Multidimensional Cyanide-Bridged Heterometallic Fe^{II}–Cu^{I} and Homometallic Cu^{I} Coordination Polymers from Solvothermal Reactions Involving either $K_3[Fe(CN)_6]$ or KCN as the Source of Cyanide Anions

Enrique Colacio,*[a] Ahderrahmane Debdoubi,[b] Raikko Kivekäs,[c] and Antonio Rodríguez[a]

Keywords: Coordination polymers / Copper / Cyanides / Heterometallic complexes / Solvothermal synthesis

The reaction between $K_3[Fe(CN)_6]$, $CuCl_2·2H_2O$ and 1,10-phenanthroline (phen) under hydrothermal conditions gives rise to the formation of the 3D cyanide-bridged heterometallic Fe^{II}–Cu^{I} complex $[Fe(CN)_4(phen)_2Cu_2]$ (**1**). Its 3D network structure is constructed from two types of fused cyanide-bridged 10- and 14-metal-membered centrosymmetric rings (Fe_2Cu_8 and Fe_2Cu_{12}), which are defined by the general sequences $\{(Cu^{I})_4\text{-}Fe^{II}\text{-}(Cu^{I})_4\text{-}Fe^{II}\}$ and $\{(Cu^{I})_6\text{-}Fe^{II}\text{-}(Cu^{I})_6\text{-}Fe^{II}\}$, respectively. The copper(I) and iron(II) atoms exhibit distorted triangular planar and distorted octahedral coordination environments, respectively. Complex **1** is the first example of a 3D cyanide-bridged bimetallic complex prepared by hydrothermal methods. The use of methanol as solvent, KCN as source of cyanide anions and 2,2′,6,6′-bipyrimidine as the bridging ligand results in the isolation of the 2D homometallic copper(I) complex $[Cu_2(CN)_2(bpym)]·H_2O$ (**2**). Its structure consists of neutral 2D (6,3) honeycomb layers in the *ab* plane made of fused $Cu_6(CN)_4(bpym)_2$ rings, in which the copper(I) atoms exhibit a distorted tetrahedral geometry. The layers are interdigitated in such a way that the bpym ligands lie above and below the ring cavities of neighbouring networks, with an ABCD repeat sequence of layers. Water molecules are located in the free space between the A/D and B/C layers. Under the same conditions as used for **1**, but with 4-methyl-2,2′,6,6′-bipyrimidine 2-oxide instead of phen, the 3D complex $[Cu_2(CN)_2(mbpym]$ (**3**) was obtained (mbpym = 4-methyl-2,2′,6,6′-bipyrimidine). During the reaction the oxygen atom of the *N*-oxide group is eliminated and the novel ligand mpym formed. Its structure consists of distorted tetrahedral copper(I) atoms connected by cyanide and mpym bridging ligands to give rise to a 3D chiral network.

Introduction

Research on multidimensional polymetallic coordination polymers is currently of great interest because of their fascinating structural diversity and potential applications as functional materials in fields such as electrical conductivity, molecule-based magnets, molecular absorption, ion-exchange, heterogeneous catalysis, etc.[1] Among these materials, cyanide-bridged bimetallic complexes deserve special attention as they exhibit, among others, interesting electrochemical, zeolitic, magnetic and photomagnetic properties.[2] These compounds can be prepared either by assembling cyanometallates and metal complexes or by multicomponent self-assembly of cyanide, metal ions and multidentate ligands. Although the majority of these systems are still being prepared by conventional solution routes, attention has recently turned to solvothermal techniques. In this regard, we and others have recently reported homo- and heterometallic cyanide-bridged complexes, which were assembled through hydrothermal reactions with azine and diazine ligands and either CuCN or hexacyanometallate anions as sources of cyanide anions.[3–8] As an extension of our work in this field, in this paper we report three novel coordination polymers that have been constructed from simple phenanthroline and bipyrimidine ligands, namely $[Fe(CN)_4(phen)_2Cu_2]$ (**1**; phen = 1,10-phenanthroline), $[Cu_2(CN)_2(bpym]·H_2O$ (**2**; bpym = 2,2′-bipyrimidine) and $[Cu_2(CN)_2\ (mbpym)]$ (**3**; mbpym = 4-methyl-2,2′-bipyrimidine).

Results and Discussion

Solvothermal reactions are typically carried out in the 100–260 °C temperature range under autogenous pressure. Under these conditions, the reduced viscosity of the solvent enhances diffusion processes, thus favouring the solvent extraction of solids, the self-assembly of the precursors and the crystal growth from the solution. In fact, a rich variety of 1D to 3D polymetallic systems with intriguing structures and topologies have been recently prepared by solvothermal

---

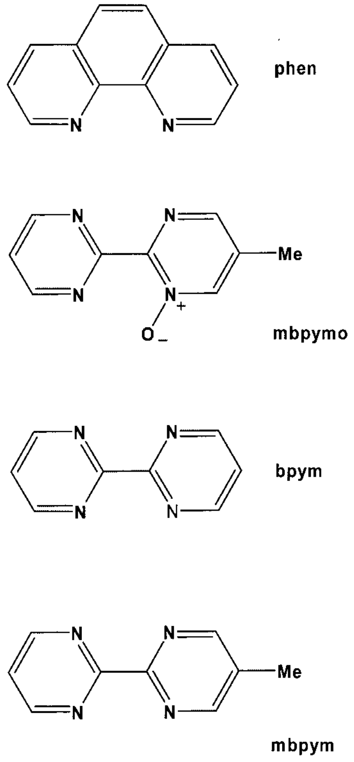
[a] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada,
18071 Granada, Spain
Fax: +34-958-248526
E-mail: ecolacio@ugr.es
[b] Unité de Calorimétrie et Materiaux, Université Abdelmalek Essaadi, Faculté des Sciences,
P. O. Box 2121, Tétouan 93002, Morocco
[c] Department of Chemistry, Laboratory of Inorganic Chemistry,
P. O. Box 55, 00014, University of Helsinki, Finland
E-mail: raikkok@saunalahti.fi

DOI: 10.1002/ejic.200401000

reactions, the great majority of them being hometallic in nature. The complexity of these reactions, in principle, prevents the control and prediction of crystal structures. Nevertheless, it is clear from empirical observations that the architecture of these multidimensional materials depends strongly on the subtle interplay between the characteristics of the metal ion (oxidation state, coordination preferences, plasticity of the coordination sphere, available coordination positions, redox capability, etc.), ligand (type and number of donor groups, bridging capability, connectivity, steric constraints, etc.) and reaction conditions (temperature, heating time, solvent, etc.). In this regard, Zubieta's group has prepared in the last few years a variety of multidimensional cyano-bridged complexes with simple diimine ligands. For these systems both changes of the ligand and the steric constraints imposed by the ligand substituents often give rise to the formation of quite different architectures.[4] As expected, a change in the reaction stoichiometry and/or counterion may also have a direct influence on the structure of the final product. For instance, the hydrothermal reaction of $Cu(CH_3COO)_2\cdot H_2O$, $K_3[Fe(CN)_6]$ and phen in a 2:1:1.5 molar ratio give rise to the 1D homometallic compound $[Cu_6(CN)_6(phen)_4]$.[5] However, the use of $CuCl_2\cdot 2H_2O$ instead of $Cu(CH_3COO)_2\cdot H_2O$ and a 1:1:1 molar ratio allowed us to isolate $[Fe(CN)_4(phen)_2Cu_2]$ (**1**), an interesting 3D bimetallic complex. As far as we know, this compound is only the second example of a cyano-bridged bimetallic complex prepared by solvothermal techniques, and the first example of such a compound exhibiting a 3D structure.

While chelating donor ligands, such as phen, act as passivating agents by blocking metal coordination sites, bridging ligands are expected to favour the propagation of the structure. In a previous paper,[3] we reported that the solvothermal reaction of $K_3[Fe(CN)_6]$, $CuCl_2\cdot 2H_2O$ and bpym, a bisdidentate ligand, in methanol leads to a 2D material made of honeycomb layers with alternating bpym and cyanide bridges. However, under the same solvothermal conditions, the use of KCN instead of $K_3[Fe(CN)_6]$ as a source of cyanide anions resulted in the formation of a different 2D homometallic compound $[Cu_2(CN)_2(bpym)]\cdot H_2O$ (**2**).

Recently, we have prepared the compound 4-methyl-2,2′-bipyrimidine 2-oxide (mbpymo, see Scheme 1), which, in principle, might bridge two metal ions to produce polynuclear complexes. However, all attempts to obtain this kind of compound were unsuccessful.[9] In view of this, we decided to use hydrothermal methods to force their preparation. Thus, by following the same synthetic procedure as that for **2**, but using $K_3[Fe(CN)_6]$ instead of KCN, the 3D complex $[Cu_2(CN)_2(mbpym)]$ (**3**), which contains cyanide and 4-methyl-2,2′-bipyrimidine (mbpym) bridging ligands was obtained (when KCN is used as a source of cyanide anions no definite compound could be isolated). During the hydrothermal reaction the *N*-oxide group of the ligand is lost and mbpym formed. This fact, and the reduction of iron(III) and copper(II) ions to iron(II) and copper(I), respectively, are a consequence of the high pressure and temperature used in the hydrothermal reactions for preparing complexes **1**–**3**. Cyanide groups, from either KCN or the dissociation of $[Fe(CN)_6]^{3-}$, are probably responsible for the reduction process, yielding cyanogen as the oxidation product. Moreover, it is well known that copper(I) cyanide species are more stable at elevated temperatures and pressures than those of copper(II).[4]



Scheme 1.

X-ray Structures

The asymmetric unit of the structure of **1**, together with the atomic labelling scheme, is given in Figure 1; selected bond lengths and angles are gathered in Table 1. The structure is constructed from two types of 10-metal-membered (Fe_2Cu_8) and two types of 14-metal-membered (Fe_2Cu_{12}) centrosymmetric rings, which fuse out of plane into an intricate 3D network. Within these rings, which are defined by the general sequences $\{(Cu^I)_4\text{-}Fe^{II}\text{-}(Cu^I)_4\text{-}Fe^{II}\}$and $\{(Cu^I)_6\text{-}Fe^{II}\text{-}(Cu^I)_6\text{-}Fe^{II}\}$, respectively, the metal centres are bridged by cyanide groups (Figure 1, middle). The Fe_2Cu_8 rings are similar to those observed in the 2D Fe^{II}–Cu^I compound $[Fe(bipy)_2(CN)_4Cu_2]$.[3] There are four independent Cu^I atoms in the structure, all of which exhibit a distorted trigonal-planar geometry with Cu–X bond lengths and X–Cu–X angles (X = C or N) in the ranges 1.872–1.975 Å and 104.49(12)–140.68(13)°, respectively. Each of these Cu^I atoms is connected by cyanide groups to two Cu^I atoms and one Fe^{II} atom, with Cu···Cu and Cu···Fe distances in the ranges 4.8736(6)–4.9456(6) Å and 4.7773(8)–4.9683(6) Å, respectively. There are two crystallographically independent Fe^{II} atoms in the structure (Fe1 and Fe2),

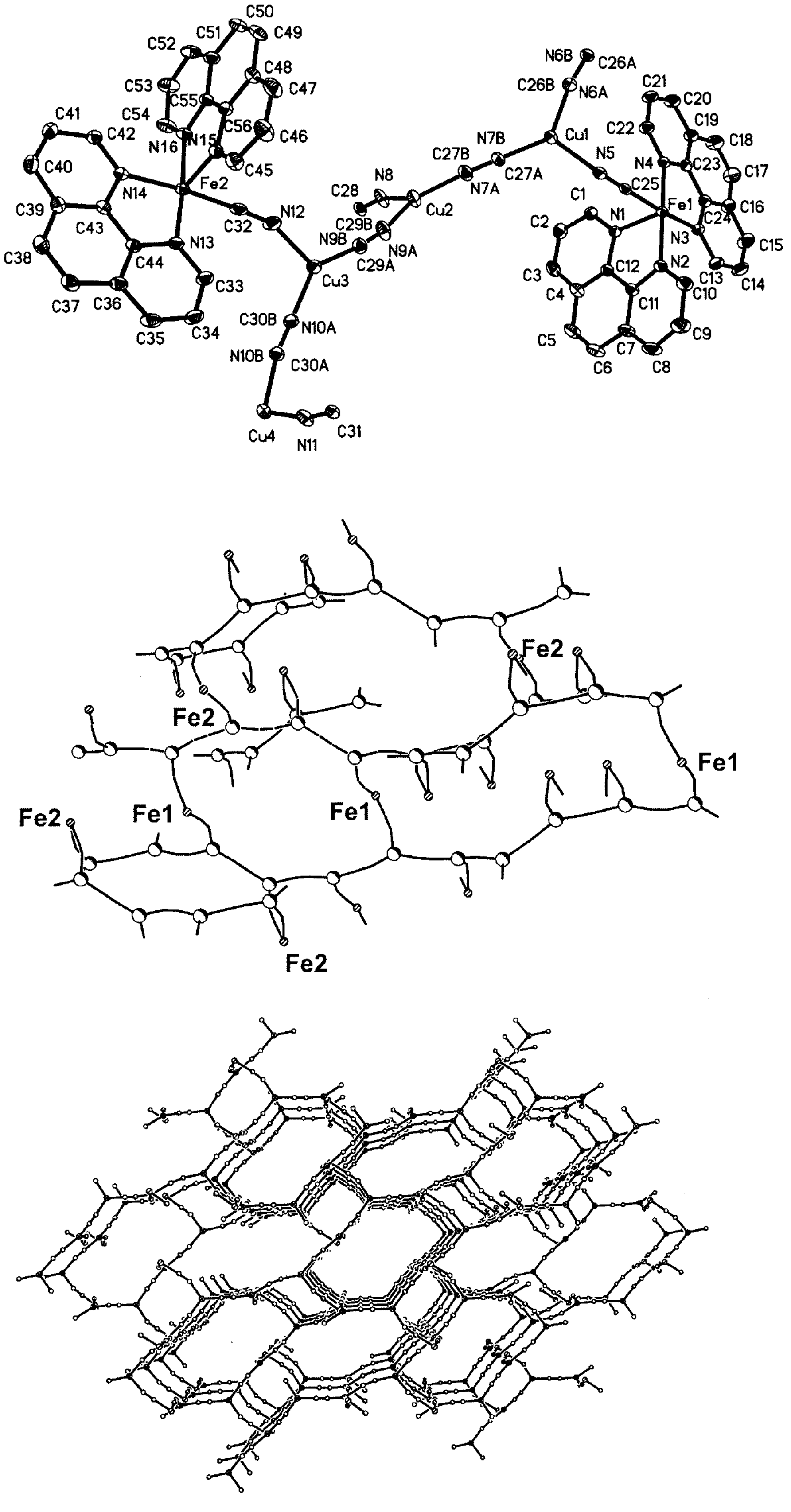


Figure 1. Asymmetric unit of **1** with the disordered CN bridging groups labelled as X (top). A fragment of the structure showing the two types of fused Fe_2Cu_8 and Fe_2Cu_{12} rings (middle); grey and black balls represent Cu and Fe atoms, respectively. View down the *b* axis of the 3D network of **1** (bottom). In the two latter views phen ligands have been omitted for clarity.

which exhibit a distorted octahedral FeN_4O_2 coordination environment. Each Fe^{II} atom is coordinated by four nitrogen atoms belonging to two bidentate phen ligands and to two carbon atoms from cyanide groups, these latter bridging each Fe^{II} atom to two Cu^I atoms and displaying a *cis* orientation. As expected for the Fe–CN–Cu coordination, the Fe–C–N angles [171.3(3)–177.3(3)°] are closer to linearity than the Cu–N–C angles [148.5(3)–165.3(2)°]. This is due to the stronger covalent interaction between C and Fe^{II} atoms. The bond lengths and angles in the Fe(CN)(phen) unit are similar to those found for the $Fe(bipy)(CN)_2$ unit in the 2D compound $[Fe(bipy)_2(CN)_4Cu_2]$ and the molecular squares $[Fe_2Cu_2(\mu\text{-}CN)_4(bipy)_6](PF_6)_4\cdot 2H_2O$ and $[Fe_2Co_2(\mu\text{-}CN)_4(bipy)_6]\cdot 2CHCl_3\cdot CH_3NO_2$.[10]

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

Cu1–X1	1.918(4)	X3–Cu1–X1	132.38(13)
Cu1–X3	1.872(3)	X1–Cu1–N5	106.52(12)
Cu1–N5	1.974(3)	X3–Cu1–N5	120.65(12)
Cu2–X4	1.883(3)	X4–Cu2–X5	131.25(13)
Cu2–X5	1.930(4)	X7–Cu3–X6	139.99(14)
Cu2–N8	1.936(3)	X5–Cu2–N8	105.92(12)
Cu3–X6	1.878(4)	X6–Cu3–N12	115.50(13)
Cu3–X7	1.913(3)	X7–Cu3–N12	104.49(12)
Cu3–N12	1.951(3)	X2[a]-Cu4–X8	140.68(13)
Cu4–X2[a]	1.878(3)	X2[a]-Cu4–N11	113.46(12)
Cu4–X8	1.907(3)	X8–Cu4–N11	105.84(11)
Cu4–N11	1.975(3)	N2–Fe1–N1	81.96(10)
Fe1–N1	1.996(2)	N4–Fe1–N3	81.68(10)
Fe1–N2	1.978(2)	N14–Fe2–N13	82.12(10)
Fe1–N3	2.011(3)	N16–Fe2–N15	82.03(10)
Fe1–N4	1.982(2)		
Fe1–C25	1.910(4)		
Fe1–C31[b]	1.891(3)		
Fe2–N13	1.987(2)		
Fe2–N14	1.990(2)		
Fe2–N15	1.991(2)		
Fe2–N16	1.982(2)		
Fe2–C28[c]	1.891(4)		
Fe2–C32	1.894(4)		

[a] Equivalent positions: $x - 1/2, -y + 3/2, z + 1/2$. [b] $-x + 1, -y + 2, -z + 1$. [c] $-x + 3/2, y - 1/2, -z + 3/2$.

The Fe1 and Fe2 centres are chiral and display opposite absolute configurations, therefore the crystal as a whole is racemic. One of the Fe_2Cu_8 rings contains two Fe1 atoms and the other one two Fe2 atoms, with approximate dimensions 11 × 18 Å^2 and 8 × 18 Å^2, respectively. The Fe_2Cu_{12} rings containing Fe1 and Fe2 have approximate dimensions 8 × 23 Å^2 and 13 × 25 Å^2. Cavities created by the out-of-plane fusion of the rings are filled by the coordinated phen ligands. Within the rings the maximum deviation from the mean plane corresponds to the iron(II) atoms. It should be noted that **1** is the first example of a 3D cyanide-bridged bimetallic complex prepared by hydrothermal methods.

We have shown that the related 2D Fe^{II}–Cu^I bimetallic compound $[Fe(bipy)_2(CN)_4Cu_2]$[3] exhibits a high spin:low spin equilibrium with 96% of the Fe^{II} atoms in the low-spin state ($S = 0$) at room temperature. Likewise, it has been shown recently that a series of cyanide-bridged Fe^{II}–M systems (M = Pd^{II}, Pt^{II}, Ni^{II}, Au^I, Ag^I) exhibit thermal-, pressure-, and light-induced spin crossover transitions.[11] In the case of **1**, however, the magnetic measurements reveal that the compound is diamagnetic at room temperature, thus indicating that the ligand field is strong enough to force all the Fe^{II} atoms to be in the low-spin state.

The structure of **2** (Figure 2) is very similar to that previously reported by us for the dehydrated compound $[Cu_2(CN)_2(bpym)]$[3] and consists of neutral 2D(6,3) honeycomb layers in the *ab* plane made of fused $Cu_6(CN)_4(bpym)_2$ rings and water molecules. The structure can be alternatively described as constructed from zig-zag $\{Cu(CN)\}_4$ chains linked by bisdidentate bridging bpym ligands generating the (6,3) net topology. Selected bond lengths and angles are given in Table 2. Two major differences between the structure of **2** and its dehydrated complex are observed: a) in **2**, the mean plane of the bpym ligand is almost perpendicular to the layers, with a dihedral angle of 90.2° (or 89.8°), whereas in the dehydrated complex this dihedral angles is only 73°; b) in **2**, the layers are stacked in such a way that bpym ligands are interdigitated and aligned above and below one sheet with the cavities in neighbouring layers, giving rise to an ABCD repeat pattern of layers (Figure 3). The bpym ligands of layers A and B are parallel.

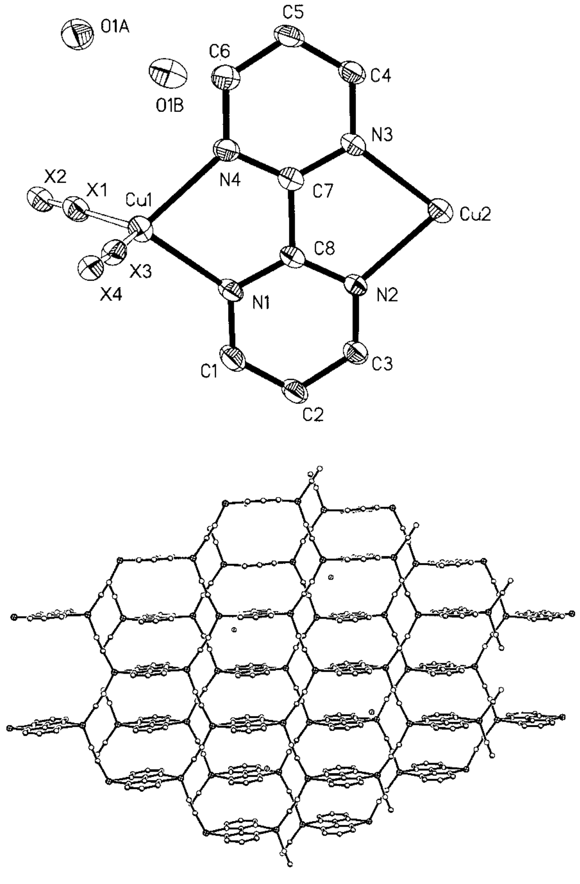


Figure 2. Perspective view of the asymmetric unit of **2** with the disordered CN bridging groups labelled as X (top). View down the *c* axis of two neighbouring layers with the same orientation of the bpym ligands (bottom).

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

Cu1–N1	2.102(4)
Cu1–N4	2.140(4)
Cu1–X1	1.888(7)
Cu1–X3	1.909(7)
Cu2–N2	2.129(4)
Cu2–N3	2.131(4)
Cu2–X2[a]	1.899(7)
Cu2–X4[b]	1.873(7)
X1–Cu1–N1	117.22(19)
X3–Cu1–N1	107.52(17)
N4–Cu1–N1	78.04(15)
X3–Cu1–X1	125.7(2)
X1–Cu1–N4	111.89(19)
X3–Cu1–N4	105.85(18)
X4[b]-Cu2–X2[a]	126.0(2)
N2–Cu2–N3	78.14(15)
X2[a]–Cu2–N2	113.33(18)
X4[b]–Cu2–N2	109.68(17)
X2[a]–Cu2–N3	110.08(18)
X4[b]–Cu2–N3	109.33(17)

[a] Equivalent positions: *x*, *y* + 1, *z*. [b] *x* – 1/2, *y* + 1/2, *z*.

Likewise, the mean planes of the layers C and D are also parallel but form a dihedral angle of 47.5° with those of layers A and B. Thus, layers are arranged in couples, with interlayer distances of about 4 Å and 6 Å for layers of the same couple (AB and CD) and different couples (BC and DA), respectively. In **2**, however, the repeat pattern of layers is of the ABAB type. Water molecules are located in the free space between the layers of different couples.

In **2**, Cu1 and Cu2 exhibit distorted tetrahedral coordination environments, which are formed by the coordination of two bridging cyano groups and one bridging bisdidentate bpym ligand, with Cu–X(cyano) (X = C or N) and Cu–N(bpym) bond lengths in the ranges 1.873(7)–1.909(7) Å and 2.102(4)–2.140(4) Å, respectively. As expected, the small bite of the bpym ligands leads to distorted tetrahedral coordination geometries with bond angles in the range 78.04(15)–125.7(2)°. The Cu···Cu distances across the cyanide ligands are 4.9431(12) Å and 4.9614(12) Å, whereas that across the bpy ligand is 5.6686(11) Å. The Cu_6 ring

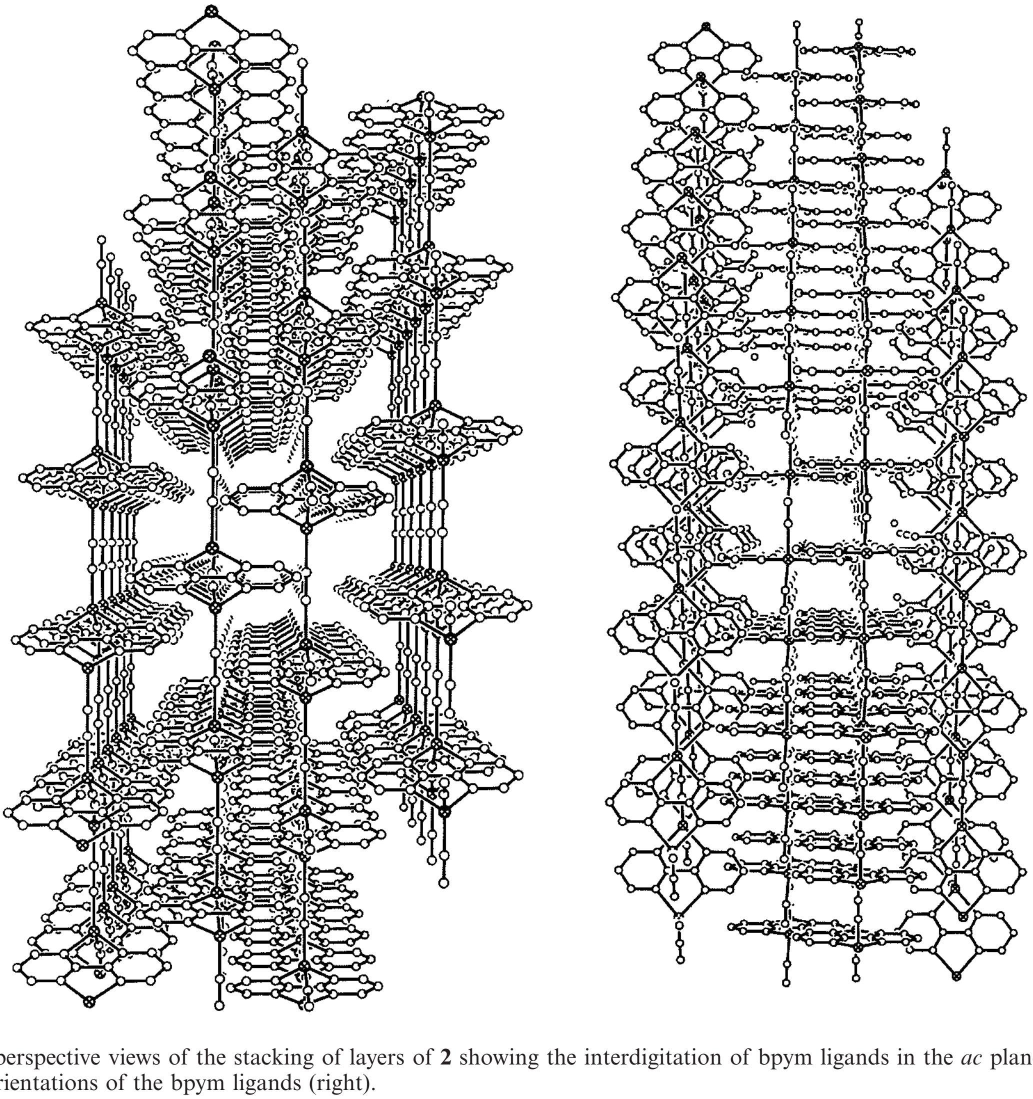


Figure 3. Two perspective views of the stacking of layers of **2** showing the interdigitation of bpym ligands in the *ac* plane (left) and the two different orientations of the bpym ligands (right).

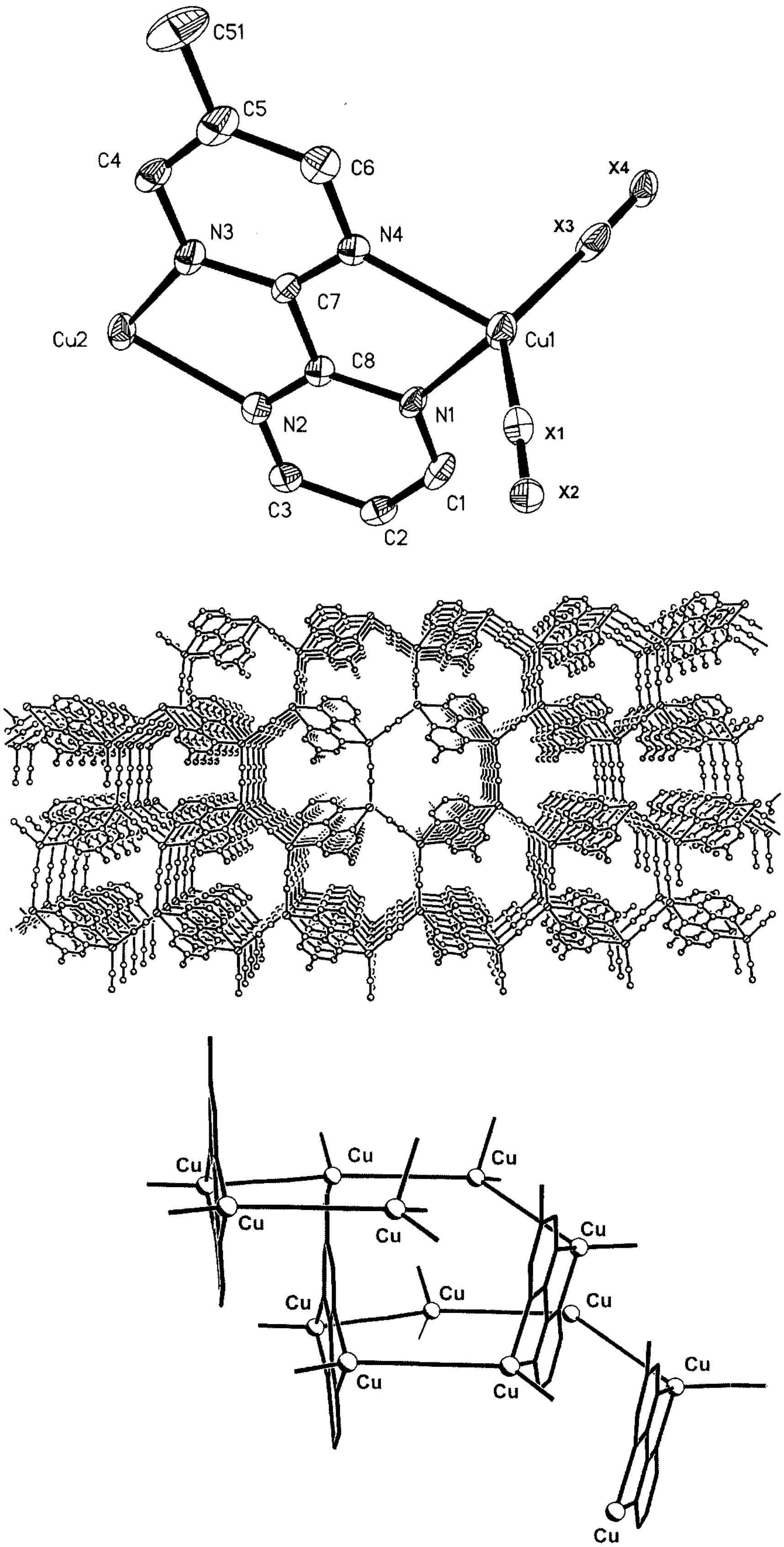


Figure 4. Asymmetric unit of **3** with the disordered CN bridging groups labelled as X (top). View of the 3D network down the *a* axis (middle). Spiral distribution of Cu^{I} atoms along the *a* axis (bottom).

has approximate dimensions of 8.8×11 Å^2, with Cu···Cu distances across the ring in the range 9.917(17)–10.9254(16) Å.

The asymmetric unit of the structure of $[Cu_2(mbpym)(CN)_2]$ (**3**) is given in Figure 4; selected bond lengths and angles are listed in Table 3. There are two crystallographically independent distorted tetrahedral copper(I) atoms in the structure, which are coordinated, as in **2**, by two bridging cyano groups and one bisdidentate bridging mbpym ligand. In contrast to **2**, the join of the Cu^I atoms does not take place in the same plane, therefore the structure is 3D. When viewed down the *a* axis, the structure seems to be made of fused hexagonal rings (Figure 4, middle). However, a closer examination reveals that these rings are not closed (Figure 4, bottom), and the Cu atoms are distributed in the *a* direction in a spiral manner leading to a 3D chiral network with hexagonal channels of approximate dimensions 9×9.5 Å^2. The space filling is achieved by orientation of the mbpym ligands in such a way that the methyl groups lie on the channels. The bond lengths and angles are similar to those observed in **2**. The Cu···Cu distance across the mbpym is 5.7311(10) Å, whereas the Cu···Cu distances across the cyanide ligands are 4.9526(9) Å and 4.9590 (9) Å.

Table 3. Selected interatomic distances [Å] and angles [°] for **3**.

Cu1–N1	2.154(6)
Cu1–X1	1.874(10)
Cu1–X3	1.903(8)
Cu1–N4	2.143(5)
Cu2–N2	2.166(6)
Cu2–X2[a]	1.915(9)
Cu2–N3	2.150(7)
Cu2–X4[b]	1.900(7)
X1–Cu1–N1	109.5(3)
X3–Cu1–N1	107.2(3)
X3–Cu1–X1	132.5(3)
N4–Cu1–N1	76.9(2)
X1–Cu1–N4	109.7(2)
X3–Cu1–N4	107.1(2)
X2[a]–Cu2–N2	109.1(2)
N3–Cu2–N2	78.1(2)
X4[b]–Cu2–N2	106.0(3)
X4[b]–Cu2–X2[a]	135.0(2)
X2[a]–Cu2–N3	105.9(3)
X4[b]–Cu2–N3	108.1(3)

[a] Equivalent positions: $x - 1/2$, $-y + 3/2$, $z - 1/2$. [b] $x + 1/2$, $y - 1/2$, z.

Concluding Remarks

From the above results the following conclusions can be drawn: (i) The use of hexacyanoferrate(III) as a precursor together with $CuCl_2 \cdot 2H_2O$ and polydentate ligands in simple hydrothermal reactions allows the isolation of homo- and heterometallic cyanide-bridged complexes with intriguing 3D architectures. (ii) The introduction of sterically demanding substituents in the bisdidentate ligand bpym leads to the formation of different structures (compound **2** vs. compound **3**). (iii) Solvothermal chemistry is a versatile and useful synthetic tool to prepare cyanide-bridged polymers.

Solvothermal reactions between other cyanometallate precursors, metal salts and a wide variety of polydentate ligands are currently under examination in our laboratory.

Experimental Section

4-Methyl-2,2′-bipyrimidine was prepared by condensation of 2-cyanopyrimidine with hydroxylamine·HCl and further condensation with 3-ethoxy-2-methylpropenal.[9] The rest of the reagents are commercially available and were used without further purification.

$[Fe(CN)_4(phen)_2Cu_2]$ (1): A mixture of $CuCl_2 \cdot 2H_2O$ (0.21 g, 1.22 mmol), phen (0.22 g, 1.22 mmol), $K_3[Fe(CN)_6]$ (0.4 g, 1.22 mmol) and water (8 mL) was added to a Teflon-lined stainless steel Parr acid digestion vessel and heated at 180 °C for 2 d under autogenous pressure. Slow cooling of the resulting solution to room temperature afforded dark red crystals of **1**. Yield: 0.22g (55%). IR (KBr): ν_{CN} = 2090, 2096 and 2119 cm^{-1}. $C_{28}H_{16}Cu_2N_8Fe$: calcd. C 51.90, H 2.49, N 17.31; found C 51.55, H 2.56, N 17.09. A Fe/Cu ratio of 0.51 was determined by SEM (scanning electron microscopy).

$[Cu_2(CN)_2(bpym] \cdot H_2O$ (2): Dark red crystals of **2** were grown from the hydrothermal treatment of $CuCl_2 \cdot 2H_2O$ (0.054 g, 0.32 mmol), 2,2′-bipyrimidine (0.050 g, 0.32 mmol), KCN (0.123 g, 1.92 mmol) and methanol (8 mL) in the same conditions as for **1**. Yield: 0.026g (47%). IR (KBr): ν_{CN} = 2116 cm^{-1}. $C_{10}H_8Cu_2N_6O$: calcd. C 33.78, H 2.27, N 23.65; found C 33.75, H 2.09, N 23.75.

$[Cu_2(CN)_2(mbpym]$ (3): This compound was prepared as dark red crystals under the same hydrothermal conditions as above with $CuCl_2 \cdot 2H_2O$ (0.098 g, 0.57 mmol), 4-methyl-2,2′-bipyrimidine 2-oxide (0.1 g, 0.57 mmol), $K_3[Fe(CN)_6]$ (0.189 g, 0.57 mmol) and methanol (8 mL). Yield: 0.032g (32%). IR (KBr): ν_{CN} = 2071 cm^{-1}. $C_{11}H_8Cu_2N_6$: calcd. C 37.58, H 2.30, N 23.92; found C 37.51, H 2.36, N 23.52.

Physical Measurements: Elemental analyses were carried out at the Instrumentation Scientific Centre of the University of Granada on a Fisons–Carlo–Erba analyser model EA 1108. IR spectra were recorded on a MIDAC progress IR spectrometer using KBr pellets.

X-ray Crystallography: Single-crystal diffraction data for **1**–**3** were measured on a Bruker Smart Apex diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). All data sets were corrected for Lorentz and polarisation effects, and absorption corrections were made with SADABS.[12] A total of 45034, 7827 and 7832 reflections giving 7791, 2902 and 3101 unique reflections were collected (R_{int} = 0.0402, 0.0359 and 0.0260) for **1**, **2** and **3**, respectively.

The structures were solved by direct methods and refined on F^2 with the SHELXL97 program.[13] For each compound, refinement of each CN bridge between two Cu^I atoms indicated disordering with respect to the C and N termini. When site occupation parameters of the bridging CN atom positions did not differ markedly from the ratio 50:50 the parameters were fixed to 50% C and 50% N. The disordered CN atom positions are labelled in tables and drawings with X1, X2, X3 etc. For example, in compound **1** the first atom position: 0.5 N6a + 0.5 C26b = X1; second 0.5 N6b + 0.5 C26a = X2; third 0.5 N7a + 0.5 C27b = X3, etc. For all structures, the non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

For **1**, the asymmetric unit of the structure consists of four Cu^I atoms, two Fe^{II} atoms, eight cyanide ions and four phen ligands. Four of the cyanide ions bridging the copper atoms are disordered.

For **2**, in addition to the disordered bridging cyanide groups, the oxygen atom of the water molecule is disordered over two sites. Site occupation parameters for the atoms were refined, but the hydrogen atom of the disordered water molecule could not be reliably located.

Complex **3** has a lot of pseudo-symmetry and the structure can be solved and refined both in centrosymmetric space group *C*2/*c* and in non-centrosymmetric space group *Cc*. Site occupation parameters for each disordered CN atom position were fixed to 50% C and 50% N for both space groups. Refinement in the centrosymmetric space group resulted in a partly disordered mbpym ligand, whereas refinement in the non-centrosymmetric space group gave a fully ordered ligand. As the *R*1 value of 0.0732 in the centrosymmetric space group is markedly higher than that of 0.0477 in the non-centrosymmetric space group we report here the structure in the lower symmetry space group *Cc*. The structure of **2** was refined as a racemic mixture. The crystal data for **1** to **3** are summarised in Table 4.

Table 4. Crystallographic data and structural refinement details for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{28}H_{16}Cu_2FeN_8$	$C_{10}H_8Cu_2N_6O$	$C_{11}H_8Cu_2N_6$
Formula mass	647.42	355.30	351.31
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	*C*2/*c* (no. 15)	*Cc* (no. 9)
a [Å]	19.2111(19)	14.927(2)	6.0928(6)
b [Å]	12.6738(13)	9.3301(12)	16.8890(16)
c [Å]	23.607(2)	19.464(3)	13.4625(13)
β [°]	110.041(2)	97.491(2)	96.174(2)
V [Å^3]	5399.7(9)	2687.6(6)	1377.3(2)
Z	8	8	4
T [°C]	25	–173	–173
λ [Å]	0.71069	0.71069	0.71069
ρ [g cm^{-3}]	1.593	1.756	1.694
μ [cm^{-1}]	21.24	31.64	30.81
Goodness-of-fit	1.043	1.076	1.060
$R1$[a] $[I > 2\sigma(I)]$	0.0307	0.0572	0.0477
$wR2$[b] $[I > 2\sigma(I)]$	0.0739	0.1173	0.1168
Flack parameter x	–	–	0.47(3)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

CCDC-250057 (for **1**), -250058 (for **2**) and -250059 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Spanish Ministerio de Ciencia y Tecnología through the project BQU2001/3221 and Junta de Andalucía. A. R. thanks the Ministerio de Ciencia y Tecnología for a predoctoral fellowship.

---

[1] a) R. Robson, in *Comprehensive Supramolecular Chemistry* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon Press, Oxford, **1996**, chapter 22, p. 733; M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2000**, *39*, 3052; b) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; c) S. A. Oxtoby, N. R. Champness, *Coord. Chem. Rev.* **2003**, *246*, 145; d) S. R. Batten, *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107; e) H. Li, M. Eddaoudi, M. M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276 and references cited therein; f) H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523; g) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; h) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* **2000**, *39*, 2082 and references cited therein; i) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; j) L. C. Tabares, J. A. R. Navarro, J. M. Salas, *J. Am. Chem. Soc.* **2001**, *123*, 383; k) *Magnetism: A Supramolecular Function* (Ed.: O. Kahn), NATO ASI Series C484, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1996**; l) *Molecular Magnetism: From Molecular Assemblies to Devices* (Eds.: E. Coronado, P. Delhaés, D. Gatteschi, J. S. Miller), NATO ASI Series E321, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1996**; m) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, V. Laukhin, *Nature* **2000**, *408*, 447; n) *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001–2004**; C. Janiak, *Dalton Trans.* **2003**, 2781; o) D. Luneau, *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 123.

[2] a) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283; b) M. Verdaguer, *Science* **1996**, *272*, 698; W. Entley, G. S. Girolami, *Science* **1995**, *268*, 397; S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, M. Verdaguer, *Nature* **1995**, *378*, 701; c) M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Sciuller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, *Coord. Chem. Rev.* **1999**, *190*, 1023; d) W. P. Fehlhammer, M. Fritz, *Chem. Rev.* **1993**, *93*, 1243; e) M. Ohba, K. Okawa, *Coord. Chem. Rev.* **2000**, *198*, 313; f) A. Marvilliers, S. Parsons, E. Rivière, J. P. Audière, M. Kurmoo, T. Mallah, *Eur. J. Inorg. Chem.* **2001**, 1287 and references cited therein; g) R. J. Parker, K. D. Lu, S. R. Batten, B. Moubaraki, K. S. Murray, L. Spiccia, J. D. Cashion, A. D. Rae, A. Willis, *J. Chem. Soc., Dalton Trans.* **2002**, 3723 and references cited therein; h) J. Černák, M. Orendáč, I. Potočňák, J. Chomič, A. Orendáčová, J. Skoršepa, A. Feher, *Coord. Chem. Rev.* **2002**, *224*, 51 and references cited therein; i) H.-Z. Kou, B. C. Zhou, D.-Z. Liao, R.-J. Wang, Y. Li, *Inorg. Chem.* **2002**, *41*, 25 and references cited therein; j) D. J. Chesnut, D. Hagrman, P. J. Zapf, R. P. Hammond, R. LaDuca, R. C. Haushalter, J. Zubieta, *Coord. Chem. Rev.* **1999**, *190*, 757 and references cited therein; k) D. J. Chesnut, D. Plewak, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **2001**, 2567; l) J. S. Miller, J. L. Manson, *Acc. Chem. Res.* **2001**, *34*, 563; m) R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzée, D. Gatteschi, W. Wernsdorfer, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760; n) M. L. Toma, R. Lescouëzec, F. Lloret, M. Julve, J. Vaissermann, M. Verdaguer, *Chem. Commun.* **2003**, 1850; o) M. Pilkington, S. Decurtins, *Comprehensive Coordination Chemistry II* **2004**, *7*, 177–229; p) A. Figuerola, C. Díaz, J. Ribas, V. Tangoulis, J. Granell, F. Lloret, J. Mahía, M. Maestro, *Inorg. Chem.* **2003**, *42*, 641; q) I. Muga, J. M. Gutiérrez-Zorrilla, P. Vitoria, P. Román, L. Lezama, J. I. Beitia, *Eur. J. Inorg. Chem.* **2004**, 1886.

[3] E. Colacio, J. M. Domínguez-Vera, F. Lloret, J. M. Moreno-Sánchez, R. Kivekäs, A. Rodríguez, R. Sillanpää, *Inorg. Chem.* **2003**, *42*, 4209.

[4] a) D. J. Chesnut, D. Hagrman, P. J. Zapf, R. P. Hammond, R. LaDuca, R. C. Haushalter, J. Zubieta, *Coord. Chem. Rev.* **1999**, *190*, 757 and references cited therein; b) D. J. Chesnut, D. Plewak, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **2001**, 2567; c) D. J. Chesnut, A. Kusnetzow, R. Birge, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **2001**, 2581; d) D. J. Chesnut, A. Kusnetzow, R. Birge, J. Zubieta, *Inorg. Chem.* **1999**, *38*, 5484; e) D. J. Ches-

nut, A. Kusnetzow, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **1998**, 4081; f) D. J. Chesnut, J. Zubieta, *J. Chem. Soc., Chem. Commun.* **1998**, 1707.

[5] J.-H. Yu, J.-Q. Xu, Q.-X. Yang, L.-Y. Pan, T.-G. Wang, C.-H. Lü, T.-H. Ma, *J. Mol. Struct.* **2003**, *658*, 1.

[6] D.-Q. Chu, L.-M. Wang, J.-Q. Xu, *Mend. Commun.* **2004**, *1*, 25–27.

[7] T. Pretsch, I. Bridgam, H. Hans, *Z. Anorg. Allg. Chem.* **2004**, *630*, 353–360.

[8] Y. Kang, Y.-G. Yao, Y.-Y. Qin, J. Zhang, Y.-B. Chen, Z. J. Li, Y.-H. Wen, J.-K. Cheng, R.-F. Hu, *Chem. Commun.* **2004**, *9*, 1046.

[9] E. Colacio, A. Debdouibi, A. Romerosa, unpublished results.

[10] a) H. Oshio, H. Onodera, O. Tamada, H. Mizutani, T. Hikichi, T. Ito, *Chem. Eur. J.* **2000**, *6*, 2523; b) H. Oshio, O. Tamada, H. Onodera, T. Ito, T. Ikoma, S. Tero-Kubota, *Inorg. Chem.* **1999**, *38*, 5686.

[11] a) J. A. Real, A. B. Gaspar, V. Niel, M. C. Muñoz, *Coord. Chem. Rev.* **2003**, *236*, 121; b) Y. García, V. Niel, M. C. Muñoz, J. A. Real, *Top. Curr. Chem.* **2004**, *233*, 229.

[12] G. M. Sheldrick, SADABS, a program for empirical absorption corrections, University of Göttingen, Germany, **1996**.

[13] G. M. Sheldrick, SHELX97, University of Göttingen, Germany, **1997**.

Received: December 03, 2004