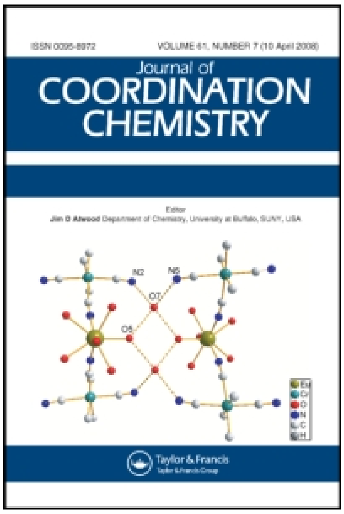

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# Syntheses, properties and X-ray structures of $[Ni(ntb)(N_3)_2]\cdot CH_3OH$ and $[Cu(ntb)(SCN)]Cl\cdot 3CH_3OH$ (ntb = *tris*(2-benzimidazolylmethyl)amine)

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# Syntheses, properties and X-ray structures of $[Ni(ntb)(N_3)_2] \cdot CH_3OH$ and $[Cu(ntb)(SCN)]Cl \cdot 3CH_3OH$ (ntb = *tris*(2-benzimidazolylmethyl)amine)

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The complexes $[Ni(ntb)(N_3)_2] \cdot CH_3OH$ (**1**) and $[Cu(ntb)(SCN)] \cdot 3CH_3OH$ (**2**), where ntb = *tris*(2-benzimidazolylmethyl)amine, were synthesized and their crystal structures determined. Complex **1** is monoclinic, space group $P2_1/c$ space group with $a = 12.777(4)$, $b = 9.928(3)$, $c = 21.623(7)$ Å, $\beta = 103.145(6)°$. The central Ni(II) ion is coordinated to four nitrogen atoms of ntb and two $N_3^-$ ions with slightly distorted octahedral geometry. Complex **2** crystallizes triclinic, space group $P\bar{1}$, with $a = 11.11(2)$, $b = 13.18(3)$, $c = 13.52(3)$ Å, $\alpha = 63.97(3)$, $\beta = 66.32(3)$, $\gamma = 85.55(3)°$. Cu(II) is five-coordinate with an $N_5$ ligand donor set comprising four nitrogen atoms of ntb and a nitrogen-bonded $SCN^-$ ion, and adopts distorted square pyramidal geometry. In the complexes, hydrogen bonds and $\pi \cdots \pi$ interactions are important in stabilising three-dimensional networks. IR, electronic and ESR spectra are discussed, together with magnetic properties at room temperature.

*Keywords: Tris*(2-benzimidazolylmethyl)amine; Nickel(II); Copper(II); X-ray structure; $\pi \cdots \pi$ interactions; ESR; Magnetic properties

## 1. Introduction

Imidazole is a typical heterocylic ligand with nitrogen as the donor atom as well as a component of biologically important molecules. Thus the coordination chemistry of related ligands has been the subject of numerous investigations [1]. Among them, the coordinating behavior of chelating benzimidazole ligands has been studied by several groups [2–6]. *Tris*(2-benzimidazolylmethyl)amine (ntb) is a versatile tripodal and potentially tetradentate ligand containing benzimidazole groups and a number of its complexes are known [7–16]. In this article, we report the structures of two new complexes of ntb with Ni(II) and Cu(II).

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## 2. Experimental

### 2.1. *Starting materials*

The ligand ntb was synthesized using a published procedure [17]. All other starting materials and solvents were of analytical grade and used without further purification.

### 2.2. *[Ni(ntb)($N_3$)$_2$] · $CH_3OH$ (1)*

The ligand ntb (0.1018 g, 0.25 mmol) was dissolved in 10 $cm^3$ of hot methanol and added to a solution of $NiCl_2 \cdot 6H_2O$ (0.0594 g, 0.25 mmol) in 5 $cm^3$ of methanol. To this solution was added an aqueous solution (1 $cm^3$) of $NaN_3$ (0.0163 g, 0.25 mmol). The resulting solution was allowed to stand for several days when green prismatic crystals of complex **1** were obtained. Anal. Calc. for $C_{25}H_{25}N_{13}NiO$ (%): C, 51.57; H, 4.33; N, 31.27. Found: C, 51.42; H, 4.28; N, 31.45.

### 2.3. *[Cu(ntb)(SCN)]Cl · 3$CH_3OH$ (2)*

The ligand ntb (0.1018 g, 0.25 mmol) was dissolved in 10 $cm^3$ of hot methanol and added to a solution of $CuCl_2 \cdot 2H_2O$ (0.0427 g, 0.25 mmol) in 5 $cm^3$ of methanol. To this solution was added a methanol solution (1 $cm^3$) of KSCN (0.0243 g, 0.25 mmol). The resulting solution was allowed to stand for several days when blue prismatic crystals of complex **2** were obtained. Anal. Calc. for $C_{28}H_{33}ClCuN_8O_3SCu$ (%): C, 50.91; H, 5.03; N, 16.96. Found: C, 50.67; H, 4.99; N, 17.08.

### 2.4. *X-ray crystallography*

Suitable single crystals were selected for diffraction analysis. Data collections were performed on a Bruker SMART 1000 CCD diffractometer using Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. Data collection and reduction were performed using the SMART and SAINT software [18]. An empirical absorption correction (SADABS) was applied to raw intensities [19]. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $F^2$ using the SHELXTL program package [20]. Non-hydrogen atoms were refined anisotropically. Details concerning data collection refinement are given in table 1.

## 3. Results and discussion

### 3.1. *Crystal structures*

ORTEP drawings of the two structures are shown in figures 1(a) and 2(a). Selected bond lengths and angles are listed in tables 2 and 3. For **1**, the crystal structure consists of a neutral, mononuclear [Ni(ntb)($N_3$)$_2$] unit and a lattice methanol molecule. Ni(II) is coordinated to four nitrogen atoms of ntb and two $N_3^-$ groups with distorted octahedral geometry. The square plane is completed by N2, N4 and N6 from ntb and N11 from $N_3^-$ with Ni1 lying 0.2825 Å out of the plane. The angles N2–Ni1–N4, N4–Ni1–N6, N6–Ni1–N11, N11–Ni1–N2 are 87.55(10), 90.60(10), 88.92(12) and 89.52(12)°, respectively. The axial positions are occupied by N1 and N8, with N1–Ni1 2.244(3) and

Table 1. Crystallographic data and refinement details for the complexes.

| | **1** | **2** |
|---|---|---|
| Emprical formula | $C_{25}H_{25}N_{13}NiO$ | $C_{28}H_{33}ClCuN_8O_3S$ |
| $M$ | 582.29 | 660.67 |
| Temperature | 293(2) K | 293(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| Unit cell dimensions | $a = 12.777(4)$ Å<br>$b = 9.928(3)$ Å<br>$c = 21.623(7)$ Å<br>$\beta = 103.145(6)^\circ$ | $a = 11.11(2)$ Å<br>$b = 13.18(3)$ Å<br>$c = 13.52(3)$ Å<br>$\alpha = 63.97(3)^\circ$<br>$\beta = 66.32(3)^\circ$<br>$\gamma = 85.55(3)^\circ$ |
| Volume | 2671.0(15) Å$^3$ | 1618(6) Å$^3$ |
| $Z$ | 4 | 2 |
| Calculated density | 1.448 Mg m$^{-3}$ | 1.356 Mg m$^{-3}$ |
| Absorption coefficient | 0.773 mm$^{-1}$ | 0.864 mm$^{-1}$ |
| $F(000)$ | 1208 | 686 |
| Crystal size | 0.30 × 0.25 × 0.20 mm | 0.30 × 0.25 × 0.20 mm |
| Limiting indices | $-14 \le h \le 14$, $-11 \le k \le 9$, $-24 \le l \le 21$ | $-12 \le h \le 11$, $-14 \le k \le 14$, $-13 \le l \le 15$ |
| Reflection collected | 8917 | 5081 |
| Independent reflection | 3846 [$R_{\text{int}} = 0.0404$] | 4456 [$R_{\text{int}} = 0.0920$] |
| Max.and min. transmission | 0.8608 and 0.8013 | 0.8462 and 0.7817 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3846/0/363 | 4456/0/394 |
| GOF | 1.028 | 0.934 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.0375, 0.0794 | 0.0722, 0.1563 |
| $R1$, $wR2$ (all data) | 0.0674, 0.0906 | 0.1371, 0.1838 |
| Largest diff. peak and hole | 0.282 and −0.217 e Å$^{-3}$ | 0.620 and −0.513 e Å$^{-3}$ |

N8–Ni1 2.053(3) Å; the N1–Ni1–N8 angle is 176.35(11)°. Two kinds of weak hydrogen bonds between the imino-nitrogen atom of the benzimidazole ring and an azide nitrogen atom (N10B···N5AD, 2.858 Å; N11B···N7AA, 2.972 Å), give rise to a 1D chain as shown in figure 1(b). In addition, the methanol molecule is also involved in forming hydrogen bonds with ntb (O1AE···N3AK 2.768 Å) and with azide (O1AE···N13A 2.786 Å), giving rise to a two-dimensional layer as shown in figure 1(c). These two-dimensional layers are further strengthened by weak $\pi \cdots \pi$ interactions (*ca* 3.9 Å) between benzimidazole groups.

In **2**, the structure consists of a $[Cu(ntb)(SCN)]^+$ cation, a chloride ion and three lattice methanol molecules. Cu(II) is five-coordinate with an $N_5$ ligand donor set including four nitrogen atoms of ntb and a nitrogen atom of $SCN^-$ to form a distorted square pyramidal geometry. The basal plane is defined by N1, N2 and N4 from ntb and N8 from $SCN^-$ with Cu1 lying 0.2496 Å out of the plane. The bond distance between copper and the tertiary nitrogen N1 is 2.192 Å, which is longer than normal. This elongation is also observed in other metal complexes of ntb [7–9,11]. The axial Cu1–N6 distance (2.145 Å) is considerably longer than the distance between copper and the other two imidazolic nitrogen atoms (Cu1–N2, 1.985 Å; Cu1–N4, 1.967 Å), while, in other trigonal bipyramidal complex of ntb [10], the distances between the central atom and three imidazolic nitrogen atoms are essentially identical. Bond angles at Cu1 fall in the range 81.0–172.3° and are comparable to those of other reported tetragonal pyramidal complex of copper [10,17]. A notable feature of **2** is

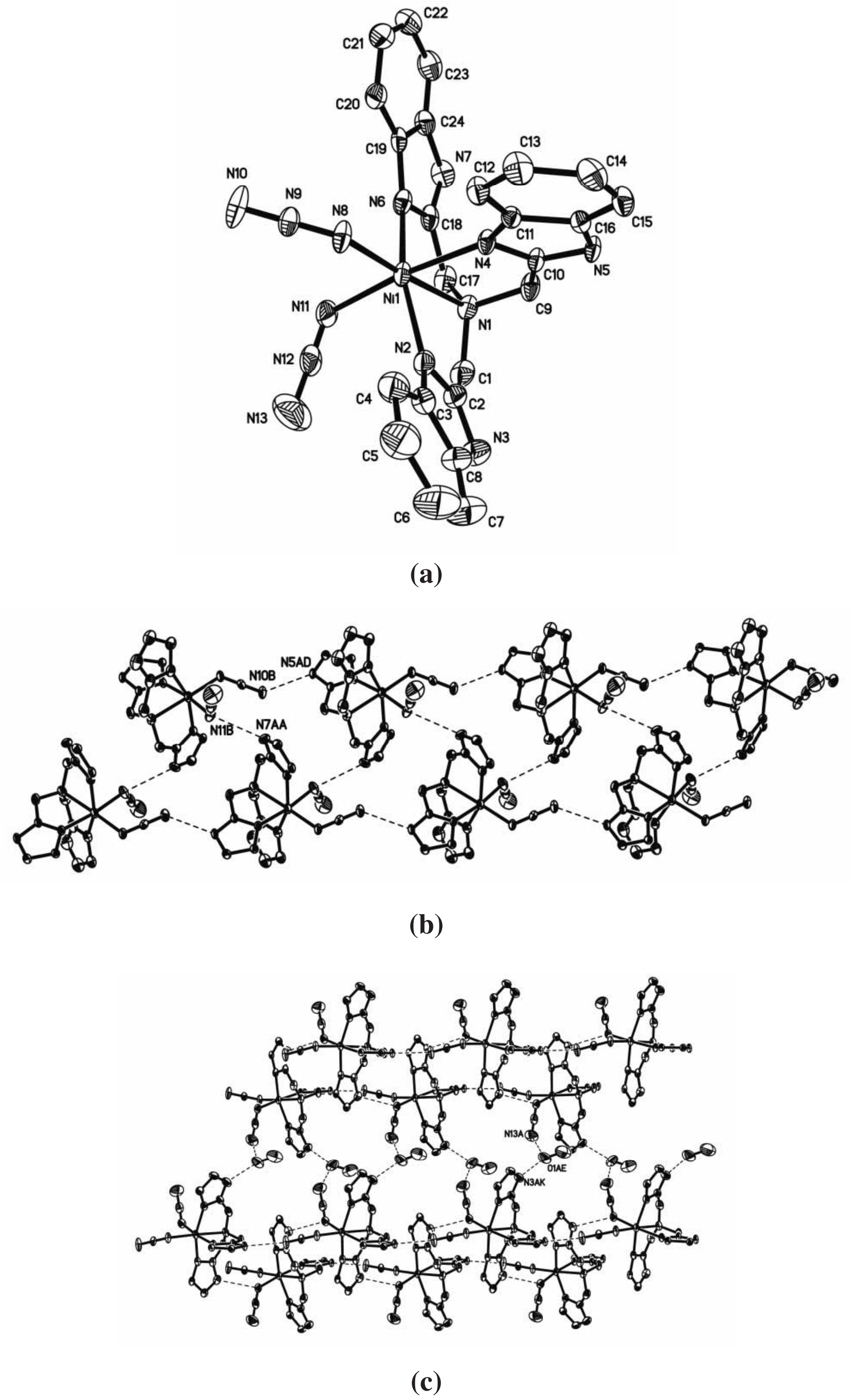

Figure 1. (a) An ORTEP drawing of **1** with the atom numbering scheme; (b) view of the one-dimensional chain built up by hydrogen bonds (four C atoms in each benzimidazole group have been omitted for clarity); (c) view of the two-dimensional layer built up by hydrogen bonds (four C atoms in each benzimidazole group have been omitted for clarity).

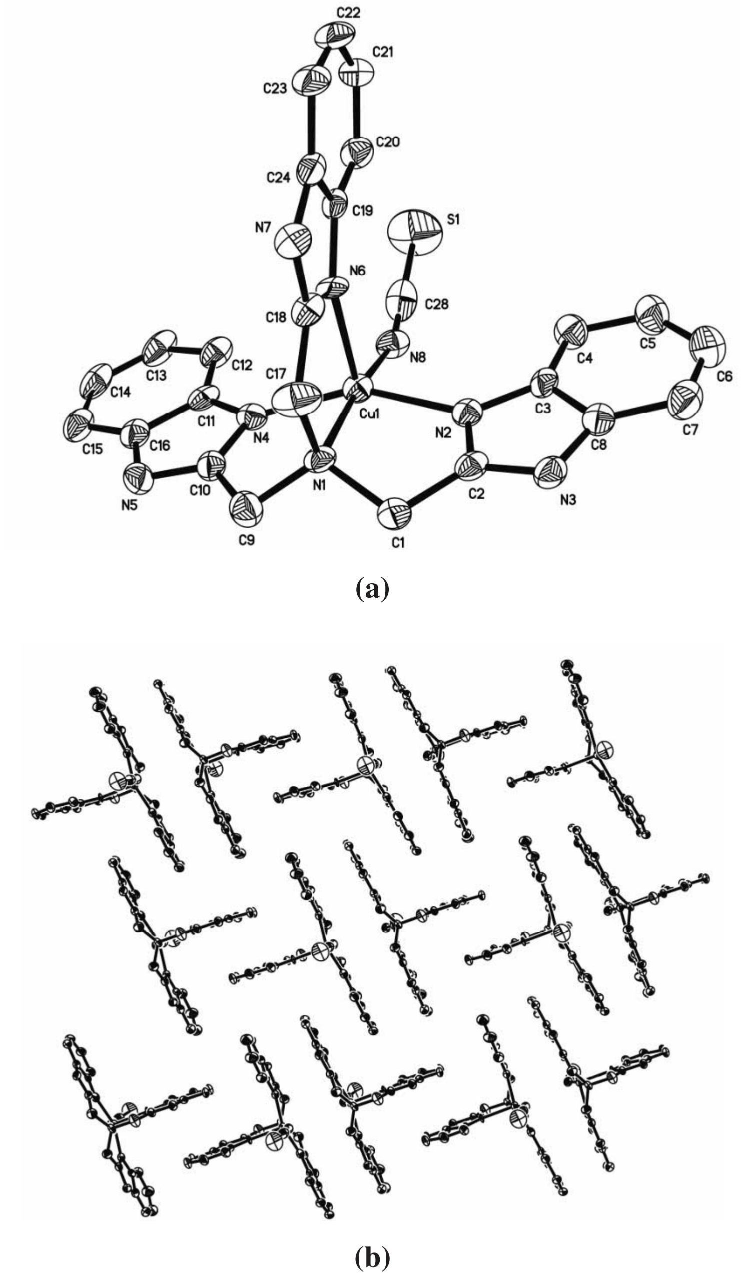

Figure 2. (a) An ORTEP drawing of **2** with the atom numbering scheme; (b) view of the stacking giving rise to $\pi \cdots \pi$ interactions between the benzimidazole groups.

that the T-shaped cations are stacked in a layer with benzimidazole–benzimidazole $\pi \cdots \pi$ interactions (*ca* 3.4–3.5 Å) as shown in figure 2(b); this serves to enhance the stability of the complex. In addition, hydrogen bonds connect lattice methanol and ligand groups (2.730–2.806 Å) as well as lattice methanol and $Cl^-$ ions (2.835–2.914 Å).

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**.

| | | | |
|---|---|---|---|
| Ni(1)–N(8) | 2.053(3) | Ni(1)–N(4) | 2.053(2) |
| Ni(1)–N(6) | 2.094(3) | Ni(1)–N(11) | 2.164(3) |
| Ni(1)–N(2) | 2.062(3) | Ni(1)–N(1) | 2.244(3) |
| N(8)–Ni(1)–N(4) | 96.29(11) | N(8)–Ni(1)–N(2) | 102.26(12) |
| N(8)–Ni(1)–N(6) | 100.10(11) | N(4)–Ni(1)–N(6) | 90.60(10) |
| N(4)–Ni(1)–N(2) | 87.55(10) | N(2)–Ni(1)–N(6) | 157.63(11) |
| N(8)–Ni(1)–N(11) | 92.54(12) | N(4)–Ni(1)–N(11) | 171.10(11) |
| N(2)–Ni(1)–N(11) | 89.52(12) | N(4)–Ni(1)–N(1) | 80.28(10) |
| N(6)–Ni(1)–N(11) | 88.92(12) | N(8)–Ni(1)–N(1) | 176.35(11) |
| N(2)–Ni(1)–N(1) | 78.94(11) | N(6)–Ni(1)–N(1) | 78.77(10) |
| N(11)–Ni(1)–N(1) | 90.91(11) | | |

Table 3. Selected bond lengths [Å] and angles [°] for complex **2**.

| | | | |
|---|---|---|---|
| Cu(1)–N(4) | 1.967(7) | Cu(1)–N(2) | 1.985(7) |
| Cu(1)–N(8) | 1.998(8) | Cu(1)–N(1) | 2.192(7) |
| Cu(1)–N(6) | 2.145(6) | | |
| N(4)–Cu(1)–N(2) | 153.2(2) | N(4)–Cu(1)–N(6) | 100.6(3) |
| N(4)–Cu(1)–N(8) | 98.5(3) | N(2)–Cu(1)–N(8) | 96.3(3) |
| N(2)–Cu(1)–N(6) | 96.4(2) | N(8)–Cu(1)–N(6) | 106.6(3) |
| N(2)–Cu(1)–N(1) | 81.3(3) | N(8)–Cu(1)–N(1) | 172.3(2) |
| N(4)–Cu(1)–N(1) | 81.0(3) | N(6)–Cu(1)–N(1) | 81.0(3) |

### 3.2. *IR and electronic spectra*

IR spectra in the range 3200–3600 $\mathrm{cm^{-1}}$ are characterized by rather broad absorptions associated with the N–H stretch of the benzimidazole ring and the O–H stretch of lattice methanol molecules. The ligand ntb exhibits two absorptions at 1622 and 1588 $\mathrm{cm^{-1}}$, assumed to be due to CN stretching in the imidazole ring. The two complexes exhibit the same two bands, but they are shifted towards to higher wavenumbers than in the free ligand. The lower energy band falls in the range 1590–1607 $\mathrm{cm^{-1}}$ and the higher in the range 1610–1632 $\mathrm{cm^{-1}}$. Characteristic bands of $\mathrm{SCN^-}$ and $\mathrm{N_3^-}$ are observed at 2100 and 2108 $\mathrm{cm^{-1}}$, respectively.

Electronic spectra of both complexes in DMF show very strong absorptions at 216, 241, 272 and 279 nm, assigned to charge-transfer transitions of the ligand. In the visible region, three strong bands can be observed at 1046, 640 and 396 nm for complex **1**, attributed to the *d–d* transitions ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, respectively. Values of $Dq$ and $B$ are 956 and 798 $\mathrm{cm^{-1}}$ respectively, and $\nu_2 = 15{,}391\ \mathrm{cm^{-1}}$, calculated from the values of $\nu_1$ and $\nu_3$ in the usual way [21]. The assignment was checked by comparing the predicted and observed positions of the second band and the agreement is satisfactory. This spectrum is typical of octahedral Ni(II) [22]. Absorption spectra of complex **2** exhibit one maximum at around 716 nm, attributed to *d–d* transitions and in accord with the observed square pyramidal coordination geometry seen in the crystal structure.

### 3.3. *ESR spectra*

X-band ESR spectra of powdered samples of complex **2** at room temperature are typical of $S = 1/2$ spin systems. Three separated $g$ values, $g_x = 2.10$, $g_y = 2.08$ and $g_z = 2.15$

were obtained by simulation. The value $g_{\text{av}} = 2.11$, and the order $g_z > 1/2(g_x + g_y) > g_e$, is indicative of axial symmetry with the unpaired electron residing in the $d_{x^2-y^2}$ orbital.

### 3.4. *Magnetic properties*

Magnetic measurement of **1** at room temperature gave an effective magnetic moment of 3.28 BM, greater than the predicted spin-only value of 2.83 BM for $\text{Ni}^{\text{II}}$ ($S = 1$). To account for the experimental results, it is necessary to consider the ligand field and spin-orbit coupling resulting in the excited state $^3T_{1g}$ or $^3T_{2g}$ mixing with the ground state $^3A_{2g}$. The magnetic behaviour of the present complex can be theoretically modeled using the following equations, (5) and (6)

$$\chi = \frac{2N\beta^2}{3kT} \times \left(2 - \frac{8\lambda}{10Dq}\right)^2$$

$$\mu = \sqrt{8}\left(1 - \frac{4\lambda}{10Dq}\right) = \mu_{\text{so}}\left(1 - \frac{4\lambda}{10Dq}\right)$$

where $\lambda$ is the spin-orbit coupling constant ($\lambda = -315\,\text{cm}^{-1}$ is the free-ion value for Ni(II)), $Dq$ is $956\,\text{cm}^{-1}$ as derived from the electronic spectrum, and the other symbols have their usual meanings. The calculative value ($\mu_{\text{eff}} = 3.21$ BM) is in fairly good agreement with the experimental value and is consistent with the crystal structure. The magnetic measurement of complex **2** is 1.76 BM at room temperature, in accord with the expected spin-only value of 1.73 BM for Cu(II) ($S = 1/2$).

## Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 185550 (**1**) and 185552 (**2**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax:+44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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