

A new one-dimensional ferromagnet based on copper(II) and hexacyanochromate(III), with a rope-ladder chain structure

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A novel 1-D ferromagnetic compound based on copper(II) and hexacyanochromate(III) with formula $\{[\text{Cu}(\text{cyclam})][\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}\}_n$ (**1**; cyclam = 1,4,8,11-tetraazacyclotetradecane) was synthesized and structurally and magnetically characterized. The compound crystallizes in the monoclinic system of the space group $P2_1/n$. The structure of **1** can be described as formed by Cu_3Cr_2 fragments that are S shaped and connected amongst them to give a rope-ladder chain structure running along the c axis. Each Cu(II) atom is coordinated to four N atoms of the macrocycle and two CN groups of the hexacyanometalate in *trans* positions. Magnetic measurements have been performed for the compound, showing a moderate ferromagnetic coupling. The best least-squares fit gives $J = 4.33 \text{ cm}^{-1}$, $g_{\text{average}} = 2.03$ and $R = 2.80 \times 10^{-4}$.

Introduction

For many years chemists have consecrated their efforts to the creation of supramolecular architectures by assembling different building units to give interesting new materials. In this field, one of the most successful examples are the cyano-bridged complexes¹ in which the cyanometalate anion serves as the bridging moiety to build multidimensional structures. The choice of cyanometalate allows to control the geometry of the complexes, giving several different geometries, such as linear derivatives with $[\text{Ag}(\text{CN})_2]^-$,^{1a,1b} trigonal complexes such as $[\text{Cu}(\text{CN})_3]^{2-}$,² tetrahedral $[\text{Cd}(\text{CN})_4]^{2-}$,³ square planar $[\text{Ni}(\text{CN})_4]^{2-}$,^{1d,4} and octahedral $[\text{M}(\text{CN})_6]^{3-}$.^{1d-1h} Taking into account the ambidentate nature of the cyanide ligand, the N atom of the CN^- can be linked to almost any metal ion in the periodic table. In this class of compounds, which can be obtained through synthetic techniques of molecular chemistry, such as starting from pre-assembled species and reacting them in solution under mild conditions, two different metal ions are present, fully connected by the bridging cyanide ions. When the cyanometalate building block is paramagnetic and it is linked to another paramagnetic center, molecular-based magnetic materials can be formed, which have attracted considerable interest among chemists. The so-called Prussian blue analogs are becoming a very fruitful area of investigation due to their potential to give rise to a large variety of molecular-based magnets. A few high-temperature molecular magnets based on cyanide building blocks were reported by Girolami⁵ and Verdager⁵ *et al.* with T_c at 230, 190, 240 and 376 K. These works show that transition metal cyanides are good candidates for the synthesis of molecule-based magnetic materials, but there are extreme difficulties in growing crystals of these cyanide-containing complexes. A new effort has been made, blocking several positions of the guest ion by multidentate ligands. Focusing our interest on Cu(II) complexes, a series of paramagnetic polycyano derivatives has been reported in the literature: $[\text{Cu}(\text{teta})(\text{H}_2\text{O})_2][\text{Cu}(\text{teta})\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ ⁶ (teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), $[\text{Cu}(\text{en})_3][\text{Fe}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$,⁷ $[\text{Fe}\{\text{CN}\}\text{Cu}(\text{tpa})_6]_2$

$[\text{ClO}_4]_8$ [tpa = tris(2-pyridylmethyl)amine],⁸ $[\text{Cu}(\text{dien})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$,⁹ $[\{\{\text{Cu}(\text{dien})\}_2\text{Cr}(\text{CN})_6\}_n][\text{Cu}(\text{dien})(\text{H}_2\text{O})\text{Cr}(\text{CN})_6]_n \cdot 4n\text{H}_2\text{O}$ ¹⁰ (dien = diethylenetriamine),¹⁰ $[\{\text{Cu}(\text{edma})\}_3\text{Cr}(\text{CN})_6]^{10} (edma = ethylenediaminemonoacetate),¹⁰ $[\text{Cu}(\text{EtOH})_2][\text{Cu}(\text{en})_2][\text{Cr}(\text{CN})_6]_2$,¹¹ $\text{K}[\text{Cu}(\text{cyclam})][\text{Fe}(\text{CN})_6] \cdot 4(\text{H}_2\text{O})$,¹² $[\text{Cu}(\text{L})][\text{Cu}(\text{L})\text{Cr}(\text{CN})_6]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ ¹³ (L = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane),¹³ $[\text{Cu}(\text{tn})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$,¹⁴ $[\text{Cu}(\text{tn})]_2[\text{Fe}(\text{CN})_6]_2 \cdot \text{KCl} \cdot 5\text{H}_2\text{O}$ ¹⁵ (tn = 1,3-diaminopropane),^{14,15} $[\{\text{Cu}(\text{ept})\}_3\text{Fe}(\text{CN})_6](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ ¹⁶ [ept = *N*-(2-aminoethyl)-1,3-diaminopropane]¹⁶ and $[\text{Cu}(\text{dmen})]_2[\text{Fe}(\text{CN})_6]^{17}$ (dmen = 2-dimethylaminoethylamine).¹⁷ Here we present the synthesis, structure and magnetic properties of a new complex in this series, $\{[\text{Cu}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}\}_n$ (**1**).$

Experimental

Materials and methods

All the reagents were used as received from commercial suppliers without further purification. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nicolet 520 FTIR spectrophotometer. Magnetic measurements were carried out on polycrystalline samples with a SQUID susceptometer at a field of 1000 G. The independence of the magnetic susceptibility *versus* the applied field was checked at room temperature. Diamagnetic corrections were estimated from Pascal Tables.

Synthesis

Caution! Perchlorate salts are potentially explosive. Only a small amount of material should be prepared and this should be handled with care.

$\{[\text{Cu}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}\}_n$ (1**).** A concentrated solution of potassium hexacyanochromate(III) (0.32 g, 1 mmol) in water (20 ml) was added dropwise to a stirred aqueous solution (30 ml) of $[\text{Cu}(\text{cyclam})](\text{ClO}_4)_2$ (0.61 g, 1.5 mmol) previously prepared as described in the literature.¹⁸ Compound **1**

Table 1 Crystallographic data for **1**

Empirical formula	C ₄₂ H ₈₀ Cr ₂ Cu ₃ N ₂₄ O ₄
FW	1279.92
T/K	293(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.945(3)
<i>b</i> /Å	33.559(8)
<i>c</i> /Å	9.959(15)
β /°	96.389(10)
<i>U</i> /Å ³	2971(5)
<i>Z</i>	2
μ (MoK α)/mm ⁻¹	1.470
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0571
<i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1289
<i>R</i> ₁ ^a (all data)	0.0804
<i>wR</i> ₂ ^b (all data)	0.2131

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

precipitated immediately as a violet-brown microcrystalline powder. The compound was filtered, washed with water and acetone and air dried. Finally, **1** was recrystallized in dimethylformamide. The yield of pure compound was 66.4%. Very slow evaporation of the DMF solution produced good quality crystals for X-ray determination. Anal. calcd (%) for C₄₂H₈₀Cr₂Cu₃N₂₄O₄: C 39.4, H 6.3, Cr 8.125, Cu 14.89, N 26.3; found C 39.2, H 6.7, Cr 8.2, Cu 14.2, N 26.1.

X-Ray crystallography

A prismatic crystal (0.1 × 0.1 × 0.2 mm) of **1** was selected and mounted on a Enraf–Nonius CAD4 four-circle diffractometer. The crystallographic data, conditions retained for the intensity data collection, and some features of the structure refinements are listed in Table 1. Unit cell parameters were determined from automatic centering of 25 reflections (12° < θ < 21°) and refined by least-squares methods. Intensities were collected with graphite monochromated MoK α radiation, using the $\omega/2\theta$ scan technique. A total of 9078 reflections were measured in the range 2.15° < θ < 29.95°, of which 1544 reflections were assumed as observed applying the condition *I* > 2 σ (*I*). Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz polarization correction was made but no absorption corrections were made. The structure was solved by direct methods, using SHELXS-97 computer program¹⁹ and refined by the full-matrix least-squares method with SHELXL-97 computer program determination of the crystal structure²⁰ using 8540 reflections (very negative intensities were not assumed), *R*_{int}(on *I*) = 0.0389. The function minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$ where $w = [\sigma^2(I) + (0.0573 P)^2]^{-1}$, and $P = [|F_o|^2 + 2|F_c|^2]/3$. All hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. The final goodness-of-fit is 0.771 for all observed reflections. The number of refined parameters was 343. Maximum shift/esd = 0.00. Maximum and minimum peaks in the final difference synthesis were 0.674 and -0.401 e Å⁻³.

CCDC reference number 197530. See <http://www.rsc.org/suppdata/nj/b2/b211276k/> for crystallographic files in CIF or other electronic format.

Results and discussion

Structural description of {[Cu(cyclam)]₃[Cr(CN)₆]₂·4H₂O}_n (**1**)

An ORTEP drawing of the unit of the compound **1** with the atom labeling scheme is given in Fig. 1. The structure consists of an

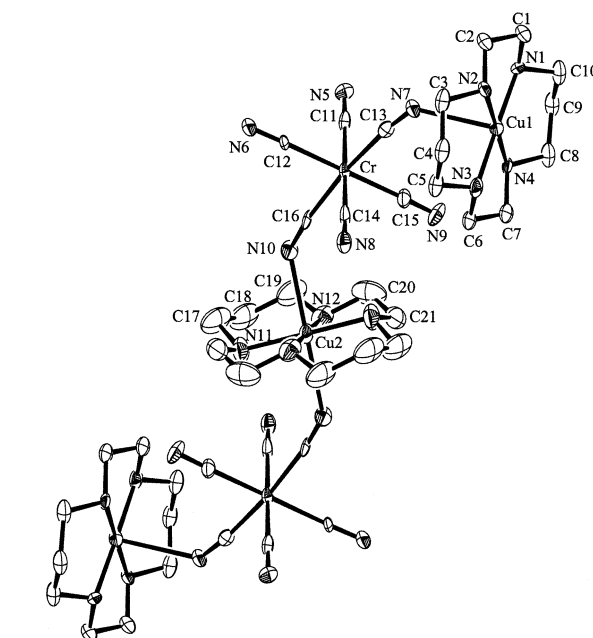


Fig. 1 ORTEP drawing of the asymmetric part of {[Cu(cyclam)]₃[Cr(CN)₆]₂·4H₂O}_n (**1**) showing atom labeling scheme. Ellipsoids at the 50% probability level. H₂O molecules are omitted.

infinite number of pentanuclear fragments, [(Cu(cyclam))₃[(Cr(CN)₆]₂], that are S shaped and which are placed in a parallel fashion along the *c* direction. Each fragment is connected to its neighbor to form a rope-ladder chain structure (Fig. 2). The copper Cu2 ion is localized at the special equivalent position (1/2, 1/2, 1/2), generating an inversion center. Each chromium ion is connected to three different copper ions by the cyanide groups (Figs. 1 and 2). The Cu···Cr separations are 5.274(8), 5.176(8) and 5.451(8) Å. In the structure each Cu(II) is octahedrally (elongated) coordinated by four nitrogen atoms of the macrocycle and two nitrogen atoms of cyanide group. The Cu–N distances vary between 1.981(8)–2.012(8) Å for (Cu–N_{cyclam}) and between 2.474(9)–2.638(8) Å for Cu–N_{CN}. The Cr–C distances range from 2.006(11) to 2.086(11) Å. Whereas, as expected, the Cr–C–N bond angles vary only over a small range between 171.4(9)–177.7(10)°, the corresponding Cu–N–C bond angles deviate significantly from linearity and are found to be 132.6(4)°, 136.9(8)° and 141.1(8)° in Cu1–N7–C13, Cu2–N10–C16 and Cu1#B–N6–C12, respectively. The water molecules are situated in the inter-fragment space. The main bond distances and angles are given in Table 2.

IR spectra

The spectrum of this complex presents a wide band centered at 3385 cm⁻¹ and assigned to the water molecule. The stretching

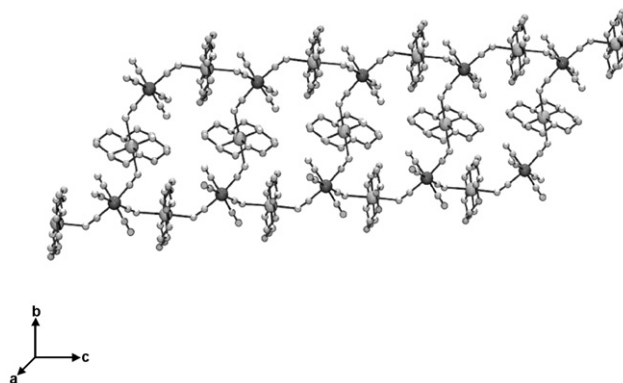


Fig. 2 Projection of the structure of the complex **1** along the *c* axis.

Table 2 Selected bond lengths (Å) and angles (°) for **1**^a

Cu1–N1	2.012(10)	Cr–C13	2.069(11)
Cu1–N2	1.981(8)	Cr–C14	2.006(11)
Cu1–N3	2.002(8)	Cr–C15	2.086(11)
Cu1–N4	2.006(8)	Cr–C16	2.076(10)
Cu1–N7	2.607(8)	N5–C11	1.138(11)
Cu2–N10	2.474(9)	N6–C12	1.144(10)
Cu2–N11	2.011(9)	N7–C13	1.176(11)
Cu2–N12	2.008(12)	N8–C14	1.170(10)
Cr–C11	2.069(11)	N9–C15	1.140(11)
Cr–C12	2.082(10)	N10–C16	1.124(10)
Cu1#B–N6	2.638(8)		
N1–Cu1–N2	84.8(4)	N11#A–Cu2–N12#A	95.5(5)
N1–Cu1–N3	179.0(3)	C11–Cr–C12	88.6(4)
N1–Cu1–N4	94.6(4)	C11–Cr–C13	90.7(4)
N1–Cu1–N7	88.3(1)	C11–Cr–C14	178.0(5)
N2–Cu1–N3	95.5(3)	C11–Cr–C15	88.0(4)
N2–Cu1–N4	178.7(3)	C11–Cr–C16	96.3(4)
N2–Cu1–N7	88.8(1)	C12–Cr–C13	94.2(4)
N3–Cu1–N4	85.1(3)	C12–Cr–C14	90.3(4)
N3–Cu1–N7	90.4(1)	C12–Cr–C15	175.7(4)
N4–Cu1–N7	92.1(1)	C12–Cr–C16	89.0(4)
N10–Cu2–N11	94.1(4)	C13–Cr–C14	87.7(2)
N10–Cu2–N12	86.9(4)	C13–Cr–C15	88.6(4)
N10–Cu2–N10#A	180.0(1)	C13–Cr–C16	172.4(4)
N10–Cu2–N11#A	85.9(4)	C14–Cr–C15	93.2(4)
N10–Cu2–N12#A	93.1(4)	C14–Cr–C16	85.4(4)
N11–Cu2–N12	95.5(5)	C15–Cr–C16	88.7(4)
N10#A–Cu2–N11	85.9(4)	Cu1–N7–C13	132.6(4)
N11–Cu2–N11#A	180.0(4)	Cu2–N10–C16	136.9(8)
N11–Cu2–N12#A	84.5(5)	Cr–C11–N5	174.9(12)
N10#A–Cu2–N12	93.1(4)	Cr–C12–N6	173.2(9)
N11#A–Cu2–N12	84.5(5)	Cr–C13–N7	173.6(9)
N12–Cu2–N12#A	180.0(2)	Cr–C14–N8	177.1(11)
N10#A–Cu2–N11#A	94.1(4)	Cr–C15–N9	177.7(10)
N10#A–Cu2–N12#A	86.9(4)	Cr–C16–N10	171.4(9)

^a Symmetry transformations used to generate equivalent atoms: A = $-x + 1, -y + 1, -z + 1$; B = $x, y, z + 1$.

bands of NH₂ groups of the cyclam are observed at 3246 and 3192 cm⁻¹. The band corresponding to the bending is registered at 1620 cm⁻¹. The bands assigned to the CH₂ group are located at 2941, 2877 cm⁻¹ and between 1469 and 1424 cm⁻¹. The ν(C–N) band appears at 2113 cm⁻¹ and is larger than usual, possibly due to an overlap of different ν(CN) bands (from monodentate and/or bridging CN⁻).

Magnetic studies

The magnetic behavior of complex **1** in the form of $\chi_M T$ and $1/\chi_M$ versus T plots are shown in Fig. 3. The global feature is characteristic of weak ferromagnetic interactions. The value of $\chi_M T$ at 300 K is 5.10 cm³ mol⁻¹ K, which corresponds to three isolated Cu^{II} ions with local spin $S_1 = 1/2$ and two Cr^{III} ions with local spin $S_2 = 3/2$ if we take into consideration $g_{Cu} = g_{Cr} = 2.0$. The $\chi_M T$ values smoothly increase from room temperature to ca. 45 K (5.56 cm³ mol⁻¹ K) and then quickly increase at lower temperature, reaching a maximum value of 11.25 cm³ mol⁻¹ K (9.49 μ_B) at 2 K. This is consistent with that expected for a spin-aligned ground state in which all spins are parallel, arising from the intramolecular interactions between the three Cu(II) and two Cr(III). The $1/\chi_M$ curve (Fig. 3 insert) in the range 2–100 K obeys the Curie–Weiss law with a positive Weiss constant $\theta = +1.8$ K.

The field dependence of the magnetization (0–5 T) measured at 2 K is shown in Fig. 4 in the form of M/N_{μ_B} (per Cu₃Cr₂ fragment) vs. H . The magnetization tends to 9.18 electrons, which is close to the expected value for the three Cu^{II} and two Cr^{III} ions. This feature agrees with the global weak ferromagnetic coupling within the copper(II)–chromium(III) system.

In order to interpret the magnetic properties it is convenient to represent a part of the structure to see the exchange

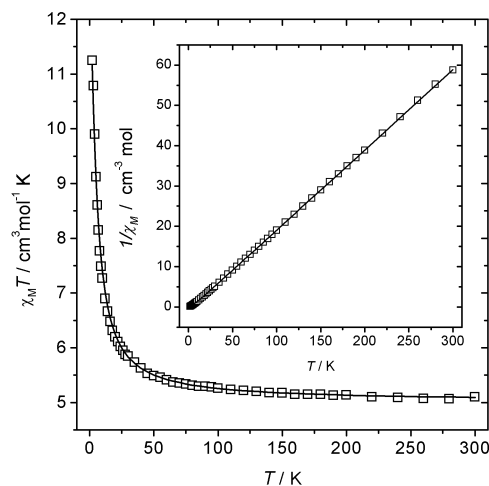


Fig. 3 Plots of observed $\chi_M T$ (□) and $1/\chi_M$ (insert) versus T of {[Cu(cyclam)]₃[Cr(CN)₆]₂·4H₂O}_n (**1**). Solid line represents the best theoretical fit (see text).

pathways and the possible Hamiltonians to use. Thus, in the light of the previous structural discussions, the coupling parameters J to be considered must be between Cu^{II} and Cr^{III} via the cyanide ligand propagated over all the structure, so we have to interpret the magnetic behavior through a model with three J parameters (J_1 , J_2 and J_3 in Fig. 5), where J_1 and J_2 are the intra-fragment (pentanuclear unit, see Figs. 1 and 2) exchange pathways and J_3 is the inter-fragment exchange pathway. A Hamiltonian with these three J parameters (along with two different g values) for this system would be impossible to solve due to the difficulties associated with the large dimensions of the calculation and the required computing time.

If we want to have an approach to the J parameters, we should take into account the following approximations. (1) The possible transmission of the coupling amongst two neighboring pentanuclear Cu₃Cr₂ fragments (J_3) is weaker than J_1 and J_2 , because the distance Cu1#B...Cr is longer. Thus, in principle we will assume J_3 is zero, even if this is not completely correct. (2) The alternating Cu1...Cr and Cr...Cu2 distances within the fragment are very similar and, thus, the corresponding J parameters will be taken to be identical ($J = J_1 = J_2$).

Based on these approximations, the experimental magnetic data can be fitted using the following isotropic Heisenberg Hamiltonian:

$$H = -J(S_{Cu1}S_{Cr} + S_{Cr}S_{Cu2} + S_{Cu2}S_{Cr\#A} + S_{Cr\#A}S_{Cu1\#A})$$

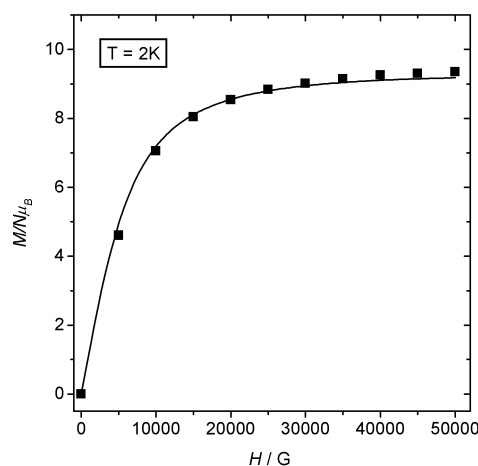


Fig. 4 The field dependence of the reduced magnetization at 2 K for {[Cu(cyclam)]₃[Cr(CN)₆]₂·4H₂O}_n (per Cu₃Cr₂). The solid line represents the best theoretical fit using the Brillouin equation.

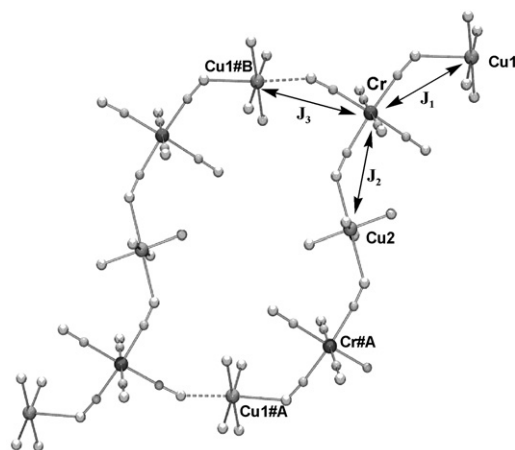


Fig. 5 Magnetic interaction pathways between the different copper(II) and chromium(III) centers. The main distances (Å) are: Cu1...Cr 5.274(8), Cu1...Cu2 9.273(8), Cu2...Cr 5.176(8), Cu1...Cu1#B 9.959(8), Cu1#B...Cr 5.451(8).

The calculations were made with the CLUMAG program, which uses the irreducible tensor operator formalism (ITO).²¹ The experimental data of **1** were fitted in the range 2–300 K with allowance for variation in all the parameters. The best least-squares fit, shown in Fig. 3, gives $J = 4.33 \text{ cm}^{-1}$, $g = 2.03$ and $R = 2.80 \times 10^{-4}$, where $R = \Sigma[(\chi_M T)_{\text{exp}} - (\chi_M T)_{\text{calc}}]^2 / \Sigma[(\chi_M T)_{\text{exp}}]^2$. The assumption of equal g values for Cu^{II} and Cr^{III} is an approximation, since g_{Cu} must be > 2.00 and g_{Cr} must be < 2.00 . This is a justified approximation, since it should not greatly affect the calculated J value (the parameter of interest).

The value of the superexchange parameter $J = +4.33 \text{ cm}^{-1}$ for compound **1** can be considered as normal, taking into account the structural and magnetic data found in the literature. The magnetic behavior of Prussian Blue analogs is well-known and the general trends of their magnetic properties are well-established. In particular, the ferromagnetic interaction between the Fe^{III} or Cr^{III} and Cu^{II} ions can be rationalized in terms of the strict orthogonality of the magnetic orbitals of these ions. According to the crystal structure and ligand-field theory, a copper(II) ion in elongated octahedral surroundings has one unpaired electron in a $d_{x^2-y^2}$ orbital (x and y axes are taken along the donor atoms), which interacts with the molecular orbitals of the cyano bridge having the same symmetry, producing a magnetic orbital with σ character. A low-spin chromium(III) ion in octahedral surroundings has unpaired electron density in the t_{2g} orbitals, which interact

with other molecular orbitals of the cyano bridge having appropriate symmetry, producing a magnetic orbital with π character. Consequently, strict orthogonality is obeyed and the interaction between Cu^{II} and Cr^{III} should be ferromagnetic. As a comparison, in Table 3, all similar Cr^{III}–Cu^{II} complexes reported in the literature, together with their magnetic characteristics, are gathered.

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Table 3 Magnetic behavior of Cu^{II}–Cr^{III} complexes reported in the literature

Compound ^a	J/cm^{-1}	Reference
[Cu(EtOH) ₂][Cu(en)] ₂ [Cr(CN) ₆] ₂	6.0	11
[{Cu(dien) ₂ Cr(CN) ₆ }] _n	$J = 7.24$, $J' = 6.41$	10
[Cu(dien)(H ₂ O)][Cr(CN) ₆] _n ·4nH ₂ O ^b		
[Cu(edma) ₃][Cr(CN) ₆]	9.16	10
[Cu(L)][Cu(L)Cr(CN) ₆ ClO ₄]	4.82	13
[Cu(tn)] ₃ [Cr(CN) ₆] ₂ ·3H ₂ O	Ferro	14
	(J not reported)	
[{Cu(cyclam) ₃ }[Cr(CN) ₆] ₂ ·4H ₂ O}] _n	4.33	This work

^a en = ethylenediamine, dien = diethylenetriamine, edma = ethylenediamine monoacetate, L = *meso*-5,5,7,12,12,14-hexamethyltetraazacyclotetradecane and cyclam = 1,4,8,11-tetraazacyclotetradecane. ^b This complex has two distinct ionic units.