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Synthesis, crystal structure, EPR and magnetic properties of a cyano-bridged Cu^{II}–Ni^{II} heterobimetallic complex: an unusual structure with long-range ferromagnetic exchange through hydrogen bonding

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A cyano-bridged Cu^{II}–Ni^{II} dimeric complex [Cu(Me$_6$Cy)][Ni(CN)$_4$] has been synthesized and characterized by its single crystal X-ray structure determination. The square planar [Cu(Me$_6$Cy)]$^{2+}$ cation is converted to a distorted trigonal bipyramidal (TBP) geometry through ligation to one of the cyano groups of [Ni(CN)$_4$]$^{2-}$ in the equatorial plane, keeping the other three as terminal. Inspection of the X-ray data reveals that the Cu–N(6)–C(6) angle of the bridging cyano group is perfectly linear (180°). The room temperature (RT) EPR spectrum of polycrystalline [Cu(Me$_6$Cy)][Ni(CN)$_4$] is typical for mononuclear copper(II) complexes of axial symmetry, where the flattened out symmetry axis is characterized by $g_\perp = 2.143 \pm 0.005$ and $g_\parallel = 2.002 \pm 0.005$. No half field ($\Delta M = 2$) signals were observed. RT EPR spectrum of polycrystalline [Cu^{II}(Me$_6$Cy)](ClO$_4$)$_2$ yields an EPR signal with $g_\parallel = 2.394 \pm 0.005$ and $g_\perp = 2.045 \pm 0.005$, indicating that this parent compound has a different geometry than [Cu(Me$_6$Cy)][Ni(CN)$_4$]. Variable temperature magnetic moment studies on [Cu(Me$_6$Cy)][Ni(CN)$_4$] indicate a very weak long-range ferromagnetic exchange through hydrogen bonding between copper(II) ions ($S = \frac{1}{2}$). The present investigation provides a unique example where the original square planar [Cu(Me$_6$Cy)]$^{2+}$ moiety rearranges itself to a trigonal bipyramidal geometry under the influence of [Ni(CN)$_4$]$^{2-}$. This is probably only the second, rare example, and perhaps the first, for a macrocyclic precursor using only one cyano group of [Ni(CN)$_4$]$^{2-}$ for bridging, leading to a discrete dinuclear complex.

Introduction

Self-assembly by H-bonding, π-π stacking and van der Waals interactions are all very important processes in the formation of biological architectures.[1] These mechanisms are being developed as efficient design tools in material sciences for organizing individual molecular motifs into highly ordered supramolecules. Transition-metal-directed self-assembly is also a powerful approach for the construction of different supramolecular architectures with unusual and interesting properties.[2] A popular approach for such constructions is to employ cyano complexes[3] like [Ag(CN)$_2$]$^-$, [Cu(CN)$_3$]$^{2-}$, [M(CN)$_4$]$^{2-}$ (M = Cd, Ni, Pd, Pt, *etc.*) and [M(CN)$_6$]$^{3-}$ (M = Cr, Mn, Fe ,*etc.*), which act as the bridging moiety to build multidimensional structures where $\sigma \rightarrow \pi$ backbonding stabilizes the resulting complexes. Such cyanometallates with various dimensionalities and containing paramagnetic central atoms often show interesting magnetic properties where the bridging cyano group forms an exchange path mediating the interaction between spins localized on paramagnetic centers.[4]

Tetracyanometallate anions [M(CN)$_4$]$^{n-}$ (M = Ni, Pd, Pt, Cu, Cd),[3c,4b,5–11] exhibit bridging character involving either one, two, three or four of the cyano groups and all four possibilities have been found. In [{Cu$_2$(medpt)$_2$Ni(CN)$_4$}(ClO$_4$)$_2$·2.5H$_2$O]$_n$[6] [medpt = bis(3-aminopropyl)methylamine] all four cyano groups have been found to be involved in bridging. Recently, it has been observed that [Ni(CN)$_4$]$^{2-}$ uses three out of four cyano groups to bridge to three Eu^{II}[7] atoms in [(DMF)$_4$EuNi(CN)$_4$][8] (DMF = *N*,*N*-dimethylformamide) or three Cu^{II} atoms in [Cu(tn)Ni(CN)$_4$] (tn = 1,3-propanediamine),[8] respectively. In *trans*-[{Cd(en)$_2$}$_2$Ni(CN)$_4$], *cis*-[{Ni(dien)}2(μ-ox){μ-Ni(CN)$_4$}] (ox = oxalate) and *cis*-[{Cd(en)$_2$}$_2$Ni(CN)$_4$][9,10] two of the four cyano groups are involved in bridging, in both cis and trans fashions. On the contrary, there is only one previous report of a complex manifesting monodentate ligation, namely in [Cu(dien)(mea)]-[Ni(CN)$_4$]·2H$_2$O [dien = *N*-(2-aminoethyl)-1,2-ethanediamine, mea = 2-aminoethanol].[11]

In this article we report the synthesis and structural characterization of Me$_6$Cy·2HClO$_4$·H$_2$O and of the cyano-bridged Cu^{II}–Ni^{II} dinuclear complex, [Cu(Me$_6$Cy)][Ni(CN)$_4$]. Here, only one cyano group of [Ni(CN)$_4$]$^{2-}$ is involved in bridging in a perfectly linear fashion. It is noteworthy that under the influence of [Ni(CN)$_4$]$^{2-}$, the [Cu(Me$_6$Cy)]$^{2+}$ moiety reshuffled itself from its original stable square-planar (SP) arrangement to a trigonal bipyramidal (TBP) geometry, but the nickel atom retains its original SP geometry. To the best of our knowledge, it is only the second, rare example,[11] and probably the first for a macrocyclic precursor, in which only one cyano group of [Ni(CN)$_4$]$^{2-}$ is involved in bridging, leading to a discrete dinuclear complex.

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Experimental

Materials and methods

All the starting materials like acetone, ethylenediamine, $HClO_4$, $NaBH_4$, *etc.* (Merck Germany) were of reagent grade and used as received. Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nickolet Magna IR 750 series-II FTIR spectrophotometer. EPR spectra of polycrystalline samples were recorded using a Bruker EMX-220 digital X-band ($\nu = 9.4$ GHz) spectrometer. Processing and initial simulation of EPR spectra was done with Bruker's WIN-EPR and SimFonia software. The variable-temperature magnetic susceptibility measurements of a crystalline sample were performed in a field of 10 kOe on an Oxford Maglab System 2000 magnetometer. Diamagnetic corrections were made using Pascal's constants.

Syntheses

Caution! *Since perchlorate salts are potentially explosive, only small amounts of the materials should be handled with care.*

The ligand *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacycloteradecane dihydrate ($Me_6Cy{\cdot}2H_2O$) and its copper(II) complex, $[Cu(Me_6Cy)](ClO_4)_2$, were prepared by using the literature methods.[12,13] $Na_2[Ni(CN)_4]{\cdot}3H_2O$ was prepared according to standard literature procedure,[14] taking NaCN instead of KCN, and further characterized by CHN analysis.

$Me_6Cy{\cdot}2HClO_4{\cdot}H_2O$ (1). A methanolic solution of $HClO_4$ (in excess) was added dropwise with constant stirring to a methanol solution of $Me_6Cy{\cdot}2H_2O$ (1 mmol, 0.32 gm) whereupon a white precipitate of the perchlorate salt of the ligand appeared. This was recrystallized from methanol to obtain single crystals suitable for X-ray analysis. Yield 68%. **1** has been characterized by CHN analysis (found: C, 38.09; H, 7.65; N, 10.95; calcd for $C_{16}H_{40}N_4O_9Cl_2$: C, 38.14; H, 7.95; N, 11.12%).

$[Cu(Me_6Cy)][Ni(CN)_4]$ (2). To a methanol solution of $[Cu(Me_6Cy]^{2+}$ ([1.0 mmol, in 30 ml MeOH, generated *in situ* by mixing equimolar quantities of $Cu(OAc)_2{\cdot}H_2O$ and $Me_6Cy]$, $Na_2[Ni(CN)_4]{\cdot}3H_2O$ (1.5 mmol, 0.394 g) dissolved in a minimum volume of water was added dropwise with stirring for 5 min. The precipitate that appeared initially was filtered off and the filtrate was allowed to undergo slow evaporation at ambient temperature whereupon dark blue shiny crystals suitable for X-ray study were obtained in a few days. Yield: 44%. Anal. found: C, 46.21; H, 6.94; N, 21.76%; calcd for $C_{20}H_{36}N_8CuNi$: C, 47.0; H, 7.0; N, 21.95%.

Crystal data collection and refinement†

Intensity data for $Me_6Cy{\cdot}2HClO_4{\cdot}H_2O$ (**1**) and $[Cu(Me_6Cy)][Ni(CN)_4]$ (**2**) were collected at 293(2) K on a Siemens P4 defractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) and the $\omega - 2\theta$ scan mode in the range $2.44° \leq \theta \leq 22.50°$ for **1** and $2.26° \leq \theta \leq 27.50°$ for **2**. As a result of the poor scattering power of **1**, reflections with $I > 3\sigma(I)$ could not be observed for $22.5° \leq \theta$. The intensities were corrected for Lorentz and polarization effects and for absorption with ψ-scans for **1** and DIFABS for **2**. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 with a rigid model for all but the N(1) and N(3) hydrogen atoms of **1**, using the PLUS-PC version of SHELXTL.[15] The N(1) and N(3) protons of **1** were located in difference syntheses and freely refined with the constraint d(N–H) = 0.95(1) Å.

Crystal data for 1. $C_{16}H_{40}Cl_2N_4O_9$, $M_w = 503.42$, monoclinic, space group $P2_1/c$, $a = 11.210(2)$, $b = 8.844(2)$, $c = 25.809(5)$ Å, $\beta = 98.39(3)°$, $U = 2531.2(9)$ Å^3, $Z = 4$, $\mu = 0.306$ mm^{-1}, 3500 reflections collected, 3302 unique ($R_{int} = 0.0370$). Final R_1 and wR_2 values for all data: 0.1742, 0.1794. R_1 and wR_2 values for 1605 reflections with $I > 2\sigma(I)$: 0.0737, 0.1400.

Crystal data for 2. $C_{20}H_{36}CuN_8Ni$, $M_w = 510.82$, monoclinic, space group $C2/c$, $a = 15.140(9)$, $b = 12.002(4)$, $c = 14.286(5)$ Å, $\beta = 115.6(4)°$, $U = 2341(2)$ Å^3, $Z = 4$, $\mu = 1.736$ mm^{-1}, 3214 reflections collected, 2570 unique ($R_{int} = 0.0550$). Final R_1 and wR_2 values for all data: 0.0906, 0.1822. R_1 and wR_2 values for 1790 reflections with $I > 2\sigma(I)$: 0.0604, 0.1568.

Results and discussion

Structure of the cation of 1

The diprotonated hexamethyl cyclam $[Me_6CyH_2]^{2+}$ in the title compound **1** possesses a monoclinic structure with the space group $P2_1/c$. Recently, several reports have appeared on the supramolecular structures of the salt type adducts formed between Me_6Cy and monocarboxylic[16] and dicarboxylic acids,[17,18] 3,5-dinitrobenzoic acid,[18] 5-hydoxyisophthalic acid and 5-nitroisophthalic acid (monoanion),[19] various diphenol, dithiophenol, hydroxybenzoic acids and phosphonoacetic acid,[20] *etc.*, yielding one-, two- or three-dimensional motifs. There is no report on the structure of a 1:2 adduct formed between Me_6Cy and an inorganic oxyacid like perchloric acid. As in many reports cited above, the $[Me_6CyH_2]^{2+}$ cation is centrosymmetric and half of the atoms of the chemical formula are unique. The ORTEP view of the cation of **1** with atom numbering is shown in Fig. 1.

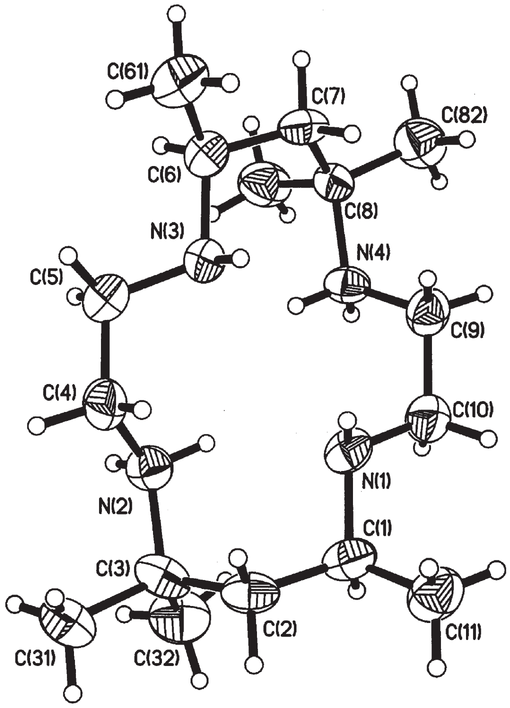

Fig. 1 ORTEP view of the cation of **1** showing the atom labelling scheme.

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† CCDC reference numbers 223767 and 231317. See http://www.rsc.org/suppdata/nj/b3/b306866h/ for crystallographic data in .cif or other electronic format.

Description of the structure of 2

The IR peaks corresponding to ν_{CN} appear at 2118(s) and 2143(m) cm^{-1} for **2** and can be assigned to the terminal and bridging cyanide groups, respectively. This indicates that the cyanide group bound to both the nickel(II) center and the copper(II) ion in $[Cu(Me_6Cy)]^{2+}$ bridges through its nitrogen atom, exhibiting an increase in its stretching frequency. The IR spectrum showed characteristic NH vibrations for the N–H···N(CN) hydrogen bonds, which appeared as a sharp peak at 3190 cm^{-1}.

Complex **2** crystallizes in the monoclinic space group $C2/c$ and exhibits crystallographic C_2 symmetry. The diad axis passes through Cu(1), N(6), C(6), Ni(1), C(8) and C(9). Fig. 2 shows the ORTEP view with atom numbering for complex **2**.

The coordination geometry about the copper atom is best described as distorted trigonal bipyramid (TBP), with two out of four macrocyclic nitrogens and the sole bridging cyano nitrogen forming the equatorial plane, and the other two macrocyclic nitrogens occupying the axial positions. The five Cu–N bond distances range from 2.123(4)–2.040(7) Å. The axial Cu(1)–N(1) = Cu(1)–N(1)#1 (where #1 refers to the symmetry transformation used to generate the equivalent atom and the corresponding symmetry code is given at the appropriate position) bond distance of 2.051(5) Å is somewhat shorter than the equatorial Cu–N(macrocyclic) distances [2.123(4) Å], which is typical for copper(II) complexes with TBP geometry coordinated *via* five nitrogen donor atoms.[21]

The N–Cu–N angles of the trigonal plane, N(6)–Cu(1)–N(2)#1 = 127.1(1)°, N(2)–Cu(1)–N(2)#1 = 105.8(2)° and N(2)–Cu(1)–N(6) = 127.1(1)°, deviate somewhat from the ideal trigonal angle (120°) but the sum of their bite angles is 360° and matches the ideal value, indicating the planarity of the trigonal plane comprising the N(2), N(2)#1 and N(6) atoms, which indirectly indicates the existence of an ideal C_2 symmetry for **2**. The axial angle N(1)–Cu(1)–N(1)#1 = 173.7 (2)° is close to 180° and manifests a regular TBP geometry. The other N–Cu–N angles range from 84.1(2)° to 92.1(2)°.

The cyano group when acting as a ligand can bind to a metal center in several modes:[4b] (a) a terminal cyano group that binds to the metal center through the carbon atom as M–C≡N; (b) a bridging cyano group (μ_2-ligand) that binds to two metal centers through both carbon and nitrogen atoms, resulting in M–C≡N–M′, and (c) in addition to the above two types of bonding CN$^-$ can also be involved in μ_3- and μ_4-type bridging though these are much less common.[22]

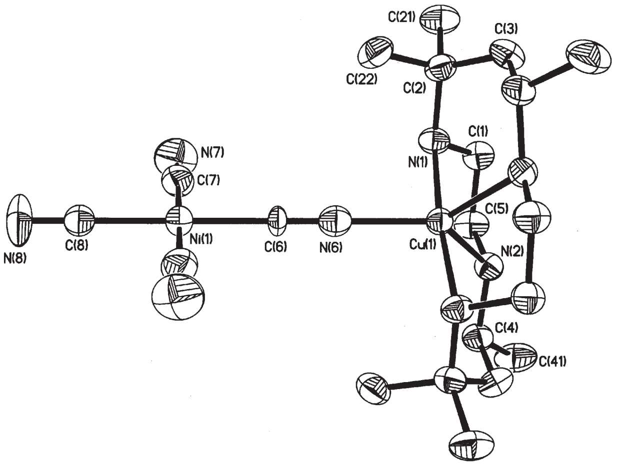

Fig. 2 ORTEP view of **2** showing the atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Cu(1)–N(1) 2.051(5); Cu(1)–N(2) 2.123(4); Cu(1)–N(6) 2.040(7); Ni(1)–C(6) 1.867(5); Ni(1)–C(8) 1.891(7); C(6)–N(6)–Cu(1) 180.0; N(6)–C(6)–Ni(1) 180.0; N(8)–C(8)–Ni(1) 180.0; N(6)–Cu(1)–N(1) 93.1(1); N(6)–Cu(1)–N(2) 127.1(1); N(1)–Cu(1)–N(2) 92.1(2); N(1)#1–Cu(1)–N(1) 173.7(2); N(1)#1–Cu(1)–N(2) 84.1(2); N(2)–Cu(1)–N(2)#1 105.8(2). Symmetry code #1: $-x$, y, $-z+1/2$.

The C-end of the cyano ligand produces a strong field effect, while the N-end behaves as a medium-strength ligand with a ligand field lower than that of NH_3. Generally, C–N distances fall in the range 1.12–1.16 Å and no difference is found between terminal and bridging ligands.[4b] In complex **2**, the C–N distances for the terminal cyanide groups lie in the range 1.129(10)–1.138(7) Å and that of the bridging cyanide C(6)–N(6) = 1.137(9) Å.

The coordination of the $[Ni(CN)_4]^{2-}$ moiety to a Cu^{II} center *via* the nitrogen atom of one of the cyanide ligands occurs in a perfectly linear fashion [Cu(1)–N(6)–C(6) = 180.0°]. In most of the cyano-bridged complexes M′–N–C is angular rather than straight and the observed angle varies from system to system. In a few cases the angles are close to but not exactly 180°. In this sense, **2** is unique as the $[Ni(CN)_4]^{2-}$ moiety bridges to a second metal center in a perfectly linear fashion.

The Ni–C bond distances in $[Ni(CN)_4]^{2-}$ fall in the range 1.868(5)–1.891(7) Å, which are very close to the ideal value of 1.86 Å.[23] The $[Ni(CN)_4]^{2-}$ moiety in **2** effectively retains its original SP geometry and this is evidenced by the fact that the all the Ni–C–N angles fall in the narrow range of 179.1(3)°–180°. Such rigidity of the SP structure is generally seen for $[Ni(CN)_4]^{2-}$ in various bridging structures, regardless of the bridging mode.

In five-coordinated Cu^{II} complexes where Cu–N distances in the equatorial plane differ from each other, a quantitative method to describe the degree of geometrical distortion has been developed.[24] According to this method, the longer Cu–N bond is assumed to be the apical bond in a square pyramidal (SqPy) structure and the percentage distortion from SqPy towards TBP geometry is defined as: $\tau = [(\theta - \pi)/60] \times 100$, where θ and π are two basal angles. τ is 100 for the ideal TBP but 0 in the SqPy geometry. In the present case, the θ and π values are 173.7(2)° and 127.1(1)° and the corresponding τ calculated to be 78%. This and the above crystallographic data confirm that the coordination geometry of complex **2** around the copper ion is quite close to TBP. This is quite different from the other five-coordinate complexes of copper and manifests the fact that the geometry of the complex is strongly affected by the ligand structures.

When $[M(CN)_x]^{n-}$ bridges to an MN_4 (N_4 = ligands coordinated through four nitrogen atoms) tetra-coordinated metal center through the nitrogen atom of a cyanide ligand, it generally occupies the axial position. But complex **2** is a unique example in which the bridging cyanide group occupies an equatorial position. Another example where the bridging cyano groups occupy both axial and equatorial positions is given by $[\{[Cu(dien)]_2Cr(CN)_6\}]_n[Cu(H_2O)(dien)Cr(CN)_6]_n \cdot 4nH_2O$, where the equatorial plane is defined by the three nitrogens of dien and one nitrogen of a $[Cr(CN)_6]^{3-}$ group and the axial position is occupied by the nitrogen of another $[Cr(CN)_6]^{3-}$ group.[25]

In the cyano-bridged bimetallic complex $[Cu(cyclen)][Au(CN)_2]_2$ (cyclen = 1,4.7,10-tetrazacyclododecane) the Cu^{II} center is bound to four nitrogen atoms of cyclen and a nitrogen atom of an $[Au(CN)_2]^-$ anion. The cations pair up to form dimeric units linked by Au···Au interactions.[26] Though in both complexes the Cu^{II} ions are penta-coordinated involving four tetraazamacrocyclic nitrogens and one nitrogen from a bridging cyanide ion, the following striking differences between $[Cu(cyclen)][Au(CN)_2]_2$ and **2** are observed: (*i*) the former is in a distorted SqPy geometry while **2** adopts a modest TBP geometry; (*ii*) as generally found, the bridging CN group occupies the axial position in the former but the unusual equatorial position in **2**; (*iii*) M′–N–C is angular (157°) in the former complex while it is perfectly linear (180°) in **2** and (*iv*) in the former, the C–N bond distances corresponding to the bridging and terminal cyano groups are 1.16 and 1.09 Å, respectively, whereas the respective bond distances in **2** are 1.137(9) and 1.129(10) Å.

The Cu^{II}–Ni^{II} units are joined together through intermolecular H-bonding between the NH protons of the macrocyclic ligand in one unit and one of the three terminal cyano groups in a $[Ni(CN)_4]^{2-}$ moiety of another unit, resulting in a dimeric structure (Fig. 3).

Magnetic properties of 2

The temperature dependence of the magnetic susceptibility of **2** over the 2–200 K range is shown in Fig. 4. The magnetic susceptibility obeys the Curie–Weiss law [$\chi_m = C/(T-\theta)$] with $C = 0.38$ cm^3 mol^{-1} K and $\theta = +2$ K. The Curie constant C corresponds to a paramagnetic Cu^{II} ion with $S = 1/2$ and $g = 2.0$ and a diamagnetic Ni(II) ion. The slight increase of $\chi_m T$ upon cooling and the small positive Weiss constant indicate a very weak ferromagnetic coupling between Cu^{II} ions.

As stated above, **2** has a dimeric structure, due to hydrogen bonding between the macrocyclic ligand and the terminal cyanide in the $[Ni(CN)_4]^{2-}$ moiety. It is to be noted that only one of the three terminal cyanide groups is involved in H-bonding. The paramagnetic Cu^{II} ($d^1_{x^2-y^2}$) is directly attached to the diamagnetic SP Ni^{II} center *via* the bridging cyanide group. As no magnetic exchange would occur between these pairs of (para-dia) ions, it is likely that exchange coupling through the N–H···N≡C pathway would be operative here. This is a long-range magnetic interaction as the Cu···Cu distance is 9.754 Å and expectedly weaker in nature. Recently, it has been shown that, in the solid state, some chromium compounds of the general formula *cis*-$[CrA_4(OH_2)(OH)]^2$ (where A_4 represents the four nitrogen ligators from an appropriate number of monodentate or polydentate ligands) have a dimeric structure in which two formula units are bound together by powerful hydrogen bonds, such that they can transmit an antiferromagnetic interaction between the two chromium centers, even though they are separated by a distance of 5 Å.[27] The proposition of antiferromagnetic coupling as an indication of hydrogen-bonded dimeric structures[28] is questionable as it was later established that antiferromagnetic coupling is also exhibited by complexes with hydrogen-bonded infinite chain structures. As hydrogen bonds have been reported to propagate *antiferromagnetic interactions* between metal centers in a variety of transition metal complexes,[27,28] the intermediate interactions through the hydrogen bonds are expected to be weakly antiferromagnetic. The observation of a positive value of θ [2.0(1) K] is indicative of a ferromagnetic behavior of **2**, which contradicts the above proposition. The present investigation provides a unique example in which a long-range magnetic interaction (Cu···Cu distance being 9.754 Å) *via* H-bonding is apparent.

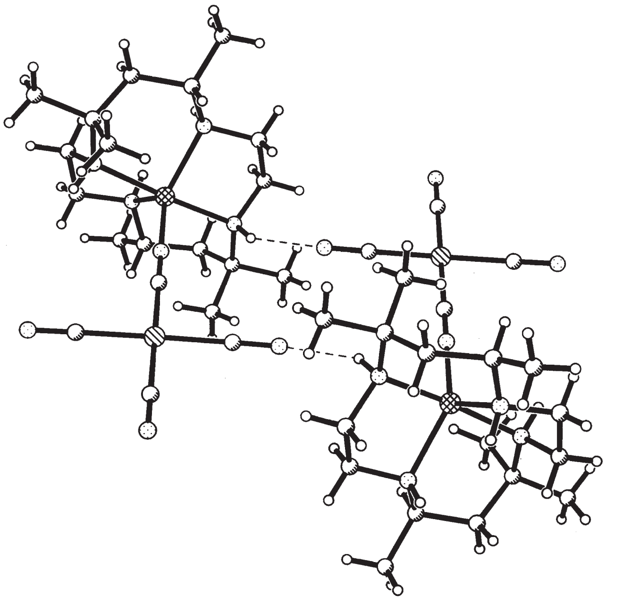

Fig. 3 Structure of **2** showing the N–H(imino)···N(cyanide) hydrogen-bonding interactions between two [Cu(Me$_6$Cy)][Ni(CN)$_4$] units. Selected hydrogen bonding parameters (Å, °) are as follows: N(1)–H(1)···N(7)^a: D–H = 0.91, H–A = 2.200, D···A = 3.006(7), DH···A = 148.00; N(2)–H(1)···N(8)^b: D–H = 0.91, H–A = 2.270, D···A = 3.149(7), D–H···A = 162.00; N(2)–H(1)···N(8)^c: D–H = 0.91, H–A = 2.270, D···A = 3.149(7), D–H···A = 162.00. Symmetry codes: $^a = x, -y, 1/2+z$; $^b = x, -1+y, +z$; $^c = -x, -1+y, 1/2-z$.

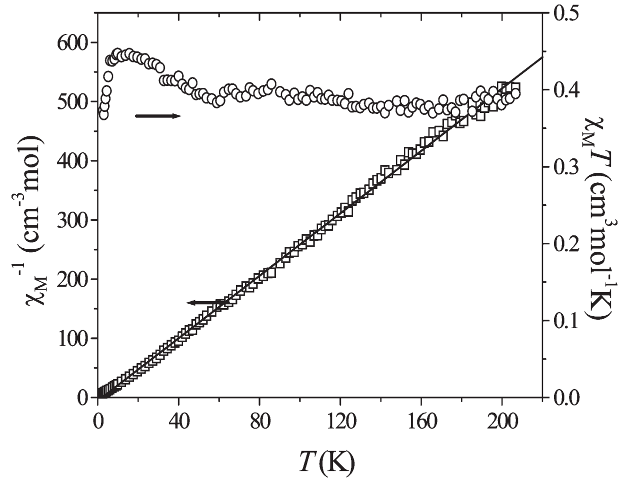

Fig. 4 Plots of $\chi_m T$ and χ_m^{-1} *vs.* T for **2**. The solid line represents the best calculated fit of the data.

EPR studies

The room temperature solid state EPR spectrum of a polycrystalline sample of **2** (Fig. 5) is typical for mononuclear Cu^{II} complexes of axial symmetry where the flattened out axis is characterized by $g_\perp = 2.143 \pm 0.005$ and $g_\parallel = 2.002 \pm 0.005$. Simulation of this signal using the Gaussian shape of the individual EPR line gives: $g_\perp = 2.152$, $g_\parallel = 2.002$, $\Delta H_{pp}^{\perp} = 7$ mT, $\Delta H_{pp}^{\parallel} = 4$ mT. In the present case $g_\perp > g_\parallel$, which for a d^9 system indicates that the axial ligand field is greater than the equatorial field,[29] as is also evidenced by their bond distances (*vide supra*). Since no "forbidden" half field ($\Delta M = 2$) signals

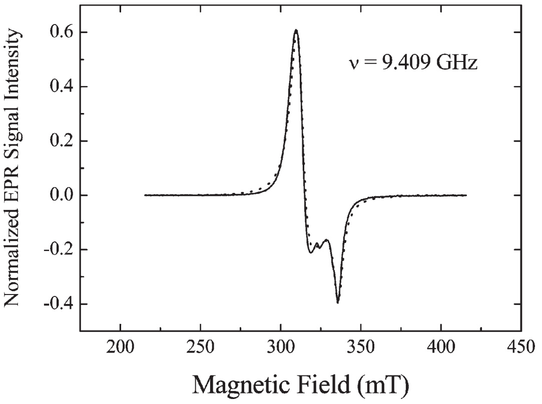

Fig. 5 Room temperature EPR spectrum of polycrystalline [Cu(Me$_6$Cy)][Ni(CN)$_4$]: (solid line) experimental spectrum, (dotted line) simulated spectrum. The weak narrow line with $g \sim 2.08$ is due to impurities.

have been observed, the absence of antiferromagnetically exchange coupled dinuclear species may be concluded. This is in line with diamagnetic $[Ni(CN)_4]^{2-}$ acting as a monodentate ligand towards $[Cu(Me_6Cy)]^{2+}$. On the other hand, the room temperature EPR spectrum of polycrystalline $[Cu^{II}(Me_6Cy)](ClO_4)_2$ yields another EPR signal [Fig. 6(a)] that, possibly, may be represented as a superposition of monomeric and dimeric signals. The main signal ($\Delta M = 1$) belongs to a monomeric species and is characterised by $g_{\parallel} = 2.394 \pm 0.005$ and $g_{\perp} = 2.045 \pm 0.005$. At higher gain a weak half field ($\Delta M = 2$) signal with $g = 4.10 \pm 0.01$ was found [Fig. 6(b)]. Its integral intensity is about of 3 orders of magnitude lower than that of the main signal. This may indicate that the sample contains a certain amount of antiferromagnetic dimeric species ($S = 1$) with an anisotropy parameter $D < 10$ mT. The EPR signal observed in the parent $[Cu^{II}(Me_6Cy)](ClO_4)_2$ compound shows that $[Cu^{II}(Me_6Cy)](ClO_4)_2$ has a different geometry than $[Cu(Me_6Cy)][Ni(CN)_4]$ and, presumably, some of these parent complexes are inclined to establish exchange-coupled dimeric species.

Conclusion

In this paper we presented a detailed study of a unique cyano-bridged Cu^{II}–Ni^{II} heterobimetallic complex, along with the synthesis and crystal structure of the perchlorate salt of the macrocyclic ligand, Me_6Cy.

The salient features of the present work are as follows: (*i*) under the influence of $[Ni(CN)_4]^{2-}$, the parent $[Cu(Me_6Cy)]^{2+}$ moiety revokes its original square planar geometry to attain a trigonal bipyramidal geometry where only one cyano group of $[Ni(CN)_4]^{2-}$ is involved in a perfectly linear bridging, and surprisingly, occupies the equatorial position, forcing the macrocyclic ligand to attain a folded conformation; (*ii*) a weak long-range (9.754 Å) ferromagnetic magnetic interaction between two copper atoms *via* H-bonding is observed. A detailed survey of the room temperature EPR study of complex **2** along with the compound $[Cu^{II}(Me_6Cy)](ClO_4)_2$ is envisaged. From this initial work the EPR spectrum of the complex with $g_{\perp} > g_{\parallel}$ has been explained by a shortening of the axial bond over the equatorial ones.

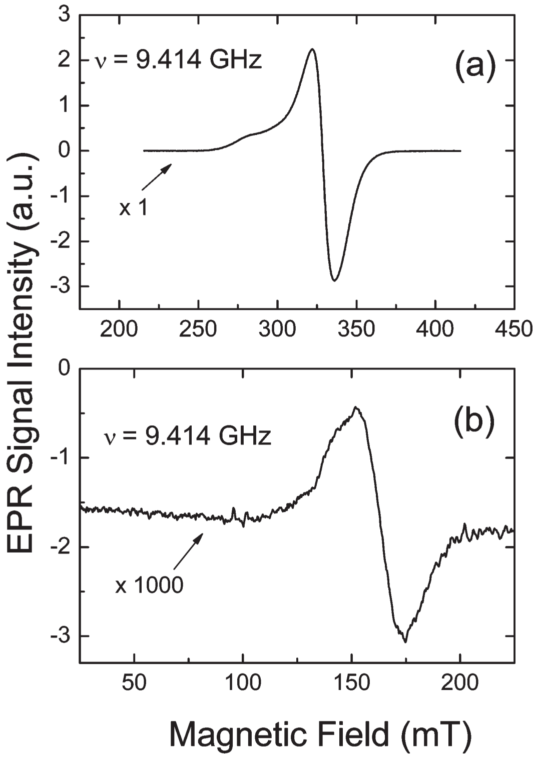

Fig. 6 Room temperature EPR spectrum of polycrystalline $[Cu^{II}(Me_6Cy)](ClO_4)_2$: (a) main ($\Delta M = 1$) signal; (b) half-field ($\Delta M = 2$) signal.

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