

# Synthesis, crystal structures and spectra properties of two new Cu(II) complexes containing thiocyanato anions as ancillary ligand

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As the result of different ratio of reactants, two novel mixed-ligand complexes with different structures have been synthesised and characterised by IR and electronic spectra. In  $[\text{Cu}(\text{L})(\text{NCS})]_2 \cdot 0.5\text{H}_2\text{O}$ , (L = N,N-dimethyl-N'-(pyrid-2-ylmethyl)ethylenediamine), there are two crystallographically independent mononuclear units which are enantiomers. The thiocyanato anions act as terminal ligands. In  $[\text{Cu}_2(\text{L})_2(\mu_2\text{-NCS})_2]_2(\text{ClO}_4)_2$ , two thiocyanato anions bridge two Cu(II) ions in the end-to-end mode.

**Keywords:** crystal structures, N, N-dimethyl-N'-(pyrid-2-ylmethyl)-ethylenediamine, copper complexes

Schiff bases and their complexes containing different central metal atoms have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects,<sup>1–4</sup> structure-redox relationships,<sup>5</sup> catalysis and magnetic properties,<sup>6,7</sup> and their important role in living beings.<sup>8–10</sup> They also act as models for biologically important species.<sup>11–13</sup> The chemistry of copper complexes with multidentate Schiff base and reduced Schiff base ligands has attracted particular attention because copper ions have an important role in many metalloproteins and biomimetic analogues, and have been shown to be very important in the elucidation of the active site of these natural compounds.<sup>14</sup> Furthermore, the thiocyanato-anion is a versatile inorganic ligand in the synthesis of coordination complexes with end-to-end or end-on coordination modes.<sup>15,16</sup> It is used to bridge metal centres to afford a number of discrete, one-, two- or three-dimensional structural assemblies.<sup>17</sup> In this paper, we report the synthesis, IR, UV-vis spectra, and crystal structures of two mixed-ligand Cu(II) complexes with N,N-dimethyl-N'-(pyrid-2-ylmethyl)-ethylenediamine (L) and thiocyanato anion.

## Experimental

### Materials and instruments:

The ligand L was synthesised according to the published procedure.<sup>18</sup> All starting materials were of analytical grade. IR spectra were recorded as KBr discs on a Shimadzu IR – 408 infrared spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region.

The ultraviolet and visible spectra were measured on a Shimadzu UV – 2101 PC spectrophotometer.

**Caution:** Perchlorate salts may be explosive when heated.

**Synthesis of  $[\text{Cu}(\text{L})(\text{NCS})]_2 \cdot 0.5\text{H}_2\text{O}$  1:** The ligand L (0.5 mmol) in methanol (5 mL) was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  or  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol) in methanol (5 mL). The solution was stirred for 10 min and  $\text{NH}_4\text{SCN}$  1.0 mmol in methanol (5 mL) was added. The solution was evaporated to dryness and the resulting powder was dissolved in acetonitrile. Blue single crystals, suitable for X-ray analysis, separated after several weeks. Anal. Calcd for  $\text{C}_{24}\text{H}_{35}\text{Cu}_2\text{N}_{10}\text{O}_{0.50}\text{S}_4$ : C, 39.65, H, 4.85, N, 19.27; Found: C, 39.71, H, 4.78, N, 19.32%. UV-vis ( $\lambda_{\text{max}}$ , nm) ( $\epsilon$ ,  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) (methanol): 628 (222).

**Synthesis of  $[\text{Cu}_2(\text{L})_2(\mu_2\text{-NCS})_2]_2(\text{ClO}_4)_2$  2:** The ligand L (0.5 mmol) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol) were dissolved in methanol (10 mL). The solution was stirred for 1 h, and  $\text{NH}_4\text{SCN}$  (0.25 mmol) in methanol (5 mL) was added. The mixture was stirred for 4 h, and then filtered. The resulting powder was washed with methanol and ethyl ether, then dissolved in 1:1 (v:v) ethanol-water solution. Blue single crystals, suitable for X-ray analysis, separated after several weeks. Anal. Calcd for  $\text{C}_{11}\text{H}_{17}\text{ClCuN}_4\text{O}_4\text{S}$ : C, 33.00, H, 4.2, N, 13.99; Found: C, 33.07, H, 4.18, N, 13.93%. UV-vis ( $\lambda_{\text{max}}$ , nm) ( $\epsilon$ ,  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) (methanol): 630 (180).

### X-ray structures

Crystal data for the two compounds are shown in Table 1. CCDC: 603161 1, 603163 2.

Single crystal X-ray diffraction studies were performed on a Bruker Smart 1000 CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

**Table 1** Data collection and processing parameters for the complexes

Complex	1	2
Empirical formula	$\text{C}_{24}\text{H}_{35}\text{Cu}_2\text{N}_{10}\text{O}_{0.50}\text{S}_4$	$\text{C}_{11}\text{H}_{17}\text{ClCuN}_4\text{O}_4\text{S}$
Formula weight	726.94	400.34
Temperature/K	293(2)	293(2)
Wavelength/nm	0.071073	0.071073
Crystal system	Monoclinic	Monoclinic
space group	$C2/c$	$P2(1)/c$
a (Å)	27.845(10)	6.663(5)
b (Å)	7.302(3)	24.429(19)
c (Å)	32.241(12)	10.289(8)
$\beta$ (°)	97.423(8)	101.120(15)
V (Å <sup>3</sup> )	6500(4)	1643(2)
Z	8	4
$D_{\text{calc}}$ (Mg·m <sup>-3</sup> )	1.481	1.618
Absorption coefficient (mm <sup>-1</sup> )	1.600	1.640
F(000)	3000	820
$\theta$ range for data collection (°)	2.89 – 25.03	2.18 – 25.35
Index ranges	$-30 \leq h \leq 29, -5 \leq k \leq 8, -6 \leq l \leq 38$	$-8 \leq h \leq 4, -29 \leq k \leq 25, -12 \leq l \leq 11$
Reflections collected	6783	5645
Independent reflection ( $R_{\text{int}}$ )	4879 (0.0608)	2782 (0.1592)
Final R indices [ $I > 2\sigma(I)$ ]	$R^1 = 0.0623, wR^2 = 0.1436$	$R^1 = 0.0747, wR^2 = 0.1485$
R indices (all data)	$R^1 = 0.1442, wR^2 = 0.1691$	$R^1 = 0.2057, wR^2 = 0.2022$

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The structures were solved by direct methods and semi-empirical absorption corrections were applied. The non-hydrogen atoms were located by direct phase determination and full-matrix least-squares refinement on  $F^2$ , while the hydrogen atoms for non-water protons were treated using the riding mode. All calculations were carried out using SHELXS-97,<sup>19</sup> and SHELXL-97<sup>20</sup> programs. Further details of the structural analyses are summarised in Table 1. The selected bond distances and angles are listed in Table 2.

## Result and discussion

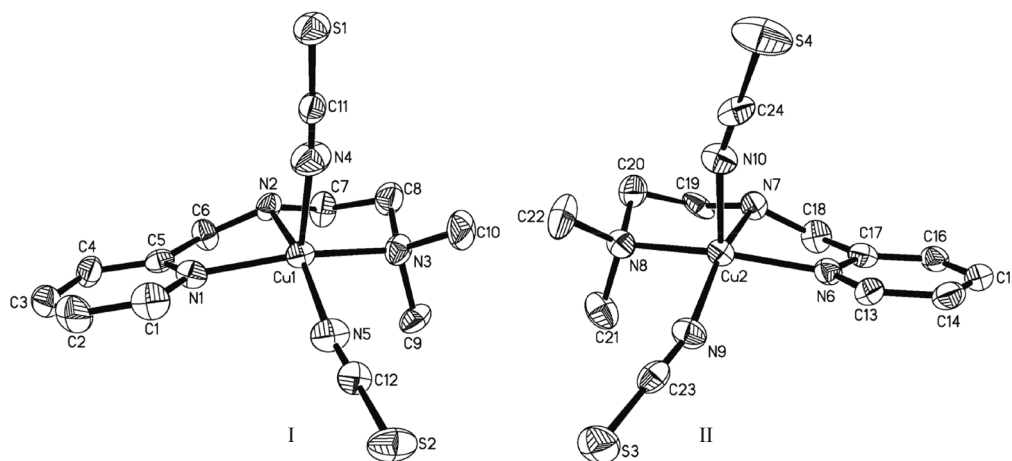
### Crystal structure of the complexes

The crystal structure of **1** consists of two crystallographically independent neutral units which are noted as I and II (Fig. 1). The two molecules coexisting in the crystal are enantiomers to form a racemic complex. The copper centres have distorted square pyramidal geometry by the  $\tau$  parameters of 0.033 for Cu1 and 0.001 for Cu2,<sup>21</sup> respectively. In the structures, the base plane is comprised of three nitrogen atoms of the tridentate ligand and a nitrogen atom of NCS<sup>-</sup>, and the nitrogen atom of another NCS<sup>-</sup> completes the coordination sphere in the apical sites.

In the two molecules, the Cu–N distances are in the range of 1.955 to 2.116 Å in which the distances of Cu–N involving the NCS<sup>-</sup> of apical sites is the longest, and the distances involving tertiary nitrogen atoms are longer than those of the other nitrogen atoms of L. The Cu(II) ion

lies over 0.3082 Å (molecule I) and 0.2867 Å (molecule II) above the base plane, respectively. The NCS<sup>-</sup> groups in the molecules of the complex are linear and also exhibits close to a linear coordination mode (N4–C11–S1/Cu1–N4–C11 = 178.1(10)°/171.1(9)° and N5–C12–S2/Cu1–N5–C12 = 179.5(10)°/170.7(9)° (molecule I), N9–C23–S3/Cu2–N9–C23 = 178.8(10)°/165.0(7)°, N10–C(24)–S(4)/Cu2–N10–C24 = 178.6(10)°/163.2(8)° (molecule II).

The structure of **2** contains one dimer [ $\text{Cu}_2\text{L}_2(\mu_2\text{-SCN})$ ]<sup>2+</sup> together with two ClO<sub>4</sub><sup>-</sup> anions. In the dimeric unit, two Cu(II) ions are bridged by two thiocyanate ligands in an end-to-end fashion with the Cu···Cu separation of 5.535 Å, which is similar to other Cu(II) complexes with double end-to-end thiocyanate bridges.<sup>22</sup> One S atom and one N atom from two different bridging thiocyanate ligands, and three N atoms from one tridentate ligand L coordinate to the Cu(II) ion to complete a distorted square pyramidal geometry by the  $\tau$  parameter of 0.073.<sup>21</sup> In the basal plane, the Cu–N bond lengths are in the range of 1.946(10) to 2.041(11) Å. The bond length of Cu1–N4 (tertiary amine) is the longest, and the distance of Cu1–N1 involving NCS<sup>-</sup> is the shortest. The S of SCN<sup>-</sup> occupies the apical position with the Cu–S distance of 2.878 Å, which is similar to that reported for thiocyanate bridging nickel complexes.<sup>15,22,23</sup> The SCN<sup>-</sup> group is linear with an S–C–N angle of 178.4°. The Cu–S–C and Cu–N–C angles for bridging SCN<sup>-</sup> groups are 94.9 and 162.8°, respectively.

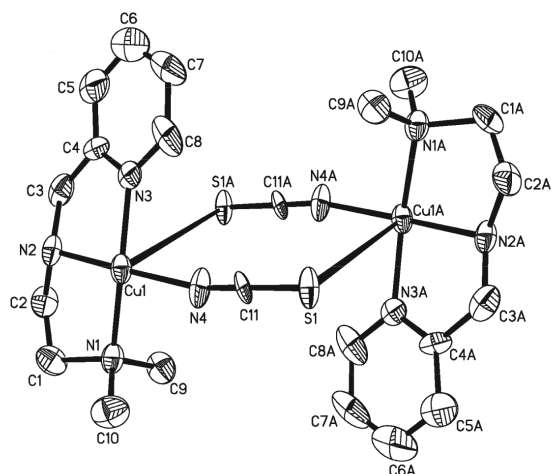


**Fig. 1** Perspective view of the crystallographically independent units of **1** with the atom numbering. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are omitted for simplicity.

**Table 2** Selected bond lengths (Å) and bond angles (°) of the complexes

Complex 1:					
Bond lengths					
Cu1–N5	1.962(9)	Cu1–N2	1.995(6)	Cu1–N1	2.027(6)
Cu1–N3	2.039(6)	Cu1–N4	2.116(10)	Cu2–N9	1.955(8)
Cu2–N6	2.000(6)	Cu2–N7	2.013(6)	Cu2–N8	2.055(6)
Cu2–N10	2.112(9)				
Bond angles					
N5–Cu1–N2	163.4(3)	N5–Cu1–N1	95.0(3)	N2–Cu1–N1	80.6(3)
N5–Cu1–N3	93.8(3)	N2–Cu1–N3	85.0(3)	N1–Cu1–N3	158.0(3)
N5–Cu1–N4	98.3(4)	N2–Cu1–N4	99.3(3)	N1–Cu1–N4	100.6(3)
N3–Cu1–N4	98.0(3)	N9–Cu2–N6	95.2(3)	N9–Cu2–N7	161.4(3)
N6–Cu2–N7	80.9(3)	N9–Cu2–N8	93.4(3)	N6–Cu2–N8	161.2(3)
N7–Cu2–N8	85.6(3)	N9–Cu2–N10	98.1(3)	N6–Cu2–N10	94.7(3)
N7–Cu2–N10	100.4(3)	N8–Cu2–N10	100.6(3)		
Complex 2:					
Bond lengths					
Cu1–N4	1.946(10)	Cu1–N3	1.973(11)	Cu1–N1	2.041(11)
Cu1–N2	1.968(10)	Cu1–S1A	2.878(11)		
Bond angles					
N4–Cu1–N2	174.4(5)	N2–Cu1–N(3)	82.9(5)	N2–Cu1–N1	85.2(4)
N4–Cu1–N3	96.4(5)	N4–Cu1–N(1)	94.0(5)	N3–Cu1–N1	161.6(5)

Symmetry transformations used to generate equivalent atoms: A: 1–x, 1–y, 1–z.



**Fig. 2** A perspective view of **2** with the atom numbering. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are omitted for simplicity.

### Spectroscopic properties

#### IR spectra

Both of the complexes **1** and **2** showed weak bands in the range of 3100–3400  $\text{cm}^{-1}$ , which can be assigned to  $\nu(\text{NH})$ . The bands in the range 2800–3000  $\text{cm}^{-1}$  are assigned to aliphatic C–H stretching vibrations. The  $\nu(\text{C}\equiv\text{N})$  absorption at 2100  $\text{cm}^{-1}$  is consistent with N-coordinated NCS groups. The  $\nu(\text{C}-\text{N})$  absorptions of **1** and **2** appear at 1565 and 1560  $\text{cm}^{-1}$ , respectively. The IR spectra show strong absorption at 1100, 1121  $\text{cm}^{-1}$ , which correspond to the vibration of dissociated  $\text{ClO}_4^-$  ions.

#### UV-Vis spectra

Complex **1** in acetonitrile and **2** in methanol show a broad band centred at about 628 and 630 nm, respectively, which is due to the electronic transitions  ${}^2\text{B}_1 \rightarrow {}^2\text{E}$  and  ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$ .<sup>24,25</sup> The spectra are typical  $d-d$  bands in the square-pyramidal Cu(II) surrounding.

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