Hexacyanidometalate molecular chemistry: di-, tri-, tetra-, penta- (*cis*/*trans*) and hepta-nuclear chromium–copper and cobalt–copper complexes†

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Numerous μ-cyanido bridged polynuclear complexes, $[M(CN)_n(CNCu^{II}L)_{6-n}]^{m+}$ (with M = Cr^{III} or Co^{III}, n = 0–5 and L = tris(2-amino)ethylamine (tren) or *N*,*N*-dimethylethylenediamine (Me_2en)), have been synthesised: $[Co^{III}(CN)_5\{CNCu^{II}(Me_2en)_2\}]^-$, $[Co^{III}(CN)_4(CNCu^{II}tren)_2]^+$/$[Co^{III}(CN)_3(CNCu^{II}tren)_3]^{3+}$, $[\{Co^{III}(CN)_6\}_2\{Cu^{II}(Me_2en)_2\}_5]^{4+}$ and $[Co^{III}(CNCu^{II}tren)_6]^{9+}$ denoted correspondingly **CoCu**, **CoCu2**/**CoCu3**, **Co2Cu5** and **CoCu6** as well as chromium derivatives: $[Cr^{III}(CN)_5\{CNCu^{II}(Me_2en)_2\}]^-$, *cis*-$[Cr^{III}(CN)_2\{CNCu^{II}(Me_2en)_2\}_4]^{5+}$, *trans*-$[Cr^{III}(CN)_2\{CNCu^{II}(Me_2en)_2\}_4]^{5+}$ and $[Cr^{III}(CNCu^{II}tren)_6]^{9+}$ denoted **CrCu**, ***cis*-CrCu4**, ***trans*-CrCu4** and **CrCu6**, respectively. All compounds have been characterised by IR spectroscopy and most of them by X-ray crystallography. The magnetic properties of the complexes have been studied and the spin and the anisotropy values as well as the intra- and inter-molecular exchange couplings evaluated. For the cobalt centred species, in first approximation, the complexes behave as one, five and six isolated copper(II) complexes, but more accurate studies allow us to evaluate the weak antiferromagnetic coupling constant between two next-nearest neighbours Cu–Co(III)–Cu. For the chromium centred species, the spin state varies from 1 to 9/2 (with ferromagnetic interaction for ***trans*-CrCu4** and **CrCu6** and weak antiferromagnetic interaction for **CrCu** and ***cis*-CrCu4**) with a negligible effective anisotropic factor. Experimentally, the exchange coupling between the μ-cyanido bridged spin carriers Cr(III) and Cu(II) varies from −2.5 to +45 cm^{-1} increasing with the C–N–Cu angle. A magneto–structural correlation allows us to rationalise the most relevant features of the exchange interaction between Cr(III) and Cu(II) through a cyanido bridge.

Introduction

The synthesis of new polynuclear complexes with large spin ground state and anisotropy is a new development in molecular magnetism.[1] It traces back to 1992 when slow relaxation of the magnetisation was discovered in a Mn_{12} complex, with formula $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2AcOH\cdot 4H_2O$, viewed as the first example of single molecule magnets.[2] The design and the studies of such species have been developed for several years[3–5] including in our laboratory.[6–10] Following a strategy which consists to use polycyanidometalate cores such as $[Cr(CN)_6]^{3-}$ and mononuclear complexes specifically designed to leave only one coordination site available, new heptanuclear complexes, such as $[Cr\{CN–Cu(tren)\}_6]^{9+}$, $CrCu_6$, $[Cr(CN–Ni(tetren))_6]^{9+}$, $CrNi_6$, and $[Cr(CN–Mn(tetren))_6]^{9+}$, $CrMn_6$, have been synthesized and characterized.[7] Despite the high spin value of these compounds (S = 9/2, 15/2 and 27/2, respectively), no single molecule magnet behaviour has been observed. This has been explained by the weak local anisotropy of the metallic ions involved in the structures and by the high symmetry of the compounds. Consequently, the uniaxial anisotropy, D, one of the important parameters to control, was equal to zero. It was then necessary to follow new synthetic routes in order to get polynuclear complexes with an effective control of the nuclearity and of the structural anisotropy. Then, starting with an hexacyanometalate precursor, we illustrated the possibility of tuning the nuclearity of the target products. A complete family of anisotropic polynuclear complexes based on hexacyanidocobaltate chemistry has been synthesised and fully characterised, $[Co(CN)_{6-x}(CN–M'L)_x]^{n\pm}$, CoNi, $CoNi_2$, $CoNi_3$, $CoNi_5$ and $CoNi_6$.[8] Recently, the spin and the anisotropy parameters were combined in a series of the μ-cyanido bridged $[Cr(CN)_{6-x}(CN–M'L)_x]^{n\pm}$, polynuclear CrNi species: nine different high-spin molecules have been characterized.[9] Some of them behave as single molecule magnets.

Similarly, changing nickel by copper ions, several polynuclear complexes $[M^{III}(CN)_n(CNCu^{II}L)_{6-n}]^{m+}$ (with M^{III} = Cr^{III} or Co^{III}, n = 0–5 and L = tris(2-amino)ethylamine (tren) or *N*,*N*-dimethylethylenediamine (Me_2en)), were synthesised:

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$[Co(CN)_5\{CNCu(Me_2en)_2\}]^-$, $[Co(CN)_4\{CNCu(tren)\}_2]^+$-$[Co(CN)_3\{CNCu(tren)\}_3]^{3+}$, $[\{Co(CN)_6\}_2\{Cu(Me_2en)_2\}_5]^{4+}$ and $[Co\{CNCu(tren)\}_6]^{9+}$ denoted correspondingly **CoCu**, **CoCu2**/**CoCu3**, **Co2Cu5**, **CoCu6** as well as chromium derivatives: $[Cr(CN)_5\{CNCu(Me_2en)_2\}]^-$, *cis*-$[Cr(CN)_2\{CNCu(Me_2en)_2\}_4]^{5+}$, *trans*-$[Cr(CN)_2\{CNCu(Me_2en)_2\}_4]^{5+}$ and $[Cr\{CNCu(tren))_6]^{9+}$ denoted **CrCu**, ***cis*-CrCu4**, ***trans*-CrCu4**, **CrCu6**, respectively. The compounds have been characterised by IR spectroscopy and X-ray crystallography and are fully described in the present paper. In addition to the magnetic properties, an EPR study of the dinuclear **CoCu** and the heptanuclear **CoCu6** complex has been included in the current work.

In the frame of polycyanometalate chemistry, the copper complexes may have an additional interest. In this regard, photoswitchable high-spin molecules based on octacyanometalate precursors have been recently observed and might be viewed as species of interest since their magnetic properties can be controlled by external stimuli.[11–13] Results have been first obtained on a polynuclear complex, MoCu6.[14] Before light irradiation, this complex behaves as six isolated paramagnetic Cu^{II} ions surrounding a Mo^{IV} diamagnetic core. After light irradiation, the magnetic properties are those of a high-spin molecule, $Mo^{V}Cu^{I}Cu^{II}_5$ ($S = 3$). The long-lived photo-produced metastable state that has been explained by a photoinduced electron transfer, is persistent up to an unusually high temperature (300 K). Furthermore, the photo-magnetic effect is thermally reversible.

The polynuclear CrCu and CoCu complexes, $[M(CN)_n(CNCuL)_{6-n}]^{m+}$ (with M = Cr or Co, $n = 0$–5 and L = polydentate ligand), might be viewed as interesting compounds in order to design new MoCu complexes. They might be considered as well as reference species for the magnetic studies of the MoCu series, not only for the ground state (diamagnetic centered compounds) but also for the metastable state (paramagnetic centered species).

After presenting the synthetic strategy that has been used in the present study, we shall discuss the main characterizations and the magnetic properties of cobalt centered complexes $[Co^{III}(CN)_{6-n}(CN–CuL)_n]^{(2n-3)+}$ (L_n = polydentate ligand, $n = 1, 2, 3, 6$) denoted **CoCu**, **CoCu2**, **CoCu3** and **CoCu6**, respectively. Additional discussion will be presented for the chromium(III) centered analogues: **CrCu**, ***cis*-CrCu4**, ***trans*-CrCu4** and **CrCu6**. The complete description of a heptanuclear "dendritic" complex, $[\{Co^{III}(CN)_6\}_2(CuL)_5]^{4+}$ compound, denoted **Co2Cu5** is also included in the present study. All the compounds reviewed in the present paper are illustrated in Fig. 1.

Results and discussion

Synthetic strategy

Hexacyanometalate chemistry has been developed in the laboratory for the design and synthesis of room temperature molecule-based magnets.[15–17] These precursors have also been used for the formation of high-spin polynuclear complexes.[7–9] The reaction of hexacyanometalate precursor $[M(CN)_6]^{3-}$ ($M = Cr^{III}$, Co^{III}), a Lewis base, with an excess of Lewis acid, *i.e.* a mononuclear complex formed by paramagnetic metal ion chelated by a multidentate terminal ligand L_n, leaving one easily accessible free coordination position only, allows the formation of the target polynuclear species $[M^{III}(CN)_{6-n}(CN–M'L)_n]^{(2n-3)+}$ ($M = Cr^{III}$, Co^{III}, $M' = Cu^{II}$) by formation of up to six M–CN–M′ coordination bonds.

The choice of the cyanide as bridging ligand is directed by several considerations that have been developed elsewhere:[17] (i) the cyano bridge is well known to bridge selectively two different transition metals in an end-to-end fashion;[18–19] (ii) the polycyanometalate precursors are often stable and inert building blocks[20] (iii) the cyanide allows strong exchange coupling between the spin carriers;[21] (iv) due to the quasi-linear configuration of the M–CN–M′ unit, it is possible to foresee the nature and to tune the value of the orbital interactions through the cyanide by choosing the metallic centers M and M′ involved and therefore the spin ground state of the molecules.

The formation of anionic or cationic complexes is another key point of our synthetic strategy. The selection of trivalent core ($M = Cr^{III}$, d^3, $S = 3/2$; Co^{III}, d^6, $S = 0$) and divalent peripheral metallic cations (M′) associated with neutral ligands (L) avoids the precipitation of neutral products in aqueous solution and favours a slow growth of crystals. Furthermore, charged complexes allow the separation of the molecular ions in the solid state by various counter-ions and an effective control of the intermolecular interactions. The possible variations of several synthetic parameters (*i.e.* the nature of the polydentate ligands, the counter anions and the stoichiometry) are another advantage of this strategy.

The peripheral transition metal ion that has been selected in the present study is copper(II) (d^9, $S = 1/2$). The selection of the terminal multidentate ligand L_n is determined by the ability of the ligand to leave only one free position accessible to the cyanide Lewis base. It must form stable and redox inactive ML_n mononuclear complexes in solution and presents a steric configuration compatible with the formation of the polynuclear species. Commercially available polyamine molecules were adopted in the present study: the tris(2-amino)-ethylamine (tren) has been used as a tetradentate ligand since it gives stable copper(II) complexes with a trigonal bipyramidal geometry. In order to support the formation of complexes adopting a different geometry (square-based pyramid), while keeping the blocking effect, we have also involved a bidentate ligand: *N*,*N*-dimethylethylenediamine (Me_2en).

Despite their hazardous reactivity, perchlorate salts have been used because we were unable to get similar compounds with equivalent properties and good quality crystals with other counter anions.

Synthesis

All the polynuclear complexes, $[M(CN)_n(CNCuL)_{6-n}]^{m+}$ ($M = Cr^{III}$, Co^{III}, L = tren or Me_2en) have been synthesized according to the following method: the mononuclear species $[M'L(H_2O)]^{2+}$ is previously generated *in situ* by addition of the copper salt into an aqueous solution of the corresponding L_n ligand, before adding the hexacyanochromate(III) or hexacyanocobaltate(III) precursors. Following this strategy and modifying the synthetic parameters such as the nature of the

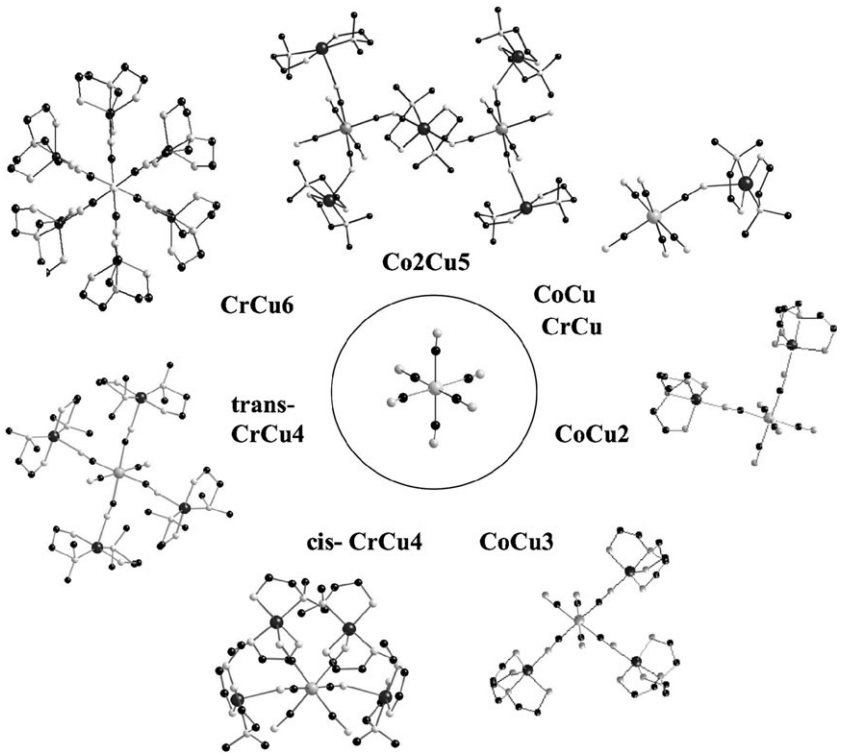

Fig. 1 Polynuclear chromium–copper and cobalt–copper complexes.

ligand, the counter anions and the stoichiometry, di-, tri-, tetra-, penta-, hexa- and hepta-nuclear complexes might be selectively obtained.

The syntheses of the dinuclear complexes, $[Cr(CN)_5\{CN–Cu(Me_2en)_2\}]^-$ and $[Co(CN)_5\{CN–Cu(Me_2en)_2\}]^-$, denoted **CrCu** and **CoCu**, respectively, have been performed with the hexacyanidometalate precursors and $[Cu(Me_2en)_2(H_2O)]^{2+}$ in stoichiometric amount, in the presence of the large tetraphenylphosphonium cation. This favours the selective crystallization of the large $[CrCu]^-$ and $[CoCu]^-$ anions. In such experimental condition, the formation of the dinuclear complex is induced whatever the nature of the ligand L around the copper. Thus, starting with the tren ligand, the corresponding **CrCu-tren** has been obtained as a powder. The dinuclear products are soluble in organic solvents such as dichloromethane, ethanol or acetonitrile.

The *cis*-trinuclear and the *mer*-tetranuclear complexes, $[Co(CN)_4\{CN–Cu(tren)\}_2]^+$ and $[Co(CN)_3\{CN–Cu(tren)\}_3]^{3+}$, briefly mentioned elsewhere,[8] have been obtained as co-crystallized species, denoted **CoCu2**/**CoCu3**. The reaction has been performed in water–acetonitrile solution by addition of the tren ligand to a copper perchlorate, forming *in situ* the mononuclear complex, before adding the $[Co(CN)_6]^{3-}$ precursor. In this reaction the stoichiometry plays an important role and the Cu : Co ratio must be smaller than 4 : 1, in order to avoid the formation of the heptanuclear **CoCu6** complex.

The pentanuclear complexes, *cis*-$[Cr(CN)_2\{CN–Cu(tren)\}_4]^{5+}$ and *trans*-$[Cr(CN)_2\{CN–Cu(tren)\}_4]^{5+}$ (denoted ***cis*-CrCu4** and ***trans*-CrCu4**, respectively) have been obtained using the bidentate ligand: *N*,*N*-dimethylethylenediamine (Me_2en). The reaction was performed in presence of the ligand and copper perchlorate, before adding the $[Cr(CN)_6]^{3-}$ precursor. Starting with a Cu : Cr ratio of 8 : 1, crystals with the co-crystallisation of the two isomers were first obtained, denoted **CrCu4**. Playing with the experimental conditions but without precise control of selectivity, we succeeded in getting the pure *trans* isomer of the pentanuclear compound, denoted ***trans*-CrCu4**.

In similar conditions, but starting with $[Co(CN)_6]^{3-}$ instead of the chromium precursor, a heptanuclear compound was obtained $[\{Co(CN)_6\}_2\{Cu(Me_2en)_2\}_5]^{4+}$, denoted **Co2Cu5**, in which one of the copper unit adopts a bridging position between two $CoCu_2$ fragments. The difference between hexacyanocobaltate and hexacyanochromate chemistry might be explained by a difference of solubility already mentioned elsewhere.[7–9]

The heptanuclear complexes $[M\{CN–Cu(tren)\}_6]^{9+}$, **CrCu6** and **CoCu6**, were obtained by a dropwise addition of a potassium hexacyanometalate(III) solution (Cr or Co) to the mononuclear copper(II) complex generated *in situ* from the ligand, tris(2-aminoethyl)amine (tren) and Cu^{II} perchlorate salt. Partial evaporation of the solvent leads to hexagonal blue crystals. As discussed previously,[7] the X-ray diffraction structure reveals not only the presence of the expected heptanuclear compound but also of a "contaminating" co-crystallized trinuclear complex $[tren(Cu(tren))_3]^{6+}$. The pure isolated **CrCu6** was also obtained as very thin platelets similar to those obtained for the cobalt centered analogue, **CoCu6** and the characterizations of the product are in good agreement with the expected structure.

Characterization

Infrared spectroscopy. The characterisation of the polynuclear complexes performed by IR spectroscopy indicates

clearly similarities between the samples. For all species, except for the **CrCu** and **CoCu** complexes, the distinctive bands of the perchlorate salts (1090 cm^{-1}) demonstrate the presence of positively charged complexes. The relative intensity of these bands gives accurate estimation on the total charge of the products varying from one (trinuclear), five (pentanuclear) up to nine counter ions for the heptanuclear complexes. For the **CoCu** and **CrCu** compounds, the presence of characteristic bands of the tetraphenylphosphonium confirms the negative charge of the target product. The 2000–2200 cm^{-1} range is characteristic of the antisymmetric stretching vibration of the free and bridging cyanido groups. **CoCu** exhibits a weak band at 2141 cm^{-1} relative to the bridging cyanide and a more intense one at 2122 cm^{-1} assigned to the free cyanides. Similarly, **CrCu** presents bands at 2131 and 2120 cm^{-1} and **CrCu-tren** bands at 2160 and 2131 cm^{-1}. For comparison, the corresponding values for the cyanide of the potassium salts of hexacyanochromate(III) and hexacyanocobaltate(III) anions are 2131 and 2130 cm^{-1}, respectively.[22]

The spectrum of the co-crystallized complexes $[Co(CN)_4\{(CN–Cu(tren)\}_2]^+/[Co(CN)_3\{(CN)Cu(tren)\}_3]^{3+}$, **CoCu2**/**CoCu3**, displays a band at 2162 cm^{-1} that is attributed to the bridging cyanido groups. Two other bands at 2126 and 2132 cm^{-1} are ascribed to the free cyanido ligands. Similar results have been obtained for the pentanuclear complexes $[Cr(CN)_2\{(CN)Cu(Me_2en)_2\}_4]^{5+}$, **CrCu4** and ***trans*-CrCu4**, with the characteristic antisymmetric stretching vibrations of the cyanide at 2150 and 2133 cm^{-1} and without differences between the two samples. Only one single band is visible on the spectrum of the heptanuclear complexes at 2181 and 2188 cm^{-1} for **CrCu6** and **CoCu6**, characteristic of unique bridging cyanido group. Concerning **Co2Cu5**, surprisingly, the infrared spectrum displays a unique ν_{CN} band at 2127 cm^{-1} without any differentiation between the cyanide ligands.

The comparison of the antisymmetric stretching vibration values of the bridging cyanido group for all the complexes suggests that the distortion of cyanido bridge is more important (i) in the species of low nuclearities compared to heptanuclear species and (ii) in the compounds where copper adopt a square-based pyramid geometry, compared to a trigonal bipyramid one, as confirmed by structural studies.

Structural studies. The X-ray crystallographic structures of the **CoCu6** and **CrCu6** complexes have been previously published.[7] Concerning, the trinuclear *cis* and the tetranuclear *mer* complexes, **CoCu2** and **CoCu3** as well as the pentanuclear complexes **CrCu4** and ***trans*-CrCu4**, up to now, no single crystals suitable for complete refining of the crystallographic structure are available. The data collected for these structures were of poor quality and for these reasons we have not deposited the coordinates for these structures. Nevertheless, the four products have been identified without ambiguity and the proposed structures are wholly consistent with the analytical, spectroscopic and magnetic data. The dinuclear compound, **CoCu**, as well as the heptanuclear complex, **Co2Cu5** have been fully characterised by single-crystal X-ray diffraction. For both samples, the resolution is good enough to determine the anisotropic thermal parameters for all non-hydrogen atoms.

The tetraphenylphosphonium salt of the **CoCu** complex crystallizes as parallelepipedic blue crystals (for the parameters see Table 1). In addition to the phosphorus, two heavy atoms are present in the asymmetric unit: the cobalt and the copper. The phosphorus is surrounded by four phenyl fragments of the tetraphenylarsonium cation which plays the role of the counter cation to balance the anionic charge of the heterometallic dimer. In the **CoCu** dinuclear unit (Fig. 2), the hexacyanocobaltate(III) fragment is slightly distorted compared to the potassium salt (mean Co–C distance = 1.89 Å; mean CN distance = 1.14 Å). One CN ligand bridges the unique copper ion present in the unit cell. The distances are in the range of other values published in the literature for cyano-bridged Co–Cu complexes[23–24] and in the other structures herein reported. The C–N–Cu angle (139.9°) deviates from linearity. The geometry around the copper ion is a square-based pyramid with Cu–N distances of 1.99 and 2.08 Å in the plane. The distance between the copper ion and the nitrogen in apical position (2.27 Å) is slightly longer, due to the Jahn–Teller distortion. The packing is formed by layers of dinuclear species separated by PPh_4 cations, with a distance of 12.7 Å between two adjacent layers.

The **CrCu** complex has been obtained as crystals and the unit cell parameters confirm the isostructurality with the cobalt centered analogue. The supposed molecular structures of **CoCu2** and **CoCu3** are presented in Fig. 3 and Fig. 4, respectively.

Concerning the **CrCu4** complexes (schematic views are presented in Fig. 5 and Fig. 6), the two isomers (*cis* and *trans*) have both been obtained and crystallise in different systems according to the experimental conditions. The compound **CrCu4** crystallises as blue needles in the orthorhombic system (a = 16.708, b = 17.572, c = 50.221 Å) whereas ***trans*-CrCu4** as blue parallelepipeds, belongs to the tetragonal system (a = 26.2975, b = 28.387 Å). For the compound **CrCu4**, six metallic atoms are present in the asymmetric unit: two chromium and four copper atoms that generate two molecules ***cis*-CrCu4** and ***trans*-CrCu4**. Five perchlorate ions allow the charge balance.

On the contrary, in the ***trans*-CrCu4** sample (tetragonal), three chromium atoms are located on elements of symmetry and generate, with only three copper atoms, three complete pentanuclear entities. The electroneutrality is assured by the presence of perchlorate ions.

The C–N–Cu angles vary apparently drastically from one entity to the other (from about 134.0 to 180.0°).

Concerning the **CrCu6** complex obtained as crystals (Fig. 7), the cell parameters are very unusual, especially the c value approaching 80 Å ($a = b$ = 15.169(5) Å and c = 77.305(17) Å). A trinuclear entity, $[tren(Cu(tren))_3]^{6+}$, Cu_3, is also present in the unit cell, in addition to the expected heptanuclear complex, with a $CrCu_6/Cu_3$ ratio of 1/2. Changing the experimental conditions, the **CrCu6** complex has also been obtained as thin platelets, isostructural to the **CoCu6** complex. The corresponding crystallographic structure indicates that only the heptanuclear entity is present in the unit cell, with nine perchlorate counter-ions, water and acetonitrile molecules. The metal–cyanide distances are in good agreement with the value published in the literature for analogous

Table 1 Crystallographic data of the polynuclear complexes **CoCu** and **Co2Cu5**

	CoCu	**Co2Cu5**
	$(PPh_4)[Co(CN)_5CNCu(Me_2en)_2]\cdot 7H_2O$	$[Co(CN)_6]_2[Cu(Me_2en)_2]_5(ClO_4)_4\cdot 4H_2O$
Chemical formula	$C_{38}H_{58}CoCuN_{10}O_7P$	$C_{52}H_{128}Co_2Cu_5Cl_4N_{32}O_{20}$
M_r	920.38	2099.22
Crystal shape	Needles	Parallelepiped
Crystal color	Blue	Blue
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	10.1341(8)	27.223(6)
b/Å	12.7726(13)	12.263(2)
c/Å	18.652(2)	28.284(4)
α/°	73.261(12)	90
β/°	81.953(8)	97.020(9)
γ/°	85.288(10)	90
V/Å^3	2287.0(4)	9371(3)
Z	2	4
No. data collected	22 252	69 094
No. unique data collected	10 479	13 591
No. data used in refinement[a]	10 479	13 591
R^b	0.0719	0.0644
$R_w{}^c$	0.1440	0.1136
No. variables	552	575
$\Delta\rho_{min}$/e Å^{-3}	−0.981	−1.137
$\Delta\rho_{max}$/e Å^{-3}	0.685	1.724

[a] Data with $F_o^2 > 2\sigma(F_o)^2$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

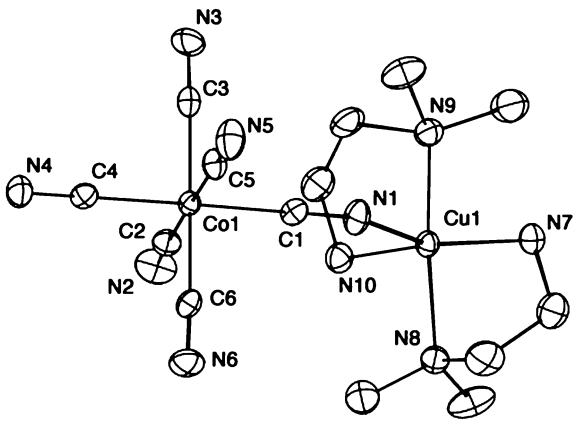

Fig. 2 X-Ray crystal structure of the $[Co(CN)_5\{CNCu(Me_2en)_2\}]^-$ entity in **CoCu** (thermal ellipsoids set at the 50% probability level).

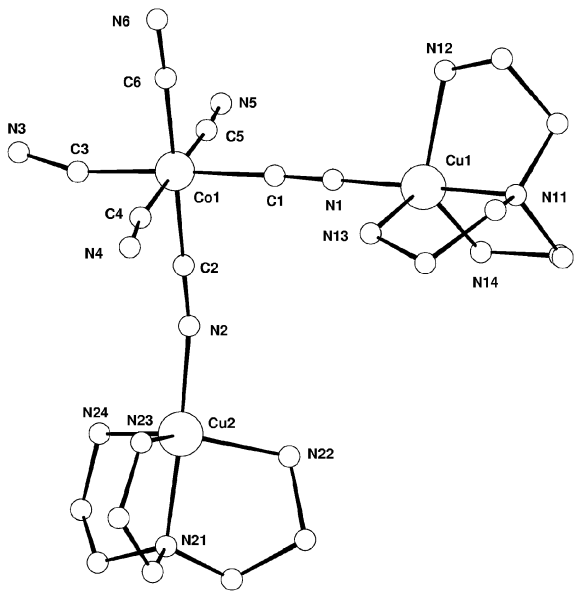

Fig. 3 Supposed structure of the $[Co(CN)_4\{(CN)Cu(tren)\}_2]^+$ entity in **CoCu2**/**CoCu3**.

compounds.[25–28] In both cases, the copper atom is in a trigonal bipyramid geometry, the cobalt or chromium atoms are in a octahedral surrounding and the cyano bridge is close to linearity with a C–N–Cu angles equal to 175.7° in **CoCu6** and 178.7° in **CrCu6**. The crystallographic structures of the **CrCu6** and **CoCu6** structures (trigonal, $R\bar{3}$) have been fully described elsewhere.[7]

The characterization by single-crystal X-ray diffraction of the **Co2Cu5** complex (Fig. 8) reveals that the system crystallizes in the monoclinic system, space group $C2/c$. One cobalt and three copper ions, associated with their respective ligands (cyanide and Me_2en) and two perchlorates anions are present in the asymmetric unit corresponding to 63 non-hydrogen atoms. The $[\{Co(CN)_6\}_2\{Cu(Me_2en)_2\}_5]^{4+}$ entity is formed by a copper atom, adopting an elongated octahedral geometry (d_{Cu-N} = 2.568 Å), located on an inversion center, playing the role of a bridge between two CoCu2 entities. The geometry of the four peripheric copper ions is described as a square-based pyramid geometry (C_{4v}). The cyano bridge appears distorted with Co–C–N angles of 176.9–177.6° and the C–N–Cu angles in the range of 131.8–134.7°. Weak interaction appears between two adjacent molecules, separated from each other by the four perchlorate ions (the shortest inter-metallic Co–Co, Co–Cu and Cu–Cu inter-chain distance are 8.9 Å, 5.3 Å and 7.0 Å, respectively). The complex might be viewed as a rare example[29] of a dendritic coordination complex made with a core (the central copper atom) and polynuclear branches (CoCu2).

EPR studies. Among all experimental techniques (optical, magnetic, *etc.*..) used to study magnetic materials, electron

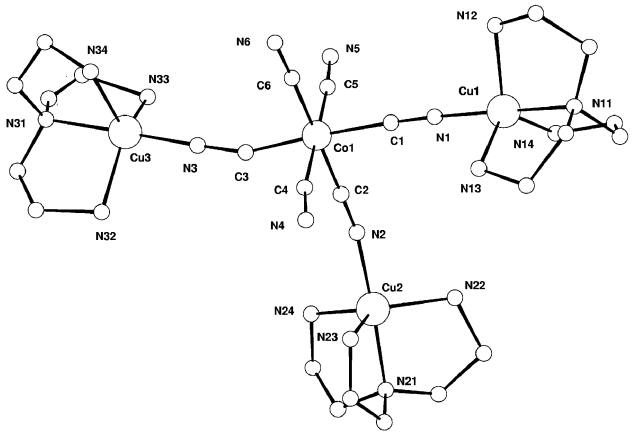

Fig. 4 Supposed structure of the $[Co(CN)_3\{(CN)Cu(tren)\}_3]^{3+}$ entity in **CoCu2**/**CoCu3**.

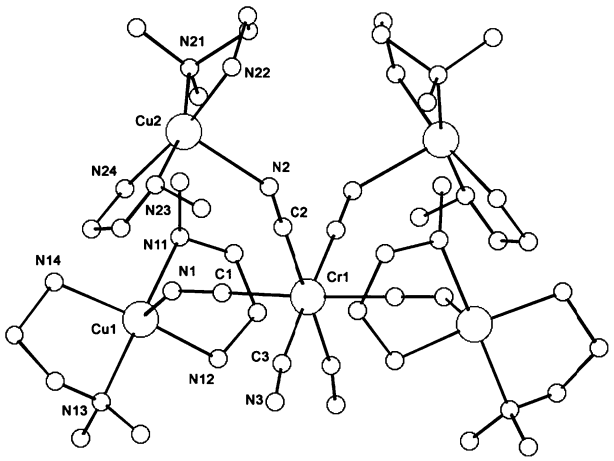

Fig. 5 Supposed structure of the *cis*-$[Cr(CN)_2\{(CN)Cu(Me_2en)_2\}_4]^{5+}$ entity in ***cis*-CrCu4**.

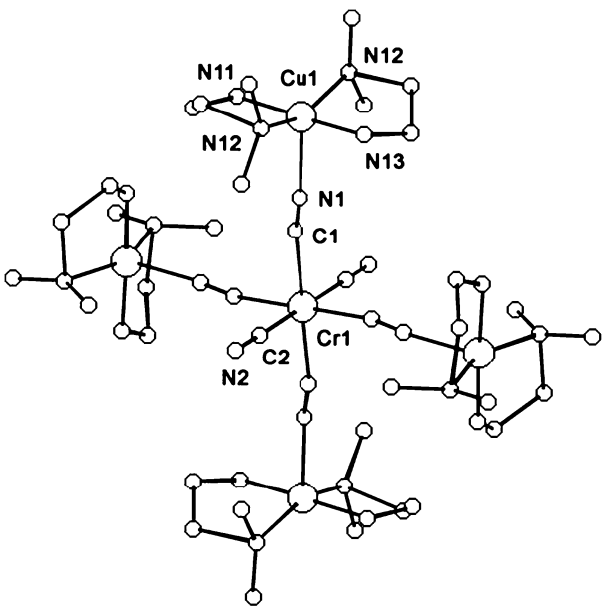

Fig. 6 Supposed structure of the *trans*-$[Cr(CN)_2\{(CN)Cu(Me_2en)_2\}_4]^{5+}$ entity in ***trans*-CrCu4**.

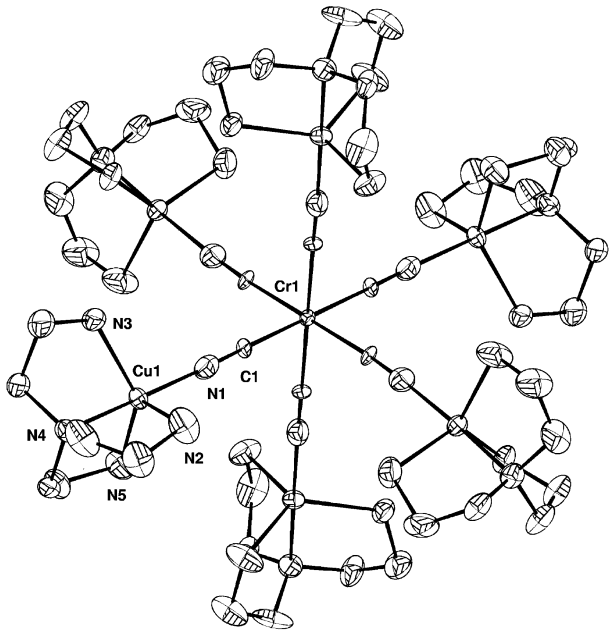

Fig. 7 X-Ray crystal structure of the $[Cr\{CN–Cu(tren)\}_6]^{9+}$ entity in **CrCu6**.

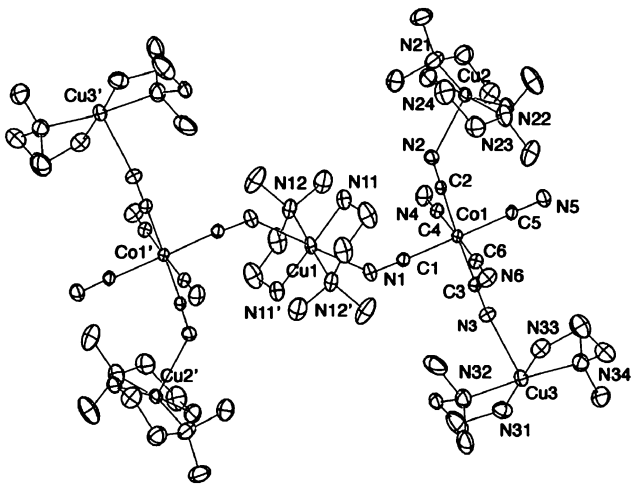

Fig. 8 X-Ray crystal structure of the $[\{Co(CN)_6\}_2\{Cu(Me_2en)_2\}_5]^{4+}$ entity in **Co2Cu5** (thermal ellipsoids set at the 50% probability level). Symmetry transformation used to generate equivalent atoms ($'$): $1/2 - x, 1/2 - y, -z$.

paramagnetic resonance, EPR, is of particular interest, owing to its sensitivity to both the magnetic state of the spin-changing ion and the crystalline structure of the compound. A brief study has been done on the dinuclear **CoCu** complex in order to have reference data for the photomagnetic compounds (and especially MoCu6 and MoCu4 complexes whose EPR spectra will be fully described elsewhere).[30] Additional data were collected for the heptanuclar **CoCu6** complexes. The choice of these two compounds is justified by the two different geometries around the copper atoms: square-based pyramid and trigonal bipyramid, respectively.

Concerning the **CoCu** prepared with Me_2en ligand, EPR measurements were performed at room temperature at X-band

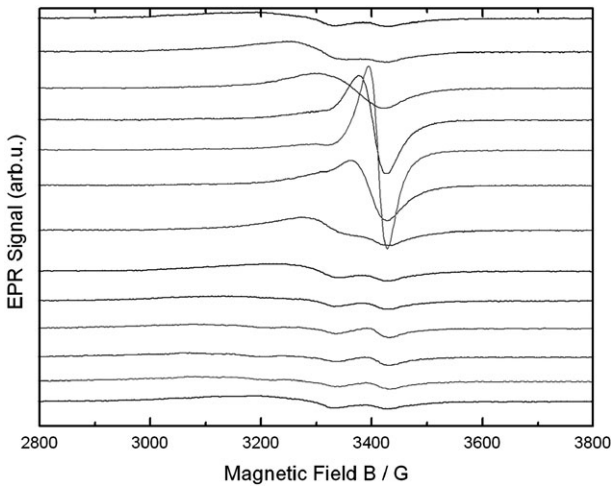

Fig. 9 EPR spectra of **CoCu** measured at room temperature for different orientations of the crystal in the magnetic field. The angle between the sample and the magnetic field is incremented by 15° from one spectrum to the other.

frequency using a Bruker ESR 300 spectrometer. A single millimetre-sized crystal presenting well-developed crystallographic facets was chosen in order to study an angular variation of the EPR signal.

Fig. 9 presents the spectra measured for different orientations of the sample in the magnetic field. The spectra are well fitted by a single anisotropic quadruplet simulated by four individual Lorentzian lines with a variable splitting. The position and splitting of the quadruplet lines depend on the crystal orientation and the four lines are cumulating at the same resonance field when the magnetic field is normal to the sample. This spectrum is attributed to isolated Cu^{2+} ions in a planar geometry, with nearly axial g tensor of $g_{zz} \approx 2.015$ and $g_{xx} \approx g_{yy} \approx 2.05$. The quadruplet arises from the anisotropic hyperfine interaction of the electronic spin $S = 1/2$ with the spin $I = 3/2$ of the copper nucleus.

The anisotropy of the spectrum shows the good crystallinity of the sample at the millimetre scale. There is no evidence for other, non-magnetically equivalent, Cu^{2+}.

Similar studies have been done on **CoCu6** viewed as a reference compound for the trigonal-bipyramidal copper complexes of the tetradentate tripodal nitrogen donor ligands, tris(2-aminoethyl)amine (tren). An EPR spectrum similar to the one already published in the literature shows that the copper complex has a ground state with a d_{z^2} unpaired electron orbital, and that it is distorted from a trigonal symmetry. This spectrum is attributed to isolated Cu^{2+} ions in a trigonal-bipyramid geometry, with axial g tensor of $g \approx 2.09$. The values are in agreement with those obtained for similar compounds already described in the literature.[31]

Magnetic properties. The magnetic studies, performed for most of the polynuclear complexes described above are discussed below. After the description of the magnetic properties of the complexes obtained with the diamagnetic hexacyanocobaltate(III), a specific attention will be paid to the polynuclear $CrCu_x$ species ($x = 1, 4, 6$) prepared from the paramagnetic $[Cr^{III}(CN)_6]^{3-}$ core.

The magnetic properties of the dinuclear **CoCu** compound, $[Co(CN)_5\{CN–Cu(Me_2en)_2\}]^-$, is in agreement for a paramagnetic species ($S = 1/2$) without anisotropy. The $\chi_M T$ product (χ_M being the magnetic susceptibility) is constant from high temperature to 4 K and then decreased continuously. The value of $\chi_M T$ (0.41 $cm^3\ mol^{-1}$ K) is higher than that calculated for an isolated $S = 1/2$ and $g = 2$ ($\chi_M T = 0.375\ cm^3\ mol^{-1}$ K). The electronic aspects of anisotropy of the mononuclear complexes, extracted from the magnetization measurements are compared to EPR data reported above (*vide supra*).

Concerning the **CoCu2**/**CoCu3** complexes, the thermal dependence of $\chi_M T$ is characteristic of a paramagnetic species. $\chi_M T$ is constant with an experimental value of 1.07 $cm^3\ mol^{-1}$ K in agreement with 2.5 isolated copper(II) metallic ions (per single cobalt ion) (the expected value is 1.01 $cm^3\ mol^{-1}$ K for 2.5 separated spin 1/2 and $g = 2.15$). At low temperature, below 30 K, the $\chi_M T$ curve decreases continuously indicating either intra- and/or inter-molecular antiferromagnetic interactions between the spin carriers. The best fit has been obtained with $J = -0.48\ cm^{-1}$ and $g = 2.15$ with an agreement factor $R = 9.6 \times 10^{-6}$ (the distinction between *cis* and *trans* CN–Co–CN bridges has not been taken into consideration).

The magnetic properties of the **Co2Cu5** compound, are consistent with that of five independent Cu(II) (d^9, $S = 1/2$) as expected from the presence of the diamagnetic Co(III) centres surrounded by paramagnetic metallic cations. The $\chi_M T$ product remains constant (1.97 $cm^3\ mol^{-1}$ K down to 30 K) in agreement with isolated Cu(II) ions (well comparing with the expected value of 1.968 $cm^3\ mol^{-1}$ K calculated for five independent spin 1/2 and $g = 2.1$). Below 30 K, the decrease of the $\chi_M T$ product is indicative of either intra- and/or inter-molecular antiferromagnetic interactions between the spin carriers. The exchange coupling value has been estimated to be $J = -0.33\ cm^{-1}$.

For the **CoCu6** compound, the thermal dependence of $\chi_M T$ is characteristic of a paramagnetic species. $\chi_M T$ is constant with an experimental value of 2.33 $cm^3\ mol^{-1}$ K in agreement with six isolated copper(II) metallic ions (2.36 for six independent spin 1/2 and $g = 2.1$). At low temperature, below 40 K, the $\chi_M T$ curve decreases indicating inter- or intramolecular antiferromagnetic interactions between the spin carriers. The value reached at 2 K is 1.14 $cm^3\ mol^{-1}$ K and would extend to zero at lower temperature.

The magnetic studies of the hexacyanocobaltate(III) derivatives allow the evaluation of the next nearest neighbour Cu^{II}–Cu^{II} interaction, through the long diamagnetic NC–Co–CN bridge (about 10 Å). The antiferromagnetic intramolecular interactions in **CoCu2**/**CoCu3** and **Co2Cu5** (−0.48 and −0.33 cm^{-1}, respectively) are smaller than that obtained for the **CoCu6** complex ($J = -0.85\ cm^{-1}$), the difference between the coupling constants being due to the different values of the C–N–Cu angle.[9]

The $\chi_M T$ *vs.* T data recorded for the four complexes, **CoCu**, **CoCu2**/**CoCu3**, **Co2Cu5** and **CoCu6** are in agreement with 1, 2.5, 5 and 6 isolated copper ions, respectively and $g \approx 2.15$. Similar results are noticed on the first magnetization curve at 2 K with four series of data corresponding to isolated copper ions ranging from one to six according the nuclearity of the compounds (Fig. 10).

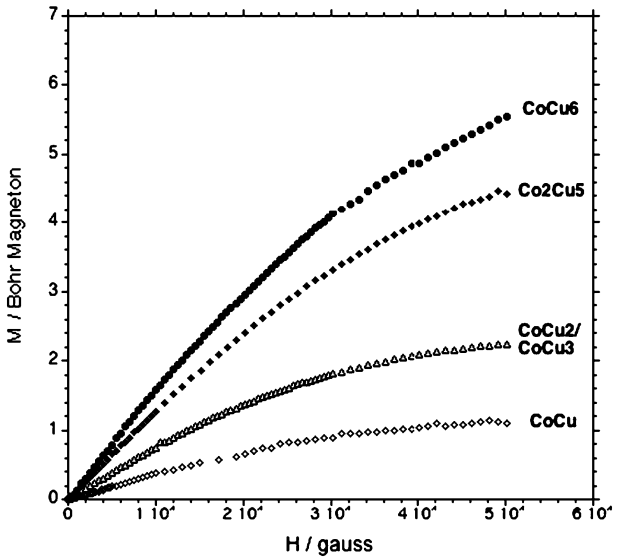

Fig. 10 Field dependence of the magnetization at 2 K for **CoCu** (◇), **CoCu2**/**CoCu3** (△), **Co2Cu5** (◆) and **CoCu6** (●).

The magnetic properties of the chromium centred complexes have been carried out and lead to the following results.

Concerning the **CrCu** compound, the $\chi_M T$ product decreases continuously when cooling down from room to low temperature. The value of $\chi_M T$ at 300 K is 2.08 $cm^3\ mol^{-1}$ K (smaller than expected for two magnetically isolated spins: 2.25 $cm^3\ mol^{-1}$ K with $g = 2.0$) and it becomes 1.56 $cm^3\ mol^{-1}$ K at 2 K. All these features are consistent with the occurrence of a weak antiferromagnetic exchange coupling between the chromium(III) and the copper(II) ions, the low-lying spin state being $S = 1$. The results is quite unusual and not in agreement with the Kahn's model of exchange between localized electrons that predict ferromagnetic interaction between Cr(III) and Cu(II) through a cyanide bridge. Taking into consideration that the magnetic orbitals (singly occupied molecular orbitals) of the spin carriers, Cr(III) (t_{2g}) and Cu(II) (d_{z^2} orbital, e_g local symmetry), are orthogonal, the model predicts that the exchange interaction should be ferromagnetic. Apparently, this is not the case in the **CrCu** compound, probably due to the strong distortion of the cyano bridge that has been observed in the X-ray structure description. Cyano-bridged chromium copper compounds exhibiting antiferromagnetic interaction are rare in the literature, but they exist.[26] Least-squares fitting of the susceptibility data by an analytical expression derived from the Hamiltonian $H = -JS_A \cdot S_B$ ($S_A = 3/2$, $S_B = 1/2$) and the van Vleck relation leads to $J = -2.5\ cm^{-1}$ and $g = 2.1$.

For the **CrCu4** complexes, the ground state spin value would be $S = 7/2$ in case of ferromagnetic interaction or $S = 1/2$ in case of antiferromagnetic interaction. The results that have been experimentally obtained on the **CrCu4** sample indicate apparently co-existence of the two magnetic behaviours. We suggest that the magnetic properties are complicated by the presence of the two isomers in the **CrCu4** sample. Similarly the magnetic properties of the *trans*-**CrCu4** isomer do not give good evidence of ferro- or antiferromagnetic interaction between the spin carriers. This is probably due to the presence of three different molecules present in the unit cell with different angle values.

The $\chi_M T$ value of the pure **CrCu6** complex (without contaminating trinuclear complex) increases continuously from room temperature to 2 K. This is consistent with a ferromagnetic interaction between the Cr^{III} and the Cu^{II} ions, in agreement with the orthogonality of the Cr^{III} $(t_{2g})^3$ and the Cu^{II} (a_{1g}) singly occupied orbitals, as predicted by Kahn's model. The value of $\chi_M T$ at 300 K is 5.4 $cm^3\ mol^{-1}$ K (significantly higher than what is expected for the magnetically isolated spins: 4.125 $cm^3\ mol^{-1}$ K with $g = 2$). At temperatures below 15 K, $\chi_M T$ reaches a plateau and becomes 12.3 $cm^3\ mol^{-1}$ K which is the expected value for $S = 9/2$ (12.375 $cm^3\ mol^{-1}$ K, $g = 2$). The $\chi_M T$ experimental data were fitted to the analytical expression using the spin hamiltonian $H = -J_{Cr/Cu} S_{Cr} \cdot \sum_i S_{Cu}$ (i ranging from 1 to 6) and including a mean field correction zJ' for intermolecular interaction (z being the number of neighbors). The intramolecular interaction between the next-nearest neighbor Cu^{II} cations is neglected and the ground state zero field splitting, D, expected to be zero. With an agreement factor $R = 1.1 \times 10^{-3}$, the best-fit values give an exchange coupling value $J = +45.8\ cm^{-1}$, a Lande factor, $g = 1.99$, an intermolecular interaction $zJ' = 1.5 \times 10^{-3}\ cm^{-1}$ and $D \approx 0\ cm^{-1}$. The J value is high compared to exchange coupling in the other heterodimetallic μ-cyano species.

The magnetization as a function of the applied magnetic field, at 2 K, for the chromium centered species, is reported in Fig. 11. For the dinuclear **CrCu** compound, the saturation value is 2.198, in good agreement with an $S = 1$ ground state. The data obtained for **CrCu4** at 5 Tesla is 5.1 μ_B that corresponds to an intermediate value between the calculated Brillouin functions for $S = 7/2$ (ferromagnetic interaction) and $S = 1/2$ (antiferromagnetic interaction). For the heptanuclear complex, **CrCu6** the data shows a value close to saturation at 9 μ_B and gives a further demonstration of the ground spin state, $S = 9/2$. The good agreement of the data with the computed Brillouin function for a spin $S = 9/2$ shows that the ground state is the only one populated at $T = 2$ K.

As already observed in chromium–nickel complexes,[9] it can be noted that J decreases both on closing the bridging angles and on decreasing the metal–metal distance. In the chromium–copper compounds herein described or already reported in the literature, the magnetic exchange coupling is mediated by the ligand and is therefore affected by the bridging angles (Cr^{III}–C–N and C–N–Cu^{II}). The two angles control the overlap between the two magnetic orbitals centered on chromium and copper and the delocalisation of the spin density on the nitrogen atom.

The geometry around the copper complex plays also an important role on the magnetic exchange interaction.[21] The negligible coupling found in the model with square-based pyramidal coordination (C_{4v}) around the copper atoms compared to those obtained when adopting trigonal bipyramidal coordination (D_{3h}) can be easily rationalized using MO-based arguments as already published in the literature. When distorting the trigonal-bipyramidal environment to that of a square-based pyramid, the d orbital on the copper atom bearing the unpaired electron changes its character gradually

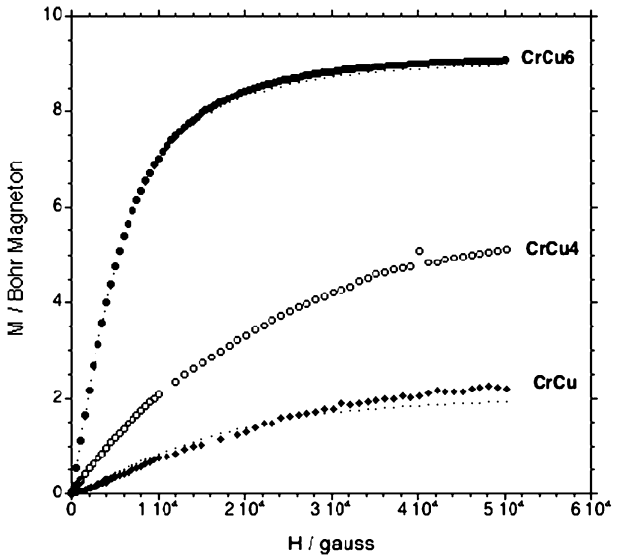

Fig. 11 Field dependence of the magnetization at 2 K for **CrCu** (◆), **CrCu4** (○) and **CrCu6** (●); the dotted lines correspond to the Brillouin functions for $S = 1$ and $S = 9/2$.

from d_{z^2}-type to $d_{x^2-y^2}$-type. The δ-type symmetry of the $d_{x^2-y^2}$ orbitals with respect to the Cr–Cu axis does not allow interaction with the orbitals of the cyanide bridge, and hence, according to the model, the ferromagnetic contribution to J becomes negligible.

Combining these three parameters (angle, distance and geometry), it seems possible to predict that chromium–copper complexes could present, *via* the cyanide ligand, not only strong ferromagnetic interaction between the spin carriers, as predicted by models, but in specific conditions, weak antiferromagnetic interaction. The **CrCu** dinuclear complex and the ***cis*-CrCu4**, herein described are probably two of such examples. The linear plot of the exchange coupling constant as a function of the N–C–Cu angle allows to determine that the maximum J value might be expected for strict orthogonality ($J_{max} = +48$ cm^{-1}) and to predict that below 140° an antiferromagnetic interaction will occur.

Conclusion

Starting with an hexacyanometalate precursor, nine different polynuclear complexes with various geometries should be obtainable associated to the corresponding pseudo-symmetry: dinuclear ($D_{\infty h}$), trinuclear-*cis* (C_{2v}), trinuclear-*trans* ($D_{\infty h}$), tetranuclear-*fac* (C_{3v}), tetranuclear-*mer* (C_{2v}), pentanuclear-*cis* (C_{2v}), pentanuclear-*trans* (D_{4h}), hexanuclear (C_{4v}) and heptanuclear (O_h) complexes. Modifying synthetic parameters, it has been possible to synthesize all of them: some have been already published,[7–9] the others have been described in the present paper. In addition to the complete family of the polynuclear complexes, the cobalt–copper and chromium copper complexes are viewed as interesting species for additional studies. We provided new examples of coordination compounds showing varying degrees of magnetic coupling, with possible relevance to other areas of molecular materials. Following a similar strategy, it should be possible to obtain a large family of polynuclear photoswichable MoCu complexes. Taking into account the magnetic properties of chromium–copper complexes in which ferro- or antiferromagnetic interaction might occur, it is possible to explain most of the corresponding photomagnetic properties. This has been already done and will be published elsewhere. In addition, with hexacyanometalate and copper precursors, we have demonstrated the feasibility to obtain a large amount of compounds with control of the structural anisotropy. With free cyanide ligands, most of the compounds herein described might be viewed as promising building blocks for the design of heterotrimetallic compounds or dendritic architectures.

Experimental

Chemicals

$K_3[Cr(CN_6)]$ was synthesised using the literature methods.[32] All other reagents were purchased as reagent grade chemicals and used without further purification. All solvents were of analytical grade quality. **CAUTION**: Perchlorate salts are potentially explosive and should be handled with care. Cyanide salts should not come into contact with acid, to avoid the formation of highly toxic hydrogen cyanide gas. The synthesis of the heptanuclear complexes **CoCu6** and **CrCu6** have been published elsewhere.[7]

Syntheses

$[PPh_4][Cr(CN)_5\{CNCu(Me_2en)_2\}]$, CrCu. To a solution of Me_2en (88 mg, 1 mmol) in water (20 ml) was added a solution of copper perchlorate (0.111 g, 0.3 mmol, in water–methanol, 1 : 1, 10 ml). The mixture was stirred for 20 min before adding hexacyanochromate potassium salt (97.6 g, 0.3 mmol) dissolved in a minimum of water. The solution was left standing for a few days in the presence of 553 mg of tetraphenylphosphonium chloride leading to blue crystals; 35% yield. Anal. calc. for $[C_{38}H_{40}N_{10}CrCuP](H_2O)_7$: C, 50.19, H, 5.99; N, 15.40; Cr, 5.72; Cu, 6.99; P, 3.41. Found: C, 55.67/55.48, H, 4.92/5.29; N, 9.47; Cr, 2.56; Cu, 4.47; P, 4.90%. IR spectrum (KBr, cm^{-1}) 2131 and 2120 (CN). X-Ray diffraction: Chemical formula: $C_{38}H_{54}N_{10}CrCuPO_7$, $M = 909.43$, crystal system: triclinic, space group = $P\bar{1}$, $a = 10.506$, $b = 12.326$, $c = 18.204$ Å, $\alpha = 89.98$, $\beta = 89.98$, $\gamma = 67.53°$, $V = 2178.42$ Å^3, $Z = 2$.

$[APh_4][Cr(CN)_5(CNCu(tren))]$ (A = As or P), CrCu-tren. Analogous complexes have been obtained with the tren ligand in presence of $AsPh_4Cl$ or PPh_4Cl following a similar procedure: 30% yield. Anal. calc. for $[C_{42}H_{32}N_{10}CrCuAs](H_2O)_7$: C, 50.78, H, 4.67; N, 14.10; Cr, 5.23; Cu, 6.40; As, 7.54%. Found: C, 51.69, H, 4.92/4.42; N, 9.41; Cr, 2.39; Cu, 4.20; As, 11.22. IR spectrum (KBr, cm^{-1}) 2160 and 2122 (CN).

Anal. calc. for $[C_{42}H_{32}N_{10}CrCuP](H_2O)_7$: C, 53.13, H, 4.88; N, 14.75; Cr, 5.48; Cu, 6.69; P, 3.26. Found: C, 55.67 or 55.48, H, 4.92 or 5.29; N, 9.47; Cr, 2.56; Cu, 4.47; P, 4.90%. IR spectrum (KBr, cm^{-1}) 2162 and 2122 (CN).

$[Co(CN)_4\{CNCu(tren)\}_2][Co(CN)_3\{CNCu(tren)\}_3](ClO_4)_4$, CoCu2/CoCu3. The details of the synthesis have been already published.[8] IR (KBr): 2126, 2132 and 2162 cm^{-1} (ν_{as}(CN)).

Anal. calc. for $C_{42}H_{98}Co_2Cu_5N_{32}Cl_4O_{20}$: C 25.89, H 5.07, N 23.00, Co 6.05, Cu 16.30, Cl 7.28; found: C 22.97, H 4.37, N 21.10, Co 5.48, Cu 14.52, Cl 8.66%. X-Ray diffraction: chemical formula: $C_{42}H_{98}Co_2Cu_5N_{32}Cl_4O_{20}$, M = 5106.36, crystal system: monoclinic, a = 8.269(3), b = 45.351(5), c = 12.200(2) Å, β = 95.3°, V = 4556(2) Å^3.

{*cis*-[Cr(CN)$_2${CNCu(Me$_2$en)$_2$}$_4$]}/{*trans*-[Cr(CN)$_2${CNCu-(Me$_2$en)$_2$}$_4$]}(ClO$_4$)$_{10}$, CrCu4. A solution of copper perchlorate (0.889 g, 2.4 mmol) in water–acetonitrile (1 : 1, 10 mL) was added to a solution of Me$_2$en (0.423 g, 4.8 mmol) in 10 mL of the same mixture. The purple solution was stirred for 10 min before adding potassium hexacyanochromate(III) (195.2 g, 0.6 mmol) dissolved in 5 mL of water. The blue solution was stirred for 10 min before filtering and the filtrate was allowed to stand for a week before collecting blue crystals.

Yield = 25%; IR (KBr): 2150 and 2133 cm^{-1}. Anal. calc. for [Cr(CN)$_2${CNCu(N$_2$C$_4$H$_{12}$)$_2$}$_4$](ClO$_4$)$_5$·2H$_2$O: C 27.12, H 5.87, N 18.31, Cr 3.09, Cu 15.10, Cl 10.53; calc. for [Cr(CN)$_2${CNCu(N$_2$C$_4$H$_{12}$)$_2$}$_4$](ClO$_4$)$_5$·4H$_2$O·KClO$_4$: C 22.66, H 5.21, N 15.30, Cr 2.58, Cu 12.62, Cl 12.32; found: C 22.69, H 4.78, N 15.74, Cr 2.24, Cu 11.27, Cl 11.48%. X-Ray structure: orthorhombic, a = 16.708(10), b = 17.572(10), c = 50.221(10) Å, V = 14744(10) Å^3.

[Cr(CN)$_2${CNCu(Me$_2$en)$_2$}$_4$](ClO$_4$)$_4$, *trans*-CrCu4. A solution of copper perchlorate (0.889 g, 2.4 mmol) in water–acetonitrile (1 : 1, 20 mL) was added to a solution of Me$_2$en (0.423 g, 4.8 mmol) in 10 mL of the same mixture. The purple solution was stirred for 5 min before adding potassium hexacyanochromate(III) (97.6 mg, 0.3 mmol) dissolved in 10 mL of water. The blue solution was stirred for 10 min before filtering and the filtrate was allowed to stand for a week before collecting blue crystals.

Yield = 30%; IR (KBr): 2150 and 2133 cm^{-1}. Anal. calc. for [Cr(CN)$_2${CNCu(N$_2$C$_4$H$_{12}$)$_2$}$_4$](ClO$_4$)$_5$·2H$_2$O: C 27.12, H 5.87, N 18.31, Cr 3.09, Cu 15.10, Cl 10.53; found: C 22.69, H 4.78, N 15.74, Cr 2.24, Cu 11.27, Cl 11.48%. X-Ray structure: tetragonal, a = b = 26.297, c = 28.387 Å, V = 19630 Å^3.

[{Co(CN)$_6$}$_2${Cu(Me$_2$en)$_2$}$_5$](ClO$_4$)$_4$, Co2Cu5. A solution of copper perchlorate hexahydrate (1.296 g , 3.5 mmol) in water–acetonitrile (1 : 1, 10 mL) was added to a solution of Me$_2$en (0771 g, 8.75 mmol) in water–acetonitrile (1 : 1, 10 mL). The purple solution is stirred for 10 min before adding K$_3$[Co(CN)$_6$] (0.166 g, 0.5 mmol) dissolved in 10 mL of water. The resulting blue solution was allowed to stand for a couple of days before collecting blue crystals. Yield = 24%.

Anal. calc. for Co$_2$(CN)$_{12}${Cu(N$_2$C$_4$H$_{12}$)$_2$}$_5$(ClO$_4$)$_4$(H$_2$O)$_4$: C 29.75, H 6.15, N 21.35, Co 5.61, Cu 15.14, Cl 6.76. Found: C 29.57, H 5.75, N 21.06, Co 5.61, Cu 14.04, Cl 7.01%. IR (KBr) 2127 cm^{-1} (CN asymmetric stretching). X-Ray diffraction: chemical formula: $C_{52}H_{128}Co_2Cu_5Cl_4N_{32}O_{20}$, M = 2099.22, crystal system: monoclinic, space group = $C2/c$, a = 27.223(6), b = 12.263(2), c = 28.284(4) Å, β = 97.020(9)°, V = 9371(3) Å^3, Z = 4; R (R_w), 6.44 (11.36%).

Physical characterisations

IR spectra were obtained between 4000 and 250 cm^{-1} on a Bio-Rad FTS 165 FT-IR spectrometer on KBr pellets. DC magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer equipped with a 5 T magnet and operating in the range of temperature from 2 to 400 K. The powdered samples (10 ± 50 mg) were placed in a diamagnetic sample holder and the measurements realised in a 200 Oe applied field using the extraction technique. Before analysis, the experimental susceptibility was corrected from diamagnetism using Pascal's constants[1] and from temperature independent paramagnetism (TIP) of the transition metals. The EPR measurements were performed on a single crystal with a standard X-band spectrometer and a 4–300 K variable-temperature cryostat under irradiation. EPR measurements were performed with a Bruker ESP 300 spectrometer, at X-band frequency (9.5 GHz). The magnetic field modulation frequency was set at 100 kHz and the modulation amplitude and the microwave power were both adjusted to avoid saturation. The spectra were measured at temperatures between 4 and 300 K.

Crystallographic studies

Suitable crystals for X-ray crystallography were directly obtained from the reaction medium or by recrystallization from water–acetonitrile solution.

For **Co2Cu5**, a single crystal of the compound was selected rapidly, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Unit-cell parameters determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs.[33] The structure was solved by direct methods using the SIR-92 program[34] and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, 1997). For the other structures, herein described, accurate cell dimensions and orientation matrix were obtained by least-square refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromatic Mo-Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collections. Absorption corrections were applied using Ψ-scan method. Computation was performed by the PC version of Crystals.[35] Scattering factors and corrections for anomalous dispersion were taken from Cromer.[36] The structures were solved with SHELXS 86[37] followed by Fourier maps technique and refined by full-matrix least squares with anisotropic thermal parameters for all non hydrogen atoms. Crystallographic data and details of the refinement are reported in Table 1.

CCDC 719843 (**CoCu**) and 719593 (**Co2Cu5**) contain the supplementary crystallographic data for this paper. Details of the **CoCu6** and **CrCu6** structures have already been published and the structures are in the Cambridge Structural Database (CSD) as refcodes GACLAY and GACKAX, respectively.

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