

# Copper(II) complexes of a novel ligand 4,5-dicyanoimidazole: structural and magnetic studies

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The potential use of 4,5-dicyanoimidazolate ion (DCI<sup>-</sup>) as a bridging ligand for magnetically interesting co-ordination polymers has been explored. New Cu<sup>II</sup>-bipy complexes containing DCI<sup>-</sup> were prepared and characterised; crystal structure analysis revealed DCI<sup>-</sup> co-ordinated Cu<sup>II</sup> in one of the complexes. The ESR and magnetic susceptibility studies showed that the compounds are nearly Curie paramagnetic or weakly antiferromagnetic. A polymeric structure is proposed for one of the complexes.

## Introduction

Molecule-based magnetic materials is an area of immense research activity today. Based on theoretical ideas such as the negative spin density product model,<sup>1</sup> configuration interaction in charge transfer complexes<sup>2</sup> and topological models,<sup>3</sup> several experimental investigations<sup>4-7</sup> have been carried out to fabricate molecular magnetic materials. Extensive work carried out on high spin species based on carbene and nitrene radical centres<sup>8</sup> indicates that the high chemical reactivity often leads to low spin concentrations in the bulk material. One of the strategies to overcome this problem is to replace the reactive radical sites based on light atoms by metal ion spin centres. Ferromagnetic coupling between the metal spin centres can be achieved using superexchange interactions<sup>9</sup> or by the orthogonality of the metal ion spin orbitals through proper design of the bridging ligands.<sup>10</sup>

Magnetic materials based on transition metal co-ordination polymers with molecular bridging ligands investigated in earlier studies<sup>11</sup> were mostly based on one-dimensional systems. Copper(II) ions assembled in 2-D and 3-D networks have also been reported<sup>12</sup> taking cognisance of the necessity to go beyond one-dimensional systems for achieving phase transitions at finite temperatures.<sup>13</sup> However these systems have shown anti-ferromagnetic interactions. An interesting case of ferromagnetic spin coupling between vanadyl centres mediated by pyrimidine ligands has been reported by Iwamura and co-workers.<sup>14</sup> The current interest in the exploration of different molecular species as mediators of magnetic interactions between metal ion spins may be juxtaposed with the extensive studies of magnetic coupling units, motivated by topological models for ferromagnetism in organic radical systems. In the spirit of the simple spin coupling schemes we have developed,<sup>15</sup> it may be envisaged that, if a molecular ligand bridging two paramagnetic metal ions provides a short odd  $\pi$ -electron path, it could serve as a ferromagnetic coupling unit for the metal ion spins, provided the metal ion spin orbitals are in conjunction with the ligand  $\pi$  system. The pyrimidine ligands mentioned above are an illustrative example. Imidazole, pyrazine, etc. are popular bridging ligands for metal ions.<sup>16</sup> However, these ligands provide 4- $\pi$ -electron pathways which probably lead to the dominant antiferromagnetic coupling of the paramagnetic metal ions observed in such systems.<sup>17</sup>

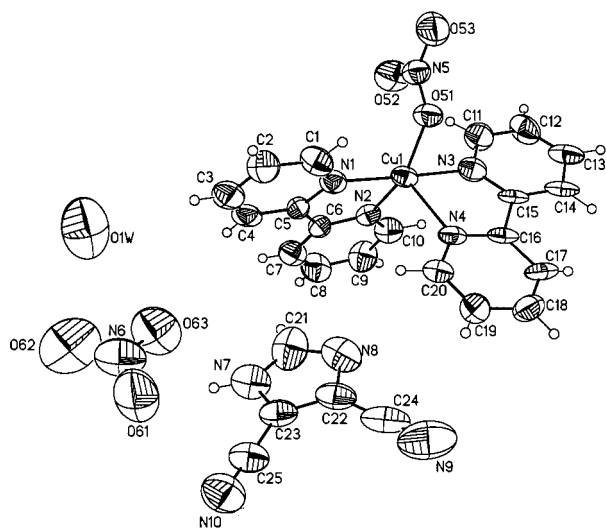
A ligand such as 4,5-dicyanoimidazole (HDCI) would be an interesting variant to investigate, since the cyano groups strongly withdraw the charge on the easily formed 4,5-dicyanoimidazolate anion bridge and diminish the electron count on the  $\pi$  pathway between the metal centres. Our *ab initio* calculations at the MP2/6-31 + G\*\* level indicate that the net charge on the N-CH-N path is -0.82 in imidazolate whereas it reduces to -0.36 in 4,5-dicyanoimidazolate anion, supporting this contention. The compound HDCI could also support 2-D metal co-ordination networks. Surprisingly there are no reports of structural or magnetic characterisation of dicyanoimidazole ligated paramagnetic metal systems. The only structural study that we are aware of, involving a derivative of DCI<sup>-</sup> as a ligand, is that of a complex<sup>18</sup> of Cu<sup>I</sup> wherein one of the cyano groups of HDCI is converted into an iminoester. This paper also reported a compound with a possible polymeric structure involving HDCI-bridged copper(I) ions. Earlier studies in our laboratory<sup>19</sup> have shown that water soluble copper(II) salts readily react with HDCI to give highly insoluble complexes. Variable temperature ESR studies showed antiferromagnetic coupling between copper(II) spins in these materials. These were amorphous and no structural information could be gathered. Structural studies on some paramagnetic complexes with DCI<sup>-</sup> as the ligand could provide insight into its potential use in the design of co-ordination polymers with desired magnetism. We report here the synthesis and first structural characterisation of some DCI<sup>-</sup> complexes of Cu<sup>II</sup>; [Cu(bipy)<sub>2</sub>]<sup>2+</sup> (bipy = 2,2'-bipyridyl) was used as the precursor to limit the DCI<sup>-</sup> ligation facilitating the formation of monomeric or controlled polymeric systems. We also present magnetic studies which indicate that the magnetic interactions are either very weak or antiferromagnetic in the present systems.

## Results and discussion

Initially we carried out the simple reaction of copper(II) nitrate with bipy and HDCI. The product **1** could be grown as large prismatic crystals. The IR spectrum revealed that HDCI was indeed included in this compound. However, the cyano stretch frequency at 2239 cm<sup>-1</sup> indicated that the HDCI is not deprotonated in this complex (cyano stretch appears as a doublet at 2245 and 2258 cm<sup>-1</sup> for HDCI and at  $\approx$ 2224 cm<sup>-1</sup> for DCI<sup>-</sup>).

**Table 1** Significant bond lengths (Å) and bond angles (°) in (a) complex **1** and (b) complex **2**; standard deviations are provided in parentheses

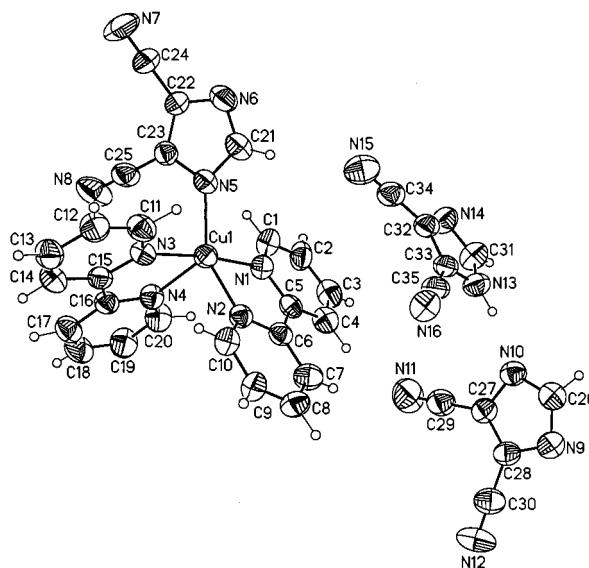
(a)			
Cu–O(51)	2.078(3)	Cu–N(2)	2.032(3)
Cu–O(52)	2.639(4)	Cu–N(3)	2.008(4)
Cu–N(1)	1.980(4)	Cu–N(4)	2.185(3)
O(51)–Cu–N(1)	92.5(1)	N(1)–Cu–N(3)	176.7(1)
O(51)–Cu–N(2)	161.5(1)	N(1)–Cu–N(4)	104.2(1)
O(51)–Cu–N(3)	88.1(1)	N(2)–Cu–N(3)	97.4(1)
O(51)–Cu–N(4)	90.8(1)	N(2)–Cu–N(4)	107.5(1)
N(1)–Cu–N(2)	81.1(1)	N(3)–Cu–N(4)	79.0(1)
(b)			
Cu–N(1)	1.993(2)	Cu–N(4)	2.162(2)
Cu–N(2)	2.043(2)	Cu–N(5)	2.001(2)
Cu–N(3)	2.003(2)		
N(1)–Cu–N(2)	80.79(7)	N(2)–Cu–N(4)	98.83(7)
N(1)–Cu–N(3)	173.04(7)	N(2)–Cu–N(5)	145.28(7)
N(1)–Cu–N(4)	96.08(7)	N(3)–Cu–N(4)	78.29(7)
N(1)–Cu–N(5)	94.16(7)	N(3)–Cu–N(5)	92.01(7)
N(2)–Cu–N(3)	95.92(7)	N(4)–Cu–N(5)	115.88(7)



**Fig. 1** An ORTEP<sup>20</sup> diagram of the molecular structure of complex **1**; 50% probability thermal ellipsoids are indicated. Only one of the disordered positions of the water oxygen atom is shown.

Single crystal analysis revealed the molecular structure shown in Fig. 1 which resembles the structure of  $[\text{Cu}(\text{dmphen})_2(\text{O}_2\text{NO})][\text{CCl}_3\text{CO}_2]\cdot\text{CCl}_3\text{CO}_2\text{H}$  (dmphen = 2,9-dimethyl-1,10-phenanthroline),<sup>21</sup> but now incorporates 4,5-dicyanoimidazole; the molecular formula is  $[\text{Cu}^{\text{II}}(\text{bipy})_2(\text{NO}_3)]\text{NO}_3\cdot\text{HDCI}\cdot\text{H}_2\text{O}$ . It is clearly seen that the HDCI does not co-ordinate to the  $\text{Cu}^{\text{II}}$ , but is present because of a hydrogen bond that links its acidic H atom to the unligated  $\text{NO}_3^-$ . The small shift of the cyano stretch frequency with respect to free HDCI appears to be the consequence of the hydrogen-bonding interaction.

Since the initial attempt failed to achieve co-ordination of  $\text{DCI}^-$  to  $\text{Cu}^{\text{II}}$  we tried two other procedures. In the first of these methods we proceeded on the basis that a strongly co-ordinating ligand such as  $\text{NO}_3^-$  in the starting copper salt would hinder the co-ordination of HDCI. Hence we used  $\text{CuSO}_4$  as the precursor material. As reported earlier,<sup>22</sup> a polymeric material containing the sulfate ion precipitated upon addition of bipy. However, using the remaining solution we were able successfully to prepare complex **2** wherein the HDCI is co-ordinated to  $\text{Cu}^{\text{II}}$ . The molecular structure from the single crystal analysis is shown in Fig. 2 and corresponds to the molecular formula,  $[\text{Cu}^{\text{II}}(\text{bipy})_2(\text{DCI})][\text{DCI}^-]\cdot(\text{HDCI})$ . The



**Fig. 2** An ORTEP diagram of the molecular structure of complex **2**; 50% probability thermal ellipsoids are indicated.

significant feature is that the sulfate ion is absent in this complex and the charge balance is maintained by two  $\text{DCI}^-$ , one co-ordinated and the other unco-ordinated to  $\text{Cu}^{2+}$ ; interestingly, a neutral HDCI is also present hydrogen bonded with the latter  $\text{DCI}^-$ . The IR cyano stretch frequency of **2** appears at  $2226\text{ cm}^{-1}$  indicating the formation of  $\text{DCI}^-$ .

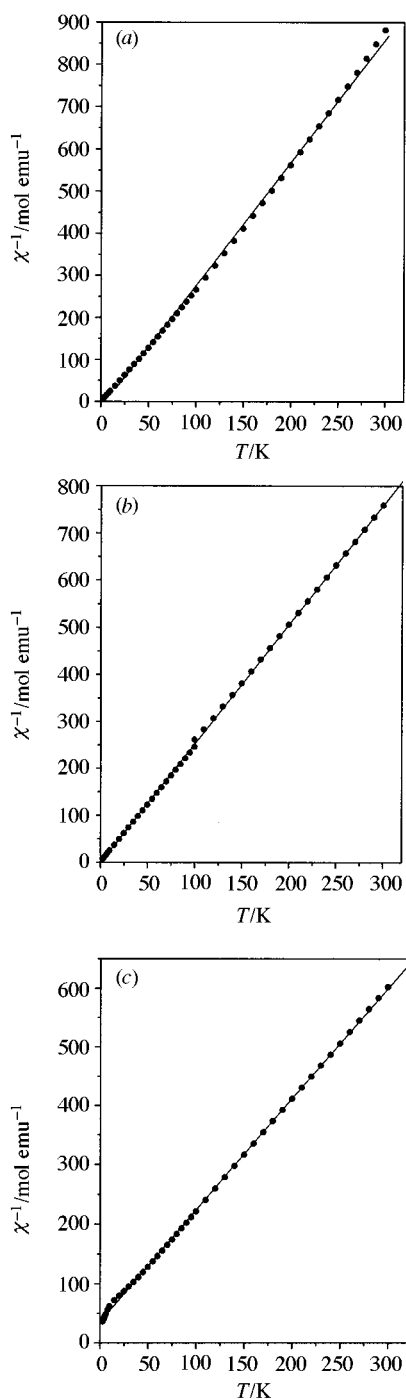
The co-ordination around  $\text{Cu}^{\text{II}}$  in complex **1** is best described as *cis*-distorted octahedral<sup>21,23</sup> with one elongated (2.639 Å) and one normal Cu–O bond and four normal Cu–N bonds [Table 1(a)]. Complex **2** has five N atoms co-ordinated to it [Table 1(b)] and the co-ordination may be described as halfway between square pyramidal and trigonal bipyramidal ( $\tau$  value based on the conventional description<sup>24</sup> of distorted five-co-ordinated geometries is  $\approx 46\%$ ). Examination of the packing diagrams of **1** and **2** shows that the  $\text{Cu}^{\text{II}}\cdots\text{Cu}^{\text{II}}$  distances are all very large, the closest being 7.1 and 8.2 Å respectively.

Since the by-product during the reaction of copper salts with HDCI is the corresponding acid, in the second strategy that we adopted to get HDCI to co-ordinate to  $\text{Cu}^{\text{II}}$  we used an acid buffer (pH  $\approx 4.0$ ) following similar procedures reported earlier.<sup>12</sup> We were not able to grow single crystals of the product **3**. However, the cyano stretch frequency at  $2227\text{ cm}^{-1}$  indicates that  $\text{DCI}^-$  is formed and the stoichiometry from elemental analysis implies that  $\text{DCI}^-$  must be co-ordinated to  $\text{Cu}^{\text{II}}$ . Based on elemental analysis the molecular formula is assigned as  $\text{Cu}^{\text{II}}(\text{bipy})(\text{DCI})_2\cdot 3\text{H}_2\text{O}$ . The peculiar hemispherical bead-like morphology and the low solubility in water and organic solvents displayed by **3** are suggestive of a polymeric structure.

To gain further insight into the local structure around  $\text{Cu}^{\text{II}}$  in complex **3**, we have investigated the ESR spectra of all three complexes as microcrystalline solids and in acetonitrile solution. The relevant characteristics at room temperature are collected in Table 2. The powder ESR spectra of **1** and **2** are very similar with  $g_{\perp} > g_{\parallel} \approx 2.0$ , indicative of an axially compressed geometry and the spin residing in the  $d_{z^2}$  orbital. The line shape and  $g$  values are similar to those found for  $[\text{Cu}(\text{bipy})_2(\text{ONO}_2)]\text{NO}_3\cdot\text{H}_2\text{O}$  which has been described as weakly six-co-ordinated bicapped square pyramidal<sup>25</sup> as well as five-co-ordinated distorted trigonal bipyramidal.<sup>26</sup> The powder ESR line shape of **3** is quite different with  $g_{\parallel} > g_{\perp}$  indicating an axially elongated case with the  $d_{x^2-y^2}$  orbital bearing the spin. Though the solution ESR of **1** did not exhibit any hyperfine structure, the solution spectra of **2** and **3** showed the typical four line hyperfine pattern expected from  $^{65}\text{Cu}$ . This can be taken as indicative of similar co-ordination around  $\text{Cu}^{\text{II}}$  in the last two cases. We believe that as in the case of **2**,  $\text{DCI}^-$  is co-

**Table 2** Room temperature magnetic moment and ESR spectral data of complexes 1–3

Complex	Microcrystals			Solution (CH <sub>3</sub> CN)		
	$\mu/\mu_B$	ESR Linewidth/G	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$	$A_{\text{iso}} (\times 10^{-4} \text{ cm}^{-1})$
1	1.66	145	2.027	2.167	2.109	—
2	1.78	180	2.014	2.172	2.099	ca. 53
3	1.99	205	2.190	2.065	2.095	ca. 56

**Fig. 3** Plots of  $1/\chi$  vs.  $T$  of complexes (a) 1, (b) 2 and (c) 3; the lines are Curie–Weiss law fits. The Weiss constants are +5.4, +0.9 and  $-19.2$  K for 1, 2 and 3 respectively ( $1 \text{ m}^3 \text{ mol}^{-1} = 4\pi \times 10^{-6} \text{ emu mol}^{-1}$ ).

ordinated to Cu<sup>II</sup> in 3 as well. This is further supported by the similar infrared spectra of these two complexes mentioned above. The difference in the ESR spectra of 2 and 3 in the microcrystalline state may arise from the different exchange mechanisms operative in the solid state; the broader signals of 3 could be taken as evidence for strong exchange interactions,

which is supported by the magnetic data presented below. The ESR spectra measured at low temperature (150 K) did not provide any further insight into the structure of the complexes.

Magnetic susceptibilities of these complexes (as powder samples) were measured on a SQUID magnetometer, from 300 to 3 K at a field of 10 kG. The room temperature magnetic moments are indicated in Table 2. The data are plotted as  $1/\chi$  against  $T$  in Fig. 3. It is seen that the behaviours in the case of 1 and 2 [Fig. 3(a) and 3(b) respectively] are very close to Curie paramagnetic. The data could be fit quite well to the Curie–Weiss law with Curie constants of 0.343 and 0.394 and Weiss constants of +5.4 and +0.9 K respectively. The data analysis indicates that the copper(II) ions in both 1 and 2 are coupled by very weak interactions, obviously a consequence of the large Cu...Cu distances in these two complexes. The magnetic susceptibility of 3 also follows a Curie–Weiss law [Fig. 3(c)] with a Curie constant of 0.532 and Weiss constant of  $-19.2$  K; the Curie constant was estimated using the molecular formula derived from elemental analysis. The larger negative Weiss constant of 3 is indicative of moderate antiferromagnetic interactions. This possibly arises from copper(II) interactions through a bridging ligand. In view of the composition, ESR and magnetic data on 3 we speculate that it has a polymeric structure involving the Cu<sup>II</sup>–DCI<sup>−</sup>–Cu<sup>II</sup> structural unit. It is quite possible that, due to the steric repulsions of the cyano groups on the DCI, these chains have strongly non-planar structures. Further, as the ESR data showed, the spin on Cu<sup>II</sup> does not reside in a d orbital that is in conjugation with the  $\pi$  system of DCI<sup>−</sup>. Hence the simple topological models for spin coupling through  $\pi$ -electron pathways may not be realised here. Further work including elucidation of the structure of a co-ordination polymer would be required to extend this scheme for the fabrication of magnetic materials.

## Conclusion

We have presented the structural characterisation of two copper(II) complexes containing 4,5-dicyanoimidazole. Ligation of DCI<sup>−</sup> to Cu<sup>II</sup> is demonstrated for the first time in one of these complexes. A third complex synthesized indicates that DCI<sup>−</sup> may be useful as a bridging ligand for co-ordination polymers. The ESR studies and magnetic susceptibility measurements on the new complexes reveal paramagnetic or weak antiferromagnetic interactions.

## Experimental

### Syntheses

The copper salts were purchased from Loba Chemie (India) whilst 4,5-dicyanoimidazole and 2,2'-bipyridyl were purchased from the Aldrich Chemical Company (USA).

**Complex 1.** The salt Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.10 g, 0.41 mmol) was dissolved in 5 ml of distilled water and warmed. A warm solution of 0.13 g (0.83 mmol) of bipy in 10 ml of ethanol was added. The pale blue copper nitrate turned to dark blue immediately. A hot solution of 0.05 g (0.42 mmol) HDCI in 5 ml of ethanol was added and stirred for 10 min. The solution was allowed to cool and then subjected to slow evaporation. Large blue prism-shaped crystals separated in 2–3 d. They were

**Table 3** Crystallographic data for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Chemical formula	C <sub>25</sub> H <sub>20</sub> N <sub>10</sub> CuO <sub>7</sub>	C <sub>35</sub> H <sub>20</sub> N <sub>16</sub> Cu
Formula weight	636.1	728.3
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.398(2)	9.803(2)
<i>b</i> /Å	13.679(3)	19.666(6)
<i>c</i> /Å	8.837(2)	9.276(1)
<i>a</i> °	100.77(1)	101.45(2)
<i>β</i> °	100.39(1)	100.11(1)
<i>γ</i> °	103.40(2)	99.36(2)
<i>V</i> /Å <sup>3</sup>	1392.4(8)	1689(1)
<i>T</i> /K	293	293
<i>Z</i>	2	2
<i>μ</i> /cm <sup>-1</sup>	8.45 (Mo-Kα)	13.09 (Cu-Kα)
Number of reflections measured	4900	5033
Number of independent reflections	4900	5033
Number of reflections with <i>I</i> > 3σ <sub><i>I</i></sub>	4249	4550
<i>R</i>	0.051	0.034
<i>R</i> '	0.066	0.054

filtered off, washed with cold ethanol and water and dried thoroughly. It was found that complex **1** could be obtained also by treating HDCI with independently prepared [Cu(bipy)<sub>2</sub>]-[NO<sub>3</sub>]<sub>2</sub> [Found (Calc. for C<sub>25</sub>H<sub>20</sub>CuN<sub>10</sub>O<sub>7</sub>): C, 47.20 (47.14); H, 3.15 (3.21); N, 22.03 (22.07)%]. IR (KBr, cm<sup>-1</sup>): 3474, 3074, 2239, 1599, 1444, 1354, 1026 and 777.

**Complex 2.** The salt CuSO<sub>4</sub>·5H<sub>2</sub>O (0.50 g, 2 mmol) was dissolved in 10 ml of water and warmed. A hot solution of 0.63 g (4 mmol) of bipy dissolved in 10 ml of distilled water was added. The pale blue precipitate which formed immediately was filtered out. Its IR spectrum matches well with the one reported<sup>22</sup> for polymeric [{Cu(bipy)(SO<sub>4</sub>)<sub>n</sub>}. A warm solution of 0.24 g (2 mmol) of HDCI in 5 ml of ethanol was added to the filtrate and stirred for 10 min. On cooling a crystalline precipitate formed. This product was recrystallised from an acetonitrile–water mixture to give pale blue platelets. These were filtered off, washed with plenty of water and dried thoroughly [Found (Calc. for C<sub>35</sub>H<sub>20</sub>CuN<sub>16</sub>O<sub>7</sub>): C, 57.72 (57.78); H, 2.75 (2.76); N, 30.79 (30.97)%]. IR (KBr, cm<sup>-1</sup>): 3109, 2226, 1601, 1442, 1109 and 769.

**Complex 3.** The salt Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.10 g, 0.41 mmol) was dissolved in 5 ml of distilled water and warmed; 2 ml of a freshly prepared acetic acid–sodium acetate buffer were added. The solution immediately turned dark blue. A warm solution of 0.13 g (0.83 mmol) of bipy in 10 ml of ethanol was added followed by 0.05 g (0.42 mmol) of HDCI dissolved in 10 ml of warm ethanol. The solution was cooled to room temperature and the solvents were slowly evaporated. Pale blue hemispherical beads separated over a period of 2–3 d. The product was filtered off, washed with water and dried thoroughly. This compound showed very poor solubility in most solvents and all efforts to grow single crystals were unsuccessful [Found (Calc. for C<sub>20</sub>H<sub>16</sub>CuN<sub>10</sub>O<sub>3</sub>): C, 47.28 (47.33); H, 3.18 (2.66); N, 27.58 (27.02)%]. IR (KBr, cm<sup>-1</sup>): 3117, 2227, 1604, 1442, 1300, 1111 and 769.

#### Magnetic and crystallographic studies

Magnetic susceptibility measurements were performed on a SQUID magnetometer (QUANTUM DESIGN MPMS5). Correction for the diamagnetism was estimated using the Pascal constants for complexes **1–3**; values are  $-326.52 \times 10^{-6}$ ,  $-396.80 \times 10^{-6}$  and  $-261.58 \times 10^{-6}$  emu mol<sup>-1</sup> respectively. The ESR studies were carried out on a JEOL JES-FE3X X-

band spectrometer employing 100 kHz modulation. Diphenylpicrylhydrazyl was used for *g* value calibration. Crystal structure data (Table 3) were collected on Philips PW1100 and Enraf-Nonius CAD4 computer-controlled diffractometers using graphite-monochromated Mo-Kα ( $\lambda = 0.71073$  Å) and Cu-Kα ( $\lambda = 1.54178$  Å) radiation respectively. Intensities were corrected for Lorentz-polarisation effects. All non-hydrogen atoms were found using direct method analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process. Refinement proceeded to convergence by minimising the function  $\sum w(|F_o| - |F_c|)^2$ .

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