# Condensed heterometallic bidimensional mixed valence $Cu^{I}/Cu^{II}/Ni^{II}$ cyanidometallate†‡

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**A 2D heterometallic mixed valence coordination network, $[Cu_2Ni(dien)(\mu\text{-}CN)_5]_n$ (1), built up from fused $[Ni(CN)_4]^{2-}$ and $[Cu(CN)_3]^{2-}$ cyanidometallate anions and $[Cu(dien)]^{2+}$ entities is reported.**

During the last few years considerable research efforts have been made on the design of compounds with the purpose of achieving materials with specific properties.[1,2] Consequently, a remarkable progress has been observed in the synthesis of coordination polymers of high dimensionality adopting the self-assembly technique.[3,4] In this context, the cyanido ligand represents an optimal group to act as terminal as well as bridging ligand.[5] Cyanidometallate anions can be diamagnetic as $[Ag(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Au(CN)_4]^-$, $[Fe(CN)_6]^{4-}$ or paramagnetic as $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Mo(CN)_8]^{4-}$, *etc.* It is observed that in general, when the second coordination centers are transition metal ions, back donation ($\sigma \rightarrow \pi$) stabilizes the resulting complexes, which make them robust. Paramagnetic entities as bridging moieties allow to build multidimensional structures with a second coordination center and the resulting complexes demonstrate unique structure and useful magnetic properties, even magnetic ordering.[6] The diamagnetic cyanidometallate entities can not give, obviously, noticeable magnetic properties, but the rigidity of such framework allows for shape and size selective inclusion of guest molecules (organic solvents, water molecules, aromatic amines, *etc.*)[7] to fill up the void space stabilizing the crystal structure. The absorption and/or desorption of the guest molecules may reveal potential applications in the areas of separation and catalysis.[8,9] As a consequence, many examples have been reported in which cyanidometallates bridge different complex entities leading to highly extended MOFs and even to discrete polynuclear entities if appropriate terminal ligands are selected to block the coordination sphere of the second coordination center. For example, several cyanidocuprate based extended systems, including some mixed valence ones, have been previously reported in which the cyanido-complexes act as bridging ligands leading to crystal structures that range from discrete oligomers to 3D polymeric architectures.[10] In spite of this structural richness, few examples apart from the classical Prussian blues and derivatives,[11] have been reported in which condensed cyanidometallates act as bridging entities between coordinatively unsaturated metal centers. Among these examples we can emphasize some such as copper(I)-zinc(II)[12] or copper(I,II)-tungsten(V)[13] condensed heterometallic cyanidometallates that present extended 2D or 3D networks. To our knowledge, we report herein the first example of a bidimensional complex with condensed $[Cu(CN)_3]^{2-}$ and $[Ni(CN)_4]^{2-}$ entities.§

The slow diffusion of a solution containing equimolecular amounts of dietilentriammine and copper(II) sulfate over an aqueous solution containing potassium tetracyanidonickelate(II) produces *in situ* partial reduction of copper(II) to copper(I) and gives rise to an unusual 2D metal–organic framework in which $[Cu(dien)]^{2+}$ (dien = dietilentriammine) subunits are simultaneously bridged by fused $[Ni(CN)_4]^{2-}$ and $[Cu(CN)_3]^{2-}$ entities. To understand the chemical processes that conduct to the synthesis of this compound we must have in mind that in aqueous solution copper(II) is easily reduced to copper(I) by cyanide, but if we choose ligands (*e.g.* amines) that have good σ-electron donor character and strongly prefer to coordinate to copper(II) rather than copper(I) ions, it could be possible to stabilize the copper(II)–CN coordination bonding.[14] In fact, the results indicate that both effects play a crucial role in the synthesis of this compound.

The crystal structure is comprised of complex sheets in which cyanide anions bridge $Cu^{I}/Cu^{II}/Ni^{II}$ metal centers (Fig. 1). The main relevant characteristic is the presence of a condensed $[CuNi(CN)_5]_n^{2n-}$ cyanidometallate anion in the form of an extended 1D polymeric chain that spreads along the crystallographic *c* axis. Tricyanidocuprate(I) and tetracyanidonickelate(II) entities alternate regularly along this chain sharing one cyanido ligand. The charge of the polymer is balanced by the presence of unsaturated $[Cu(dien)]^{2+}$ complex entities coordinated to the terminal cyanido ligands of the condensed cyanidometallate to give rise to the overall 2D framework. In this way the coordination sphere around the Cu(II) is a tetragonally elongated *mer*-$[Cu(dien)(CN)_3]$ octahedra. The cyanido bridges with longer bond distances present the highest deviation from M–CN–M linearity. The remaining cyanido bridges, those not linked to Ni(II), are almost linear. Both the tricyanidocuprate(I) and tetracyanidonickelate(II) present their usual geometrical parameters with coordination bond angles around 120 and 90°, respectively. The metal···metal distances through the $Ni^{II}\cdots Cu^{I}$ and $Cu^{I}\cdots Cu^{II}$ cyanido bridges (4.975–4.948 and 4.941 Å, respectively) are similar between them but significantly shorter than those involving cyanido bridges axially coordinated to the $Cu^{II}$ ($Cu^{II}\cdots Ni^{II}$: 5.110 and 5.605 Å). Similar

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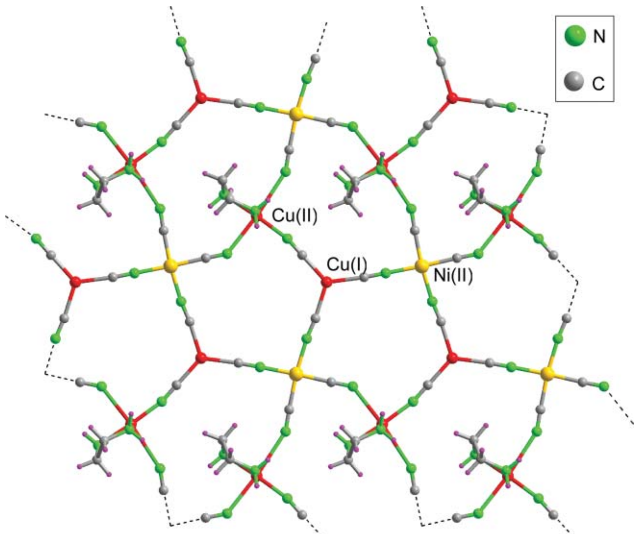
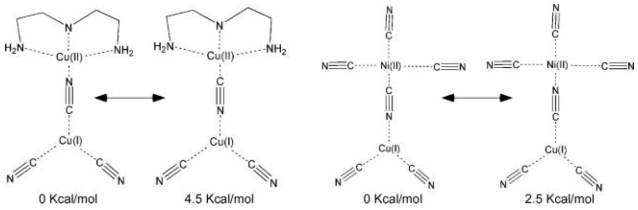


**Fig. 1** 2D framework of compound **1** showing the numbering scheme.

values have been found for other examples of cyanido bridged compounds with analogous structural characteristics.[15]

It is well known that the bridging cyanide groups usually appear as disordered entities. In the present compound however, the position of the C and N atoms of the cyanido bridged have been unambiguously located by the X-ray structural analysis and the help of DFT calculations. These calculations have been performed over dimeric models based on the X-ray crystal structure coordinates in which the energy of two models with the bridging cyanido group inverted have been calculated. The results reported on Scheme 1 indicates the following relative cyanide C-bonding preference: $Ni^{II} > Cu^{I} > Cu^{II}$. These results are in good agreement with the crystallographic X-ray analysis, which presents the lower disagreement parameters for the model corresponding to this bonding preference order (Table 1).



**Scheme 1** Relative energy values.

This fact is also reflected on the C–N bond lengthening due to the well-known retrodonation from the metal to the cyanide group. The greater retrodonation from the nickel to the cyanide leads to a more pronounced lengthening of the C–N bond (1.135–1.142 Å for Ni *vs.* 1.127 Å for Cu).

**Table 1** Crystallographic disagreement factors for different cyanide C-bonding preferences

| Cyanide C-bonding preference | $R\ (I > 2\sigma)$ | $wR\ (I > 2\sigma)$ | $R$ (all) | $wR$ (all) |
|---|---|---|---|---|
| $Ni^{II} > Cu^{I} > Cu^{II}$ | 0.0267 | 0.0621 | 0.0379 | 0.0636 |
| $Cu^{I} > Ni^{II} > Cu^{II}$ | 0.0357 | 0.0978 | 0.0478 | 0.1004 |
| $Ni^{II} > Cu^{II} > Cu^{I}$ | 0.0325 | 0.0854 | 0.0439 | 0.0873 |
| $Cu^{I} > Cu^{II} > Ni^{II}$ | 0.0412 | 0.1237 | 0.0535 | 0.1272 |
| $Cu^{II} > Cu^{I} > Ni^{II}$ | 0.0431 | 0.1343 | 0.0553 | 0.1377 |
| $Cu^{II} > Ni^{II} > Cu^{I}$ | 0.0374 | 0.1158 | 0.0492 | 0.1183 |

The crystal structure of the compound **1** is built up from an effective packing of the layers along the *b* axis. These layers are almost planar except for the dien ligands which are perpendicularly oriented outwards, in such a way that the adjacent layers are inverted and laterally displaced half unit cell along the *c* crystallographic axis to minimize the steric hindrance. As a consequence, the pile up of the sheets leads to an ABAB repetition pattern (Fig. 2).

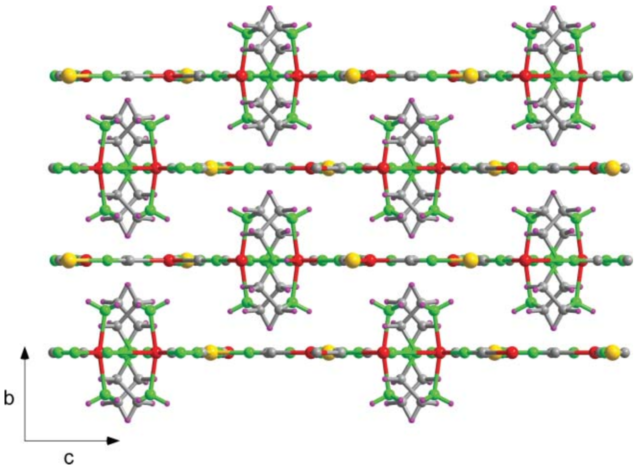


**Fig. 2** Perspective view of the lamellar crystal structure of compound **1**.

The magnetic data show very weak antiferromagnetic interactions between the Cu(II) paramagnetic centers (Fig. 3). This is in agreement with the almost negligible interactions ($|J| <$ 1 cm$^{-1}$, both ferro- and antiferromagnetic) reported for similar compounds in which copper(II) ions are linked by diamagnetic cyanidometallate complexes.[16]

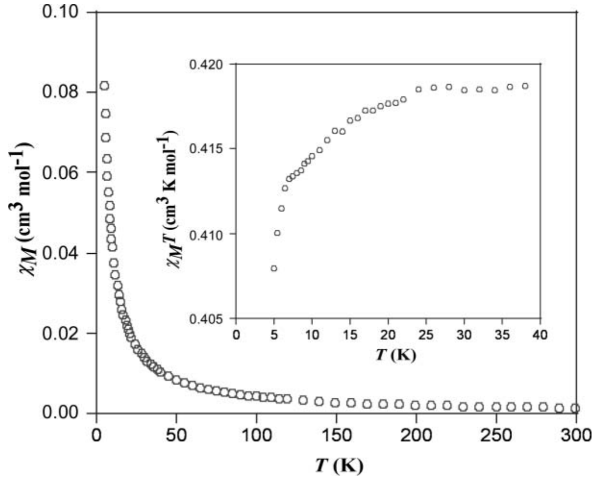


**Fig. 3** Plot showing $\chi_M$ and $\chi_M T$ curves of compound **1**.

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## Notes and references

§ Synthesis of compound **1**: purple single-crystals of compound **1** were prepared by slow diffusion of an aqueous methanol solution of $CuSO_4\cdot 5H_2O$ (0.4 mmol) and diethylenetriammine (0.4 mmol) into an aqueous solution of $K_2Ni(CN)_4$ (0.2 mmol). Crystal growth was observed six months later. Yield: 20% (based on nickel). Elemental analysis was performed with a Perkin-Elmer Analyst 100 microanalytical analyser. Metal content was determined by absorption spectrometry. Anal. calcd for $C_9H_{13}Cu_2N_8Ni$: C 25.8, H 3.1, N 26.7, Cu 30.3, Ni 14.0. Found: C 25.4, H 3.0, N 26.9, Cu 30.4, Ni 14.1. The IR spectra (KBr pellets) was recorded with a FTIR 8400S Shimadzu spectrometer in the 4000–400 $cm^{-1}$ spectral region. 3445 vs and 3290 s ($\nu$(NH)), 2152 m and 2128 m ($\nu(C\equiv N)$), 1635 m and 1585 m ($\delta(NH_2 + NH)$), 1080 s ($\nu$(C–N)), 460 m ($\nu$(M–C)). Magnetic measurement was performed on a Quantum Design SQUID susceptometer covering the temperature range 5.0–300 K at a magnetic field of 1000 G. Energy quantum mechanical calculations were carried out with B3LYP/6-31G(d) model chemistry. Diffraction data were collected at 293(2) K with Oxford Diffraction Xcalibur with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Structure was solved by direct methods using the SIR92 program[17] and refined by full-matrix least-squares on $F^2$ including all reflections (SHELXL-97).[18] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. Crystal data: $C_9H_{13}Cu_2N_8Ni$, FW = 419.06, orthorhombic, space group *Pnma*, $a = 12.8823(3)$, $b = 8.6820(2)$, $c = 13.3457(3)$ Å, $V = 1492.64(6)$ Å$^3$, $Z = 4$, $\rho = 1.865$ g $cm^{-3}$, 15 003 reflections, 1907 unique ($R_{int} = 0.0356$), $R_1 = 0.0267$ ($I > 2\sigma(I)$), $wR_2 = 0.0636$ (all data).

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