2'-dpa)}]_3[\text{Cr(CN)}_6]_2 \cdot 3\text{H}_2\text{O}$$
$$\textbf{1}$$

Table 1. Crystal Data and Structural Refinement Parameters for Complex 1

formula	$C_{48}H_{45}Cr_2Cu_3N_{21}O_3$
formula weight	1258.67
space group	$P2(1)/c$
a (Å)	18.005(4)
b (Å)	23.732(5)
c (Å)	23.235(5)
α (deg)	90.00
β (deg)	90.46(3)
γ (deg)	90.00
V (Å^3)	9927(3)
Z	4
T (K)	293(2)
λ(Mo Kα) (Å)	0.71073
ρ_{calc} (g·cm^{-3})	0.838
μ(Mo Kα) (mm^{-1})	0.878
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0889
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.2305
goodness-of-fit on F^2	0.830

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \sum\{[w(F_o{}^2 - F_c{}^2)^2]/\sum[wF_o{}^2]^2\}^{1/2}$.

method and refined by a full matrix least-squares technique based on F^2 using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, all of the hydrogen atoms except those in hydrate molecules were introduced at calculated positions as riding on a bonded atom. Crystal data, data collection, and refinement parameters for complex **1** are given in Table 1; selected bond lengths and angles are listed in Table 2.

Results and Discussion

Synthesis and Infrared Spectra. The precursor complex [Cu(2,2′-dpa)(N₃)](ClO₄) was synthesized first according to the method in the literature;[8] blue single crystals of **1** can be obtained reproducibly by diffusion of [Cu(2,2′-dpa)(N₃)](ClO₄) in DMF into K₃[Cr(CN)₆] in a H₂O−EtOH mixture. Unexpectedly, the azide ligand in the [Cu(2,2′-dpa)(N₃)]⁺ cation, which is also a very strong ligand for coordinating the copper(II) atom, was permuted by the [Cr(CN)₆]³⁻ anion during this self-assembly process. The loss of organic amine ligands from precursor complexes during synthesis procedures of 3D complex-based Prussian Blue analogues has been observed before;[6b,6i] however, the loss of azide anion from precursor complexes is quite unusual. The IR spectrum of **1** exhibits two typical C≡N bands at 2175 and 2129 cm⁻¹; the shift of ν(C≡N) to higher wavenumber compared with that of K₃[Cr(CN)₆] is in agreement with the formation of two types of C≡N bridges as revealed by the X-ray determination.

Crystal Structure. X-ray crystallography reveals that **1** is composed of a 3D polymer [Cu(2,2′-dpa)]₃[Cr(CN)₆]₂ and lattice water molecules (Figures 1 and 2). The asymmetric unit of the structure consists of three independent [Cr(CN)₆]³⁻ units [Cr(1), Cr(2), and Cr(3)] and three different types of Cu(II) centers (Cu(1), Cu(2), and Cu(3)) (Figure 2). The Cr(2) ion connects to six copper(II) ions (Cu(1), Cu(2), Cu(3), and their symmetry equivalents) through six cyanide bridges, while either the Cr(1) atom or Cr(3) atom links only two copper(II) ions (Cu(1) and its symmetry equivalent for Cr(1); Cu(2) and the symmetry equivalent of Cu(3) for Cr(3)) through two cyanide ions (C(37)≡N(10) and its symmetry equivalent for Cr(1); C(43)≡N(16) and C(48)≡N(21) for Cr(3)) in the trans position, and the other four cyano groups in these two [Cr(CN)₆]³⁻ units are nonbridging groups. Thus, two types of chromium atoms, Cr(1) (or Cr(3))

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1^a

	Bond Distances (Å)		
Cr(1)−C(37)	2.043(8)	Cr(1)−C(38)	2.099(13)
Cr(1)−C(39)	2.106(12)	Cr(2)−C(42)	2.053(7)
Cr(2)−C(41)	2.064(8)	Cr(2)−C(40)	2.086(8)
Cr(3)−C(44)	2.007(12)	Cr(3)−C(48)	2.017(8)
Cr(3)−C(47)	2.040(13)	Cr(3)−C(45)	2.053(11)
Cr(3)−C(43)	2.054(9)	Cr(3)−C(46)	2.075(11)
Cu(1)−N(10)	1.960(8)	Cu(1)−N(3)	1.992(9)
Cu(1)−N(2)	1.997(8)	Cu(1)−N(1)	2.045(9)
Cu(1)−N(13)	2.287(7)	Cu(2)−N(16)	1.938(7)
Cu(2)−N(6)	1.990(8)	Cu(2)−N(4)	2.005(8)
Cu(2)−N(5)	2.029(7)	Cu(2)−N(14)	2.239(7)
Cu(3)−N(21)	1.978(8)	Cu(3)−N(9)	2.018(9)
Cu(3)−N(7)	2.024(9)	Cu(3)−N(8)	2.028(7)
Cu(3)−N(15)#1	2.285(7)	N(15)−Cu(3)#2	2.285(7)
	Bond Angles (deg)		
N(2)−Cu(1)−N(1)	84.1(5)	N(3)−Cu(1)−N(2)	78.7(4)
N(10)−Cu(1)−N(1)	96.9(4)	N(10)−Cu(1)−N(3)	98.4(4)
N(10)−Cu(1)−N(13)	98.7(3)	N(4)−Cu(2)−N(5)	80.3(3)
N(6)−Cu(2)−N(5)	81.8(3)	N(16)−Cu(2)−N(4)	98.2(3)
N(16)−Cu(2)−N(6)	97.8(3)	N(4)−Cu(2)−N(14)	94.5(3)
N(6)−Cu(2)−N(14)	92.6(3)	N(7)−Cu(3)−N(8)	80.4(4)
N(9)−Cu(3)−N(8)	82.1(4)	N(21)−Cu(3)−N(7)	99.1(4)
N(21)−Cu(3)−N(8)	166.8(3)	N(21)−Cu(3)−N(9)	96.3(3)
C(37)−Cr(1)−C(38)	90.8(4)	C(37)−Cr(1)−C(39)	88.7(4)
C(38)−Cr(1)−C(39)	89.7(5)	C(42)−Cr(2)−C(41)	90.4(3)
C(42)−Cr(2)−C(40)	89.4(3)	C(41)−Cr(2)−C(40)	90.5(3)
C(44)−Cr(3)−C(48)	92.0(4)	C(44)−Cr(3)−C(47)	91.5(5)
C(48)−Cr(3)−C(47)	87.0(4)	C(44)−Cr(3)−C(45)	90.8(4)
C(48)−Cr(3)−C(45)	87.7(4)	C(47)−Cr(3)−C(45)	174.3(4)
C(44)−Cr(3)−C(43)	87.7(4)	C(48)−Cr(3)−C(43)	179.6(3)
C(47)−Cr(3)−C(43)	92.7(4)	C(45)−Cr(3)−C(43)	92.7(4)
C(44)−Cr(3)−C(46)	174.2(4)	C(48)−Cr(3)−C(46)	93.4(3)
C(47)−Cr(3)−C(46)	90.8(4)	C(45)−Cr(3)−C(46)	87.4(4)
C(43)−Cr(3)−C(46)	86.9(3)	N(10)−C(37)−Cr(1)	176.1(9)
N(11)−C(38)−Cr(1)	178.5(12)	N(12)−C(39)−Cr(1)	178.3(13)
N(13)−C(40)−Cr(2)	176.8(7)	N(14)−C(41)−Cr(2)	176.5(7)
N(15)−C(42)−Cr(2)	178.1(7)	N(16)−C(43)−Cr(3)	176.9(8)
N(17)−C(44)−Cr(3)	173.9(11)	N(18)−C(45)−Cr(3)	176.6(10)
N(19)−C(46)−Cr(3)	176.5(9)	N(20)−C(47)−Cr(3)	176.7(10)
N(21)−C(48)−Cr(3)	175.4(8)	C(37)−N(10)−Cu(1)	175.1(8)
C(40)−N(13)−Cu(1)	154.3(6)	C(41)−N(14)−Cu(2)	152.7(6)
C(43)−N(16)−Cu(2)	177.7(7)	C(48)−N(21)−Cu(3)	178.3(8)
C(42)−N(15)−Cu(3)#2	151.1(6)		

^{a} #1 $-x, y + {}^1/_2, -z + {}^3/_2$; #2 $-x, y - {}^1/_2, -z + {}^3/_2$.

and Cr(2), with different coordination environments exist in the crystal lattice. All of the copper atoms are five-coordinate with two cyano nitrogen atoms from two different [Cr(CN)₆]³⁻ units and three other nitrogen atoms from the ligand 2,2′-dpa, forming square-pyramidal geometries with the cyano nitrogen atoms N(13) (for Cu(1)), N(14) (for Cu(2)), and N(15) (for Cu(3)) in the axial positions. The Cu−N$_{cyanido}$ distances connected to the Cr(2) atom (average 2.271 Å) are obviously larger than those linked to the Cr(1) atom (average 1.960 Å) and the Cr(3) atom (average 1.957 Å). The Cu−N≡C bond angles connected to the Cr(2) atom (Cu−N≡C−Cr(2)) deviate significantly from linearity and lie between 152.62° and 154.19°, while those linked to the Cr(1) atom (Cu−N≡C−Cr(1), average 175.08°) and the Cr(3) atom (Cu−N≡C−Cr(3), average 177.98°) are close to linearity. The Cr(2) atom and around six cyano-connected copper(II) ions generate a heptanuclear [CrCu₆] unit (Figure 2a), which connects with other units of the same type through bidentate spacer links, Cr(1) or Cr(3) groups, forming a 3D tunnel structure, and the lattice water molecules reside in the
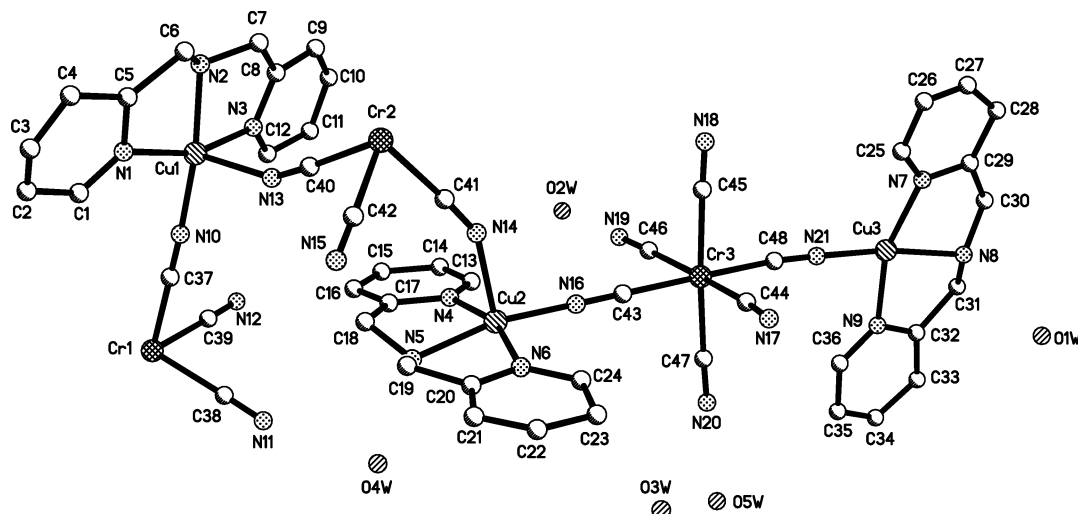
Figure 1. The asymmetric unit of **1**. All hydrogen atoms are omitted for clarity.

tunnels. This novel 3D network is quite different from reported 3D structures based on a cube formed by eight $[Fe(CN)_6]^{4-}$ anions at the corners and 12 $[Ni(L)_2]^{2+}$ (L = ethylenediamine or trimethylenediamine) cations at the edges.[6b] In complex **1**, the bent $Cu-N\equiv C-Cr(3)$ bonds induce the departure from exact cubic structure; instead, dumbbell-like tunnels are generated along the a-axis (Figure 2b). Furthermore, this 3D tunnel network structure is extended by the $Cr-C\equiv N-Cu-C\equiv N-Cr-C\equiv N-Cu-C\equiv N$ linkages, which are almost two times longer than the $Fe-C\equiv N-Ni-C\equiv N$ linkages in $[Ni(L)_2]_3$-$[Fe^{II}(CN)_6]X$ (L = ethylenediamine or trimethylenediamine, $X = PF_6^-$ or ClO_4^-);[6b] therefore, the formed tunnels are large enough and already reach nanoscale (18.0×16.6 Å^2, calculated on the basis of the distances between corner Cr(2) atoms) (Figure 3). Another complex-based Prussian Blue analogue $[Ni(tn)_2]_5[Fe^{III}(CN)_6]_3ClO_4\cdot2.5H_2O$ (tn = trimethylenediamine)[6h] also possesses long linkages ($Fe-C\equiv N-Ni-C\equiv N-Fe-C\equiv N-Ni-C\equiv N$) and exhibits 3D tunnel structure; however, the bisdentate spacer link, $[Fe(CN)_6]^{3-}$, in $[Ni(tn)_2]_5[Fe^{III}(CN)_6]_3$-$ClO_4\cdot2.5H_2O$ adopts a cis rather trans connecting mode, and differently shaped tunnels are thus generated.[6h] In addition, it is noteworthy that complex **1** is neutral, while $[Ni(tn)_2]_5$-$[Fe^{III}(CN)_6]_3ClO_4\cdot2.5H_2O$ belongs to ion-type 3D complex-based Prussian Blue analogues.

Magnetic Properties. The thermal variation of $\chi_M T$ per Cu_3Cr_2 unit of a powder sample of **1** measured under 2000 Oe is shown in Figure 4. At room temperature, the $\chi_M T$ value equals 5.648 cm^3 K mol^{-1}, which is somewhat larger than the expected value for two uncoupled Cr(III) ($S = {}^3/_2$) and three Cu(II) ($S = {}^1/_2$) (4.875 cm^3 K mol^{-1} per Cu_3Cr_2, calculated assuming $g_{Cu} = g_{Cr} = 2.00$). The $\chi_M T$ value increases slowly with deceasing temperature down to 50 K, then rapidly reaches a maximum of 22.15 cm^3 K mol^{-1} at 3 K, and then decreases again below this temperature. A plot of $1/\chi_M$ versus T in the temperature range 300 to 15 K obeys the Curie–Weiss law with $\theta = +8.27$ K and $C = 5.16$ cm^3 K mol^{-1}. The positive Weiss constant indicates the presence of ferromagnetic exchange interaction between adjacent Cu(II) and Cr(III) ions, in good agreement with other cyano-bridged Cu(II)−Cr(III) complexes. The maximum $\chi_M T$ value at 3 K is significantly higher than that of the largest possible spin state $S_T = {}^9/_2$, $\chi_M T = 12.375$ cm^3 K mol^{-1} for a ferromagnetic Cu_3Cr_2 complex, suggesting the onset of a 3D magnetic ordering. The decease of $\chi_M T$ below 3 K probably results from a saturation of the χ_M value.

The divergence of the field-cooled (FC) and the zero-field (ZFC) magnetization $M(T)$ data around 3 K confirms irreversible behavior of long-range magnetic order to produce a ferromagnet (Figure 4, inset, shown as $\chi_M T$ versus T plots). The temperature dependence of ac magnetic susceptibility measurements reveal that both the real part of ac magnetic susceptibility (χ_{ac}') and the imaginary part of ac magnetic susceptibility (χ_{ac}'') for frequency of 0.5 Hz have a peak at ca. 3 K (Figure 5), which is another indication of 3D magnetic ordering below 3 K. Interestingly, only χ_{ac}' shows peaks at the same temperature (3 K) for other frequencies of 10, 40, 100, and 800 Hz, while χ_{ac}'' is negligibly small for all corresponding frequencies. Similar trend was also observed in other magnetic ordering systems.[9] Frequency independence of χ_{ac}' excludes any spin glass behavior.

The field dependence of magnetization (0−50 kOe) measured at 1.9 K shows a sharp increase at zero field. The magnetization per Cu_3Cr_2 at 50 kOe is 7.5 $N\beta$, which is lower than the saturation value of 9 $N\beta$ expected for the ferromagnetic Cu_3Cr_2 system with $S_T = {}^9/_2$ but much higher than the theoretical value of an antiferromagnetic coupling Cu_3Cr_2 system (3 $N\beta$, $S_T = {}^3/_2$), suggesting the possible existence of spin-canted magnetism. A similar magnetic behavior had also been observed in another 3D complex-based Prussian Blue analogue, $[Ni(tren)_2]_5[Fe-(CN)_6]_3(ClO_4) \cdot 2.5H_2O$ (tren = trimethylenediamine).[6h] Furthermore, similar to another 3D complex-based Prussian Blue analogue, $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$,[6i] almost no remnant magnetization and coercive field can be detected at 1.8 K in a ±5 kOe field. However, the T_c value of complex **1** is much lower than that of $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$,[6i] which orders ferromagnetically below 57 K. Two reasons are responsible for this. First, the magnetic coupling strength of **1** is weaker due to the presence of not only comparatively long Cu−N_{cyano} bond distances but also weak Cu−N_{cyano} contacts in which the cyano nitrogen atoms are situated at the axial positions of the CuN_4 square-pyramidal configuration.[11b] Second, the number of the magnetic neighbors (average 2.8) around each metal ion in **1** is smaller than that in $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ (average 4),[6i] which would result in lower T_c value for **1** according to following expression derived by Verdaguer et al.:[10]
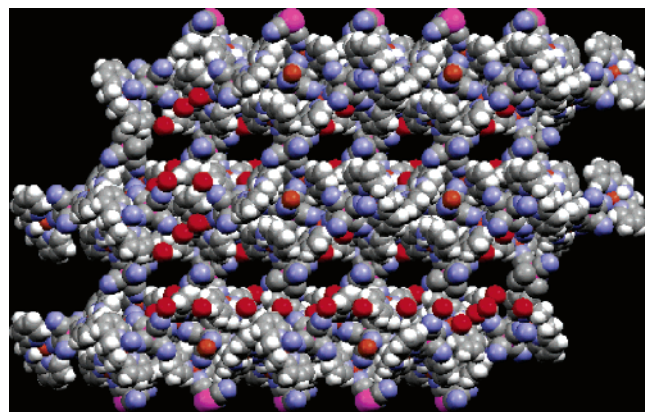
$$kT_c = (Z|J|N\beta^2g^2\sqrt{C_{Cu}C_{Cr}} \tag{1}$$

where k is Boltzmann's constant, Z is the number of magnetic

(a)

(b)
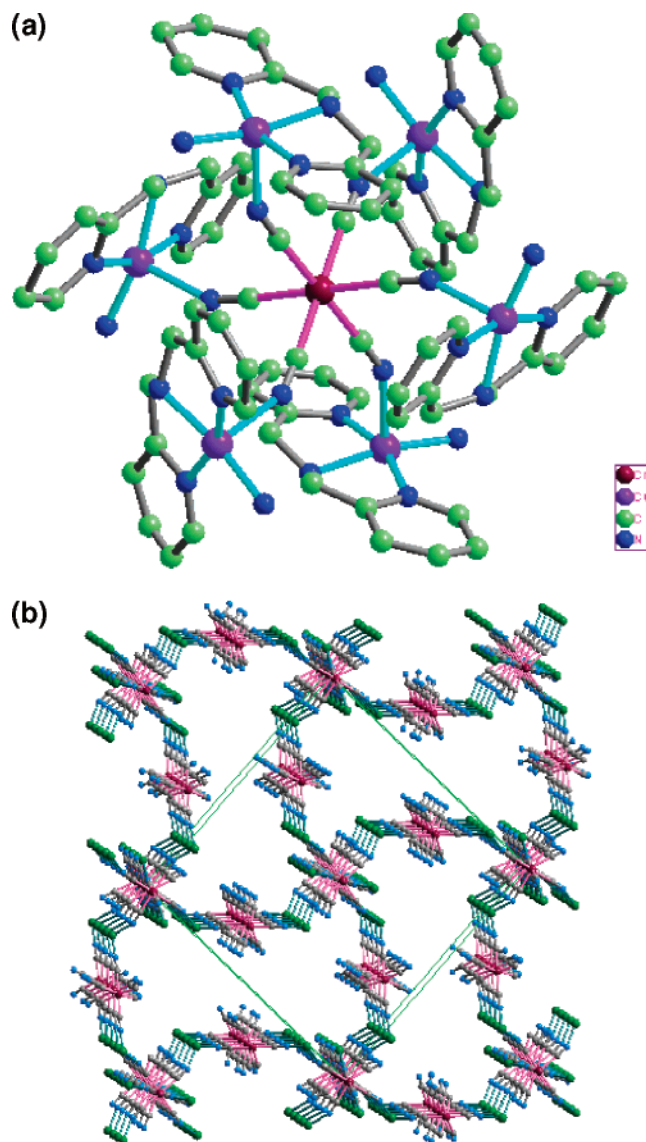
Figure 2. (a) The heptanuclear [CrCu₆] unit of **1** and (b) a view of the 3D network structure along the *a*-axis for complex **1**. 2,2′-Dipicolylamine ligands and solvent H_2O molecules are omitted for clarity.


Figure 3. A space-filling model of complex **1** viewed down the *b*-axis.

neighbors, N is the Avogadro constant, g is the mean Landé factor, β is the Bohr magneton, and C_{Cu} and C_{Cr} are the Curie constants of Cu(II) and Cr(III).
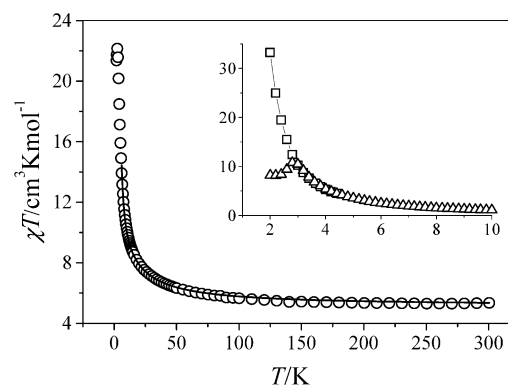
Figure 4. $\chi_M T$ versus T plot for complex **1**. The solid line represents the best-fit results with the parameters described in the text. The inset shows plots of FCM (△) and ZFCM (□) versus temperature at an applied field of 20 Oe.
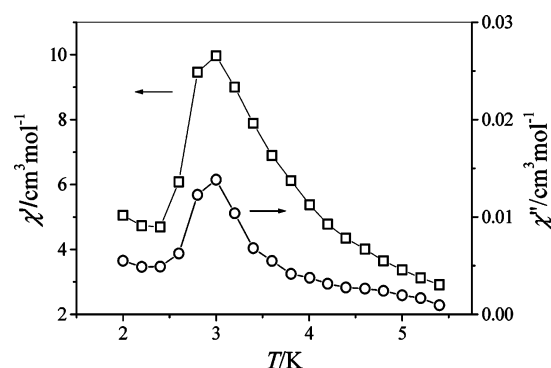
Figure 5. Real (χ') and imaginary (χ'') ac magnetic susceptibilities of **1** measured in an ac field of 3 Oe at the frequency of 0.5 Hz.

Finally, we have tried to analyze the magnitude of magnetic coupling between Cu(II) and Cr(III) ions in the complex. On the basis of the molecular structure, the complex can be described as trinuclear Cu₂Cr that contains linear cyano bridging linkages and one Cu(II)−Cr(III) ionic pair that incorporates bent cyano bridging linkages. From the magnetic viewpoint, the magnetic exchange through the bent Cr−CN−Cu linkages is negligibly small due to the inefficiency in magnetic orbital overlap and the comparatively long Cu−N$_{cyano}$ bond distances. To account for this contribution, a mean-field approximation including Weiss constant (θ) was used. However, this simplification is rough, especially for the strong bent cyano bridging in the title complex. Without any other suitable equations for the fitting, this attempt is worthwhile. Hence, the magnetic susceptibilities can be simulated on the basis of the isotropic spin Hamiltonian $\hat{H} = -2JS_{Cr}(S_{Cu(1)} + S_{Cu(2)})$ for the Cu₂Cr trimer of **1**. The fit to the experimental data in the temperature range 6−300 K gave the parameters of $J_{CuCr} = +8.1(6)$ cm⁻¹, $g = 2.09(1)$, and $\theta = +3.07(3)$ K, as shown in Figure 4.[11] The J value is reasonable; however, it should be noted that the fitting model is rough and should be treated carefully. The positive θ value suggests the presence of ferromagnetic Cu(II)−Cr(III) coupling through the bent cyano bridging, in good agreement with that previously reported for cyano-bridged Cu(II)−Cr(III) complexes.[4c,12]

Conclusions

The present work demonstrates that even aromatic amines can be utilized to construct 3D complex-based Prussian Blue analogues as capping ligands. The sterically hindered effect of

the aromatic amine tridentate ligand bis(2-pyridinylmethyl)-amine and the special coordination mode of Cu(II) induce the generation of the 3D tunnel structure of **1**. Comparatively, an infinite chainlike complex, $[\{(Cu(dien))_2Cr(CN)_6\}_n][Cu(H_2O)-(dien)Cr(CN)_6]_n \cdot 4nH_2O$, was obtained when the copper(II) complex of tridentate aliphatic amine ligand diethylenetriamine, $[Cu(dien)Cl_2]$ (dien = diethylenetriamine), was treated with $K_3[Cr(CN)_6]$.[4c] Up to now, only a few 3D Prussian Blue derivatives containing organic ligands able to organize the cyanide bridges in different ways within the same structure have been obtained.[6h,6i] Complex **1** is a new original interesting example.

Supporting Information Available: X-ray crystallographic files in CIF format, CCDC-253417. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (c) Ohab, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313.

(2) For example: (a) Verdaguer, M. *Science* **1996**, *272*, 698. (b) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (c) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593. (d) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096. (e) Sato, Y.; Ohkoshi, S.; Arai, K.; Tozawa, M.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 14590. (f) Champion, G.; Escax, V.; Cartier dit Moulin, C.; Bleuzen, A.; Villain, F.; Baudelet, F.; Dartyge, E.; Verdaguer, M. *J. Am. Chem. Soc.* **2001**, *123*, 12544. (g) Köhler, F. H.; Lescouëzec, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2571. (h) Entley, W. R.; Girolam, G. S. *Inorg. Chem.* **1994**, *33*, 5165. (i) Dong, W.; Zhu, L.-N.; Song, H.-B.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P.; Gao, S. *Inorg. Chem.* **2004**, *43*, 2465.

(3) (a) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (b) Larionova, J.; Clérac, R.; Donnadieu, B.; Willemin, S.; Guérin, C. *Cryst. Growth Des.* **2003**, *3*, 267.

(4) For example: (a) Re, N.; Gallo, E.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1996**, *35*, 6004. (b) Marvilliers, A.; Parsons, S.; Rivière, E.; Audière, J.-P.; Mallah, T. *Chem. Commun.* **1999**, 2217. (c) Fu, D.-G.; Chen, J.; Tan, X. S.; Jiang, L. J.; Zhang, S.-W.; Zheng, P. J.; Tang, W.-X. *Inorg. Chem.* **1997**, *36*, 220. (d) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Re, N.; Crescenzi, R.; Floriani, C. *Inorg. Chem.* **1998**, *37*, 255. (e) Marvilliers, A.; Parsons, S.; Rivière, E.; Audière, J.-P.; Mallah, T. *Chem. Commun.* **1999**, 2217. (f) Kou, H.-Z.; Zhou, B. C.; Gao, S.; Wang, R. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3288. (g) Colacio, E.; Dominguez-Vera, J. M.; Lloret, F.; Rodriguez, A.; Stoeckli-Evans, H. *Inorg. Chem.* **2003**, *42*, 6962.

(5) For example: (a) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. (b) Re, N.; Gallo, E.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1996**, *35*, 5964. (c) Ohba, M.; Okawa, H.; Fukita, N.; Hashimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 1011. (d) Miyasaka, H.; Matsumoto, N.; Re, N.; Gallo, E.; Floriani, C. *Inorg. Chem.* **1997**, *36*, 670. (e) Gallo, E.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1997**, *36*, 2178. (f) Miyasaka, H.; Okawa, H.; Miyazaki, A.; Enoki, T. *Inorg. Chem.* **1998**, *37*, 4878. (g) Smith, J. A.; Galan-Mascaros, J.-R.; Clérac, R.; Dunbar, K. R. *Chem. Commun.* **2000**, 1077. (h) Kou, H.-Z.; Gao, S.; Ma, B. Q.; Liao, D.-Z. *Chem. Commun.* **2000**, 713. (i) Kou, H.-Z.; Gao, S.; Ma, B. Q.; Liao, D. Z. *Chem. Commun.* **2000**, 1309. (j) Smith, J. A.; Galán-Mascarós, J.-R.; Clérac, R.; Dunbar, K. R. *Chem. Commun.* **2000**, 1077. (k) Ma, B. Q.; Gao, S.; Su, G..; Xu, G. X. *Angew. Chem., Int. Ed.* **2001**, *40*, 434. (l) Xiang, H.; Gao, S.; Lu, T.-B.; Luck, R. L.; Mao, Z.-W.; Chen, X.-M. *New J. Chem.* **2001**, *25*, 875. (m) Inoue, K.; Kikuchi, K.; Ohba, M.; Okawa, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4810.

(6) For example: (a) Salah El Fallah, M.; Rentscher, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947. (b) Fukita, N.; Ohba, M.; Okawa, H.; Matsuda, K.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 842. (c) Niu, T.; Wang, X.; Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **1998**, *37*, 5324. (d) Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1795. (e) Niu, T.; Wang, X.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1934. (f) Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1999**, *38*, 5346. (g) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775. (h) Zhang, S.-W.; Fu, D.-G.; Sun, W.-Y.; Hu, Z.; Yu, K.-B.; Tang, W.-X. *Inorg. Chem.* **2000**, *39*, 1142. (i) Kou, H.-Z.; Gao, S.; Zhang, J.; Wen, G.-H.; Su, G.; Zheng, R.-K.; Zhang, X.-X. *J. Am. Chem. Soc.* **2001**, *123*, 11809. (j) Inoue, K.; Imai, H.; Ghalsasi, P. S.; Kikuchi, K.; Ohba, M.; Okawa, H.; Yakhmi, J. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 4242. (k) Imai, H.; Inoue, K.; Kikuchi, K.; Yoshida, Y.; Ito, M.; Sunahara, T.; Onaka, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5618.

(7) (a) Berlinguette, C. P.; Galán-Mascarós, J. R.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 3416. (b) Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W.; Rey, P.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 718. (c) Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523. (d) Berlinguette, C. P.; Dragulescu-Andras, A.; Sieber, A.; Galán-Mascarós, J. R.; Güdel, H.-U.; Achim, C.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 6222. (e) Parker, R. J.; Spiccia, L.; Berry, K. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2001**, 333.

(8) Sarkar, S.; Mondal, A.; Ribas, J.; Drew, M. G. B.; Pramanik, K.; Rajak, K. K. *Inorg. Chim. Acta* **2005**, *358*, 641.

(9) Sun, H.-L.; Gao, S.; Ma, B.-Q.; Su, G.; Batten, S. R. *Cryst. Growth Des.* **2005**, *5*, 269.

(10) Verdaguer, M.; Bleuzen, A.; Train, C.; Grade, R.; Fabrizi De Biani, F.; Desplanches, C. *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 2959.

(11) Kou, H.-Z.; Zhou, B. C.; Wang, R.-J. *Inorg. Chem.* **2003**, *42*, 7658.

(12) (a) Kou, H.-Z.; Jiang, Y.-B.; Zhou, B. C.; Wang, R.-J. *Inorg. Chem.* **2004**, *43*, 3271. (b) El Fallah, M. S.; Ribas, J.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **2001**, 247. (c) El Fallah, M. S.; Ribas, J.; Solans, X.; Font-Bardia, M. *New J. Chem.* **2003**, *27*, 895. (d) Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdaguer, M. *Chem.—Eur. J.* **2003**, *9*, 1678.