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Synthesis, structure and magnetic properties of a new one-dimensional copper(II) complex with $[Cr(CN)_6]^{3-}$. Comparison with the $[Fe(CN)_6]^{3-}$ analogue

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Received 16th October 2000, Accepted 5th December 2000

A new complex of formula $\{[Cu(L)][Cu(L)Cr(CN)_6]ClO_4{\cdot}2H_2O\}_n$ **1** (L is *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has been prepared from the reaction of $[Cr(CN)_6]^{3-}$ and $[Cu(L)]^{2+}$, and its structure and magnetic properties studied. The structure consists of a discrete $[Cu(L)]^{2+}$ cation and an anionic fragment formed by $[Cu(L)Cr(CN)_6]^-$ in which the Cu^{II} is coordinated to four N atoms of the macrocycle and two CN groups of the hexacyanometalate in *trans* positions to give a one-dimensional compound. The compound shows a moderate ferromagnetic coupling. In order to describe its magnetic data a new formula was developed for the magnetic susceptibility of an isotropic ferromagnetic $S = 1/2$ and 3/2 Heisenberg chain assuming a variation of $\chi_M T$ *vs.* the length N. The best least-squares fit gives $J = 4.82$ cm^{-1}, $g = 2.02$ and $R = 1.23 \times 10^{-4}$.

Introduction

For many years chemists have devoted their efforts to assembling compounds by using and connecting building units to give supramolecular structures. A successful recent example of this process is the cyano bridge complexes[1] in which a cyanometalate anion serves as the bridging moiety to build a multidimensional structure with a second coordination center. These complexes are usually composed of a cyanometalate $[M(CN)_m]^{n-}$ (building unit) and a guest molecule. In general, the choice of cyanometalate is limiting, since the geometry of the complexes has only a few possibilities, such as linear $[Ag(CN)_2]^-$,[1a,b] trigonal such as $[Cu(CN)_3]^{2-}$,[1c,2] tetrahedral $[Cd(CN)_4]^{2-}$,[3] square planar $[Ni(CN)_4]^{2-}$,[1d,4] and octahedral $[M(CN)_6]^{3-}$.[1f–j] The second coordination center, however, can be almost any metal ion in the Periodic Table. When the cyanometalate building block is paramagnetic, molecular-based magnetic materials can be formed which have attracted considerable interest. The so-called Prussian blue analogues are becoming a very fruitful area to investigate due to the importance of their potential to give rise to a large variety of molecular-based magnets. In this class of compounds, which can be obtained through synthetic techniques of molecular chemistry, *i.e.* starting from pre-assembled species and treating them in solution under mild conditions, two different metal ions are present, fully connected by the bridging cyanide ions. A few high temperature molecular magnets based on cyanide building blocks were reported by Entley and Girolami and Verdaguer and co-workers[5] with T_c values of 230, 190 and 240 K. These works show that transition metal cyanides are good candidates for a system of molecule-based magnetic materials, but there is extreme difficulty in growing crystals of these cyanide-containing complexes. A new effort has been made, to substitute the H_2O molecules of the guest ion for ambidentate diaminoalkanes, aromatic amines, pyrazine and derivatives. These ligands are necessary to fill up the void space, stabilizing the crystal structure. Focusing our interest on copper complexes, a series of paramagnetic polycyano derivatives has been reported: $[Cu(teta)(H_2O)_2][Cu(teta)Fe(CN)_6]ClO_4{\cdot}2H_2O$[6] (teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane), $[Cu(en)]_3[Fe(CN)_6]_2{\cdot}3H_2O$,[7] $[Fe\{(CN)Cu(tpa)\}_6][ClO_4]_8$ [tpa = tris(2-pyridylmethyl)amine],[8] $[Cu(dien)]_3[Fe(CN)_6]_2{\cdot}6H_2O$,[9] $[\{(Cu(dien))_2Cr(CN)_6\}_n][Cu(dien)(H_2O)Cr(CN)_6]_n{\cdot}4nH_2O$,[10] (dien = diethylenetriamine), $[(Cu(edma))_3Cr(CN)_6]$ (edma = ethylenediaminemonoacetate),[10] $\{[Cu(en)_2][KCr(CN)_6]\}_n$,[11] $K[Cu(cyclam)][Fe(CN)_6]{\cdot}4H_2O$[12] and several Fe^{III}–CN–Cu^{II} models of cytochrome c oxidase.[13] Here we present the synthesis, structure and magnetic properties of the new complex $\{[Cu(L)][Cu(L)Cr(CN)_6]ClO_4{\cdot}2H_2O\}_n$ **1** (L = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane) and compare it with the analogous iron(III) complex **2**.

Experimental

General methods

Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nicolet 520 FTIR spectrophotometer. Magnetic measurements for complexes **1** and **2** were carried out on polycrystalline samples with a pendulum type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat, working in the temperature range 4–300 K, and a Bruker BE15 electromagnet. The magnetic field was approximately 15000 G. All magnetic measurements were performed on macroscopic crystals ground to a fine powder. Diamagnetic corrections were estimated from Pascal tables. IR spectra are similar for both compounds showing very strong bands at 3234 cm^{-1}, ν(N–H), a wide range between 2974 and 2893 cm^{-1}, ν(C–H), and the characteristic set of bands of L in the 1463–1141 cm^{-1} range. The hexacyanide ligand band ν(C–N) appears at 2123 cm^{-1}, the perchlorate bands at normal frequencies (1096 and 625 cm^{-1}).

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

DOI: 10.1039/b008314n

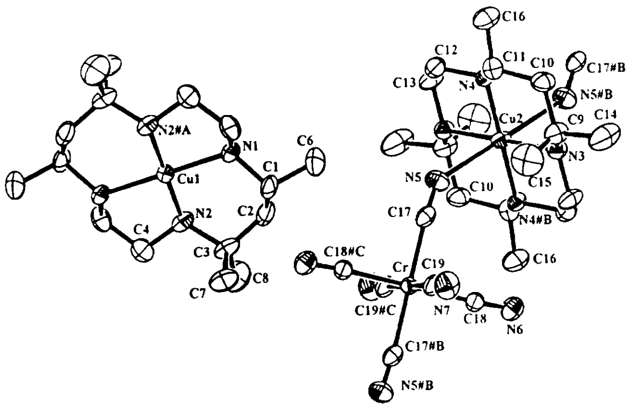

Fig. 1 An ORTEP drawing of the cationic part of {[Cu(L)][Cu(L)Cr(CN)$_6$]ClO$_4$·2H$_2$O}$_n$ **1** showing the atom labeling scheme. Ellipsoids at the 40% probability level.

Syntheses

{[Cu(L)][Cu(L)Cr(CN)$_6$]ClO$_4$·2H$_2$O}$_n$ 1. A concentrated solution of potassium hexacyanochromate(III) (0.16 g, 0.5 mmol) in water (20 ml) was added dropwise to a stirred aqueous solution (30 ml) of [Cu(L)][ClO$_4$]$_2$ (1.64 g, 3 mmol) previously prepared as described.[14] Compound **1** precipitated immediately as a violet microcrystalline powder. It was filtered off, washed with water and acetone and air-dried. The compound was recrystallized from dimethylformamide. Yield 60%. Very slow evaporation of DMF solutions produced good quality crystals for X-ray determination (Found: C, 42.4; H, 7.5; Cl, 3.3; N, 18.3. Calc.: C, 42.4; H, 7.4; Cl, 3.3; N, 18.2%).

{[Cu(L)(H$_2$O)$_2$][Cu(L)Fe(CN)$_6$]ClO$_4$·2H$_2$O}$_n$ 2. Complex **2** was obtained according to the literature method.[6]

X-Ray crystallography

The crystallographic data, conditions 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 5950 reflections and refined by least-squares methods. A total of 19097 reflections (7078 independent) were measured for complex **1** of which 6861 were assumed to be observed applying the condition 2$\sigma(I)$. The crystal structure was solved by direct methods, using the SHELXS 97 computer program,[15] and refined by full matrix least squares methods using SHELXL 97.[16]

CCDC reference number 186/2299.

See http://www.rsc.org/suppdata/dt/b0/b008314n/ for crystallographic files in .cif format.

Results and discussion

Crystal structure of {[Cu(L)][Cu(L)Cr(CN)$_6$]ClO$_4$·2H$_2$O}$_n$ 1

An ORTEP[17] plot of the basic units of compound **1** is shown in Fig. 1. The structure consists of a discrete [Cu(L)]$^{2+}$ cation, an anionic fragment [Cu(L)Cr(CN)$_6$] and perchlorate as counter anion. The local coordination of the two copper(II) ions is different: the isolated cationic part shows a square-planar arrangement, with the copper and four N-macrocycle atoms placed in the same plane while the one-dimensional system shows an elongated octahedral arrangement, with the copper and four N-macrocycle atoms placed in the same plane (short distances, 2.04 Å) and two nitrogen atoms of the cyanometalate group coordinated in *trans* fashion (long distances, 2.58 Å). The bond distances around the copper atom are very close to those reported,[6] ranging from Cu2–N3 2.038(3) to Cu2–N5 2.582(4) Å. Each cyanometalate group links the adjacent copper ion giving a one-dimensional compound. The bond angle Cu2–N5–C17 138.5(3)° is close to values in the literature.[6–12] The Cr–C17–N5 angle deviates slightly from linearity, 173.5(3)°. The perchlorate anions are placed in the interchain space and no hydrogen bonds are present between them and the chain which runs along the (100) direction. The main bond distances and angles are given in Table 2.

Table 1 Crystallographic data for complex **1**

Empirical formula	C$_{38}$H$_{80}$ClCrCu$_2$N$_{14}$O$_8$
M	1075.68
T/K	293(2)
Crystal system	Monoclinic
Space group	*P*2$_1$/*c*
a/Å	10.6760(10)
b/Å	15.4830(10)
c/Å	15.8860(10)
β/°	92.7510(10)
V/Å^3	2622.9(3)
Z	2
μ(Mo-Kα)/mm^{-1}	1.157
Reflections collected	19097
Independent reflections	7078
R(int)	0.0784
R	0.0496
wR	0.1324

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

Cu1–N1	2.028(3)	Cr–C18	2.060(3)
Cu1–N2	2.048(3)	Cr–C19	2.083(3)
Cu2–N3	2.038(3)	N5–C17	1.125(6)
Cu2–N4	2.043(3)	N6–C18	1.156(5)
Cu2–N5	2.582(4)	N7–C19	1.127(4)
Cr–C17	2.083(4)		
N1–Cu1–N2	94.74(12)	C17–Cr–C19	90.10(14)
N1–Cu1–N2#A	85.26(12)	C17–Cr–C18#C	87.98(15)
N3–Cu2–N4	93.67(11)	C17–Cr–C19#C	89.90(14)
N3–Cu2–N5	78.73(11)	C18–Cr–C19	89.53(13)
N3–Cu2–N4#B	86.33(11)	C18–Cr–C19#C	90.47(13)
N3–Cu2–N5#B	101.27(11)	Cu2–N5–C17	138.5(3)
N4–Cu2–N5	86.95(11)	Cr–C17–N5	173.5(3)
N4–Cu2–N5#B	93.05(11)	Cr–C18–N6	176.9(4)
C17–Cr–C18	92.02(15)	Cr–C19–N7	178.4(3)

[a] Symmetry transformations used to generate equivalent atoms: (A) 2 − *x*, −*y*, 2 − *z*; (B) 1 − *x*, −*y*, 1 − *z*; (C) 2 − *x*, −*y*, 1 − *z*.

Magnetic studies

The variable temperature magnetic susceptibility data for complex **1** were recorded between 290 and 4 K. A plot of $\chi_M T$ *versus* T is shown in Fig. 2. At room temperature $\chi_M T$ is equal to 2.67 cm^3 K mol^{-1}, which corresponds to two isolated copper(II) ions with local spin $S_1 = 1/2$ and one chromium(III) ion with local spin $S_2 = 3/2$ if we take into consideration $g_{Cu} = g_{Cr} = 2.017$. $\chi_M T$ increases smoothly as T is lowered, to exhibit a maximum value of 4.6 cm^3 K mol^{-1} at 4.5 K, indicating ferromagnetic coupling. To fit the magnetic data we take into consideration that one Cu^{II} of the two present in the elemental cell is isolated, following, thus, the Curie law. This part can be subtracted from the global magnetic susceptibility to give only that corresponding to the fragment Cu^{II}–Cr^{III} which is ferromagnetically coupled. No formula to reproduce such a ferromagnetic system is available in the literature, so we felt it appropriate to develop one.

Magnetic model. The Hamiltonian for a Heisenberg ferromagnetic chain with alternate spins $S_i = 1/2$ and $S_{i+1} = 3/2$ can be written as in eqn. (1) where n is the number of spin pairs

$$H = -J \sum_{i=1}^{n} S_i S_{i+1} \qquad (1)$$

and J the nearest neighbor ferromagnetic exchange interaction; J positive means ferromagnetic coupling.

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

Compound	Magnetic properties	Spin–orbit coupling of Fe^{III}	Ref.
$[Cu(teta)(H_2O)_2][Cu(teta)][Fe(CN)_6]ClO_4\cdot 2H_2O$	AF	Ignored	6
$[Cu(dien)]_3[Fe(CN)_6]_2\cdot 6H_2O$	Weak F	Ignored	9
$[Cu(en)_3][Fe(CN)_6]\cdot 3H_2O$	F	Ignored	7
$K[Cu(cyclam)][Fe(CN)_6]\cdot 4H_2O$	F	Considered	13
$[KCu(en)_2][Cr(CN)_6]$	Not reported	—	11
$[Cu(dien)]_2[Cu(dien)(H_2O)][Cr(CN)_6]_2\cdot 4H_2O$	F	—	10
$[Cu(edma)_3][Cr(CN)_6]$	F	—	10

AF = Antiferromagnetic, F = ferromagnetic.

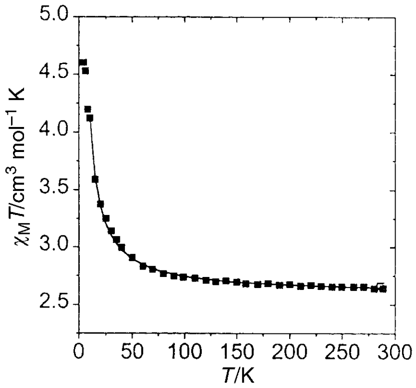

Fig. 2 Plot of observed $\chi_M T$ (■) *versus* T of $\{[Cu(L)(H_2O)_2][Cu(L)Cr(CN)_6]ClO_4\cdot 2H_2O\}_n$ **1**. The solid line represents the best theoretical fit (see text).

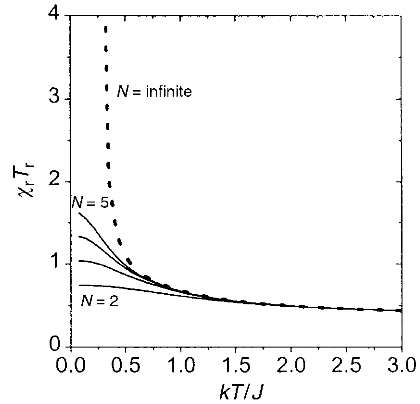

Fig. 3 Theoretical curves of $\chi_r T_r$ *versus* kT/J.

By applying the usual computational technique, based on calculation of the properties of finite rings of increasing size ($N = 2$, 3, 4 and 5) and then extrapolating them to infinity, we determined the product of the reduced susceptibility and reduced temperature ($\chi_r T_r$) (see below) of ferromagnetic chains with alternate spins $S_1 = 1/2$ and $S_2 = 3/2$. The calculations were made with the CLUMAG program, which uses the irreducible tensor operator formalism (ITO).[18] Fig. 3 shows the $\chi_r T_r$ curves of the chains when N is 2, 3, 4, 5 (solid line), and the infinite curve calculated by extrapolation (dashed line).

An expression of the product $\chi_r T_r$ which depends on T_r can easily be generated by applying a previously reported strategy,[19] *i.e.* fitting the theoretical $\chi_r T_r$ curve (N = infinite) using the rational expression (2) where $\chi_r = \chi_M J/(9/2)Ng^2\beta^2$. We assumed

$$\chi_r T_r = (AT_r^2 + BT_r + C)/(DT_r^2 + FT_r + G) \qquad (2)$$

that the local g factors were identical, $g_{Cu} = g_{Cr} = g$, and the reduced temperature T_r is given by kT/J.

The coefficients A–G are 0.855649, 0.53931, −0.261437, 2.59081, −0.904933 and 0.00887567. Eqn. (2) can be converted into the usual form to eqn. (3) where $X = J/kT = 1/T_r$. It is valid for $T_r = kT/J \geq 0.417$.

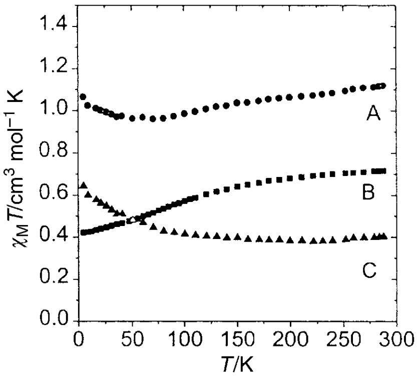

Fig. 4 Plots of observed $\chi_M T$ *versus* T of $\{[Cu(L)(H_2O)_2][Cu(L)Fe(CN)_6]ClO_4\cdot 2H_2O\}_n$ **2** (A), $K_3[Fe(CN)_6]$ (B) and the difference (C).

$$\chi_M T = (9/2)(Ng^2\beta^2/k)[(A + BX + CX^2)/(D + FX + GX^2)] \qquad (3)$$

Coupling constant calculations. The experimental data for complex **1** were fitted using eqn. (3) in the range 300–10 K. With allowance for variations in all the parameters, the best least-squares fit shown in Fig. 2 gives $J = 4.82$ cm^{-1}, $g = 2.02$ and $R = 1.23 \times 10^{-4}$. 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 value of J (the parameter of interest).

Some authors[6] have reported the structure and magnetic properties of the analogous iron(III) compound **2**. However, their interpretation leads to error. First, they did not take into account the spin–orbit coupling responsible for the decay of the $\chi_M T$ curve. Secondly, they tried to fit the magnetic data using an expression that presents an alternating antiferromagnetic interaction, which we believe to be inadequate. On the contrary, and according to our measurements, the coupling is ferromagnetic. In Fig. 4 we represent the experimental susceptibility curve of **2**, together with the corresponding susceptibility for $K_3[Fe(CN)_6]$ and the difference. The difference in values increases inversely with temperature, indicating ferromagnetic coupling. No fit of the magnetic data is possible if we take into account the spin–orbit coupling of the Fe^{III}. Only the shape is indicative of the ferromagnetism. The ferromagnetic interaction between the Fe^{III} or Cr^{III} and Cu^{II} 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 taken along the donor atom bonds) which interacts with molecular orbitals of the cyano bridge having the same symmetry, producing a magnetic orbital with σ character. A low-spin iron(III) or chromium(III) ion in octahedral surroundings has unpaired electron density in t_{2g} orbitals which interacts 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 Fe^{III} or Cr^{III} should be ferromagnetic. Quantitatively, the interactions between nearest neighbours are very weak. This might be due to the large distance between the magnetic ions. For comparison, all similar Fe^{III}–Cu^{II} and Cr^{III}–Cu^{II} complexes reported, together with their magnetic characteristics, are gathered in Table 3.

Acknowledgements

This work was supported by the Dirección General de Investigación Científica y Técnica (Spanish Government), Grant no. PB96/0163. M. S. El Fallah acknowledges support by the Generalitat de Catalunya.

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