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Synthesis and structural characterization of the new quadridentate N_3S-compound di-2-pyridyl ketone thiosemicarbazone and its binuclear copper(II) complexes

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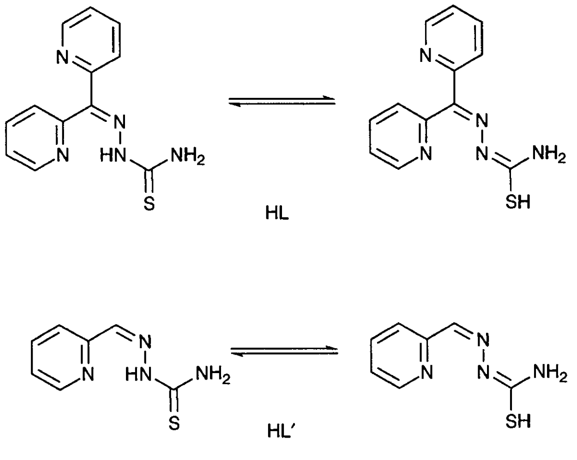
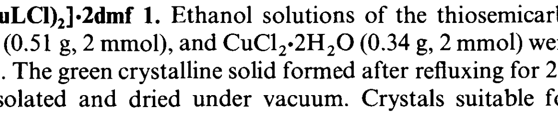
The new quadridentate N_3S-compound di-2-pyridyl ketone thiosemicarbazone (HL) has been characterized by spectroscopic techniques and single-crystal X-ray analysis. The thiosemicarbazone moiety adopts a configuration with N(1) *cis* to N(3). The chelating behaviour of the deprotonated compound (L) has been investigated in two dinuclear copper(II) complexes, $[(CuLCl)_2]\cdot2dmf$ **1** (dmf = dimethylformamide) and $[\{CuL(CN)\}_2]\cdot2MeOH$ **2**. The crystal structures of **1** and **2** were determined. The co-ordination geometry about the copper(II) in both compounds is distorted square pyramidal with one pyridine nitrogen atom, the sulfur, the imino nitrogen, and a chloro or cyano group in the basal plane; a pyridine nitrogen atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

Thiosemicarbazones belong to a large group of thiourea derivatives the biological activities of which are a function of the parent aldehyde or ketone.[1-3] It has been postulated that many α-*N*-heterocyclic carbaldehyde thiosemicarbazones act as tridentate N_2S ligands which bond to iron or copper at the active site of ribonucleotide reductase, a key enzyme in the synthesis of precursors of DNA.[4-6] A number of thiosemicarbazones and their copper and iron complexes have also been found to be active in cell destruction, as well as in the inhibition of DNA synthesis.[7-9] The solution chemistry and crystal structure of pyridine-2-carbaldehyde thiosemicarbazone (HL′),[10] the active precursor complex $[CuL'(O_2CMe)]$,[11,12] as well as many other α-heterocyclic carbaldehyde thiosemicarbazones[13-17] and their metal complexes[18-21] have been studied. The present paper deals with the synthesis and structural analysis of a new tetradentate N_3S-compound, namely di-2-pyridyl ketone thiosemicarbazone $(C_5H_4N)_2C{=}N{-}NHCSNH_2$ (HL), and two copper complexes, $[(CuLCl)_2]\cdot2dmf$ (dmf = dimethylformamide) **1** and $[\{CuL(CN)\}_2]\cdot2MeOH$ **2**, for comparison with related α-heterocyclic carbaldehyde thiosemicarbazones in regard to their steric configuration and chelating ability.



HL



HL′

Experimental

Materials and measurements

Thiosemicarbazide and di-2-pyridyl ketone (Aldrich) were used as received. Elemental analysis data were obtained using a Perkin-Elmer 240 analyser. Infrared spectra were recorded from KBr discs in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer, proton NMR spectra (in $CDCl_3$) on a Bruker Cryospec WM 250 (250 MHz) spectrometer.

Preparations

$(C_5H_4N)_2C{=}NNHCSNH_2$ (HL). Five drops of acetic acid were added to a mixture of thiosemicarbazide (0.91 g, 10 mmol) and di-2-pyridyl ketone (1.84 g, 10 mmol) in refluxing ethanol. The solution was further refluxed for 1 h and on cooling a yellowish white solid was formed. Crystals suitable for analysis were obtained by slow evaporation of a methanol solution in air (Found: C, 55.6; H, 4.4; N, 27.5. Calc: C, 56.0; H, 4.3; N, 27.2%). IR (cm^{-1}): ν(NH) 3130; ν(C=N), 1600, 1587, 1540; ν(C=S) 950. ^{1}H NMR: δ, 8.79 [$N(1)H_2$] (br, 2 H); H(C3, C8), 8.62 (d, 2 H); H(C4, C9), 7.78 (t, 2 H); H(C5, C10), 7.38 (t, 2 H); H(C_6, C_{11}), 7.98 (d, 2 H) and 6.38 [br, 1 H, N(2)H].

$[(CuLCl)_2]\cdot2dmf$ 1. Ethanol solutions of the thiosemicarbazone (0.51 g, 2 mmol), and $CuCl_2\cdot2H_2O$ (0.34 g, 2 mmol) were mixed. The green crystalline solid formed after refluxing for 2 h was isolated and dried under vacuum. Crystals suitable for X-ray analysis were obtained by slowly evaporating a dmf solution in air (Found: C, 41.7; H, 4.3; N, 20.2. Calc.: C, 42.1; H, 4.0; N, 19.6%). IR (cm^{-1}): ν(C=N) 1625, 1598 and 1513.

$[\{CuL(CN)\}_2]\cdot2MeOH$ 2. Ethanol solutions of complex **1** (0.4 g) and NaCN (0.25 g, about 5 mmol) were mixed. The dark green crystalline solid formed after refluxing for 4 h was isolated and dried under vacuum. Crystals of good quality were obtained by evaporating a methanol solution in air (Found: C, 44.9; H, 4.1; N, 21.8. Calc.: C, 44.5; H, 3.7; N, 22.2%). IR (cm^{-1}): ν(C≡N) 2135; ν(C=N), 1626, 1586 and 1508.

Crystallography

The relevant crystal data and structural parameters are summarized in Table 1. The intensities were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max}$ = 55.2°); 60 oscillation frames in the range of 0–180°, exposure 8 min per

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frame for HL; 40 frames, exposure 10 min per frame for complexes **1** and **2**; absorption corrections were made using the ABSCOR program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections.[22]

The structures of all three compounds were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares (on *F*). Hydrogen atoms of the ligand and the solvent molecules were placed in calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

All computations were carried out on a PC-486 computer, using the SHELXTL-PC program package.[23] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[24] Selected bond distances and angles are in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/156.

Results and Discussion

The new Schiff base HL was prepared by the reaction of thiosemicarbazide with di-2-pyridyl ketone in a 1 : 1 molar ratio. It can, in principle, exhibit thione–thiol tautomerism, since it contains a thioamide -HN–C=S functional group.[25–27] The ν(S–H) band at 2570 cm^{-1} is absent from the IR spectrum of the Schiff base, but ν(NH) at *ca.* 3130 cm^{-1} is present, indicating that in the solid state the ligand remains as the thione tautomer. The ^{1}H NMR spectrum in $CDCl_3$ does not show any peak at δ *ca.* 4.0 attributable to the SH proton, suggesting that the thiol tautomeric form is absent even in solution. However, in the presence of metal ions, the Schiff-base compound is rapidly converted into the thiol tautomeric form to facilitate the formation of metal complexes of the deprotonated ligand.

Structure of compound HL

Fig. 1 shows an ORTEP[28] drawing of the molecule with the atom numbering scheme. The thiosemicarbazone moiety shows an *E* configuration about both the C(2)–N(3) and C(1)–N(2) bonds as found in most thiosemicarbazides[29–31] and thiosemicarbazones.[32–34] Though non-planar as a whole, the molecule comprises three planar fragments, namely the two pyridine rings I and II plus the thiosemicarbazone moiety III. The mean deviations of sets of atoms from their best planes and the dihedral angles between them are given in Table 3.

The C–S bond distance (Table 2) of 1.682(2) Å agrees very well with those in related compounds, being intermediate between 1.82 Å for a C–S single bond and 1.56 Å for a C=S double bond.[35] The corresponding C(1)–N(2) and C(1)–N(1) [1.365(3), 1.323(4) Å] bond distances are indicative of some double-bond character, in agreement with the resonance forms **b** and **c** in Scheme 1. A comparison of the N(2)–N(3) distance of 1.354(3) Å with the corresponding N–N distances of 1.411(2), 1.395(2) and 1.431(6) Å for unsubstituted thiosemicarbazide,[29] 1-phenyl[30] and 4-phenyl[31]-thiosemicarbazides, respectively, suggests that the canonical form **d** might be important. A similar shortening of the N–N bond was reported for the weighted average distance of 1.372 Å for the thiosemicarbazones except acetone thiosemicarbazone.[36] In contrast to thiosemicarbazides and acetone thiosemicarbazone, heterocyclic carbaldehyde thiosemicarbazones have an extensively delocalized group attached to the imino nitrogen atom N(3). The inclusion of resonance forms involving pyridine ring I in HL would account for the shortening of the N–N distance through extensive electron delocalization. This expectation is supported by the slightly but significantly shortened C(2)–C(7) bond of 1.482(4) Å in pyridine ring I, as compared to C(2)–C(12) 1.495(3) Å in ring II, although the thiosemicarbazone moiety is twisted by 21.6° with respect to ring I. This result is quite similar to that observed for formaldehyde thiosemicarbazone[33] (twist angle 14.6°) and benzamide[37] (twist angle 26°) the non-planarity of which apparently arises from steric strain and possible intramolecular hydrogen bonding. The C(2)–N(3) bond distance of 1.301(3) Å might also be indicative of some single-bond character in accordance with resonance form **d**. The net result would be a small negative charge residing on the pyridine ring nitrogen N(4), which is reported to be important in terms of biological activity.[33,36]

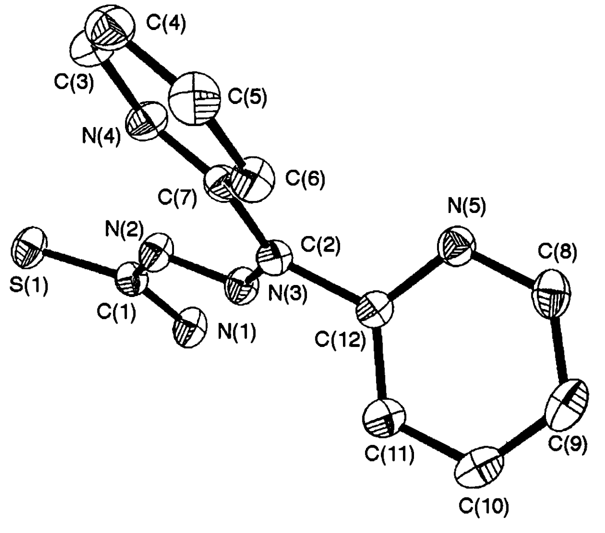
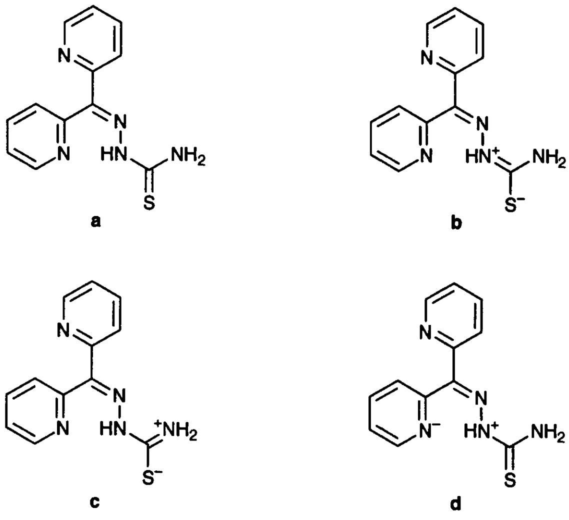


Fig. 1 Molecular structure and atom numbering of $(C_5H_4N)_2C$=NNH-$CSNH_2$ (HL). Thermal ellipsoids are drawn at the 30% probability level



Scheme 1

The compound HL commonly adopts a configuration in which the N(3) atom is *trans* to S(1). Rotation of the H_2NCS fragment by 180° about the C(1)–N(2) bond places the sulfur atom, the imino nitrogen N(3), and the pyridine nitrogen N(4) all on the same side, thus enabling the compound **1** to function as a planar tridentate N_2S anionic ligand as found for most thiosemicarbazones such as pyridoxal thiosemicarbazone,* methyl pyruvate thiosemicarbazone, formaldehyde thiosemicarbazone and their derivatives. It has also been suggested that the

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* Pyridoxal = 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde.

planar mononegative tridentate nature of the active thiosemicarbazones is likely an essential feature for antitumour activity.[1,36]

The three hydrogen atoms attached to amino nitrogen atoms N(1) and N(2) have the potential to form donor hydrogen bonds. The intermolecular hydrogen bonds which link the molecules together in the solid state are shown in Fig. 2, featuring a cyclic arrangement (similar to those in dimeric carboxylic acids and pyridine-4-carbaldehyde thiosemicarbazone) consolidated by hydrogen bonds of the type N(1)–H ··· S(1a) ($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$), which are rather weak since the N ··· S separation 3.473(5) Å is at the upper end of the range summarized by Srinivasan and Chacko.[38] The dimer-like units are linked into an infinite chain by N(1)–H ··· N(5b) ($1 - x, y, \frac{3}{2} - z$) hydrogen bonds; the N ··· N distance of 3.065(5) Å agrees well with that of the NH_2 ··· N(ring) distance reported by Fuller.[39] The H(2A) ··· N(4) distance of 2.031 Å, which is less than a normal van der Waals contact, suggests a possible intramolecular hydrogen bond, and both the N–H ··· N angle of 131° and the H–N ··· N angle of 35° support this hypothesis. The chain conformation is further stabilized by π–π interaction between adjacent pyridyl rings related by a two-fold axis, the centres of which are 3.64 Å apart (Fig. 2).

Structures of the copper(II) complexes

Complexes **1** and **2** have analogous dimeric structures with crystallographically imposed $\bar{1}$ symmetry. The co-ordination geometry about the copper(II) ion is square pyramidal as illustrated in Figs. 3 and 4. The pyridine nitrogen N(4), the imino nitrogen N(3) and the thiosemicarbazone S(1) atoms, together with a chloro or cyanide group, comprise the basal plane, whereas the apical position is occupied by pyridine nitrogen N(5a) [Cu(1)–N(5a) 2.369(6) for **1** and 2.565(3) Å for **2**] of the symmetry-related half of the dimer. In compound **1**, the basal plane shows appreciable tetrahedral distortion (mean deviation from the best plane > 0.2 Å) which deforms the square-pyramidal co-ordination polyhedron toward trigonal-bipyramidal geometry, as described by structural parameters according to the models of Gillespie[40] and Muetterties and Guggenberger.[41] On the other hand, in **2** the basal plane shows only a very slight tetrahedral distortion, and the copper(II) is displaced 0.189 Å out of the plane towards the pyridine nitrogen N(5a) at the apex of the pyramid. In thiosemicarbazonato complexes of copper(II) with the empirical formula [Cu(NS)X], where the ligand NS is pyruvate thiosemicarbazone,[16] pyridoxal thiosemicarbazone[18] or pyridine-2-carbaldehyde thiosemicarbazone[11] and X is bromide or chloride, dimeric structures are also present; however, the apical position is always occupied by a halide[18] or sulfur[9,11] ligand which serves as a bridging atom instead of the pyridine nitrogen atom. The bond lengths in the basal plane for **1** and **2** (Table 2) agree well with those generally found in copper(II) complexes containing thiosemicarbazone derivatives which act as mononegative tridentate ligands.[11,16,18,42–44] It has also been suggested that the strong co-ordinating ability of the basal ligand X weakens the interaction of the metal with the axial ligand and thus leads to a less distorted square geometry about the copper(II). This is supported by the observed bond angles at the copper atom (Table 2) and the least-squares planes data (Table 3). In **2** the stronger electron-withdrawing ability of CN^-, as compared to Cl^- in **1**, significantly weakens the binding of the metal to the axial ligand. The extent of planarity of the basal plane in **1** and **2** is also supportive of the same conclusion. In fact, the apical co-ordination site of **2** is very soft [Cu(1)–N(5a) 2.565(3) Å] and may well be omitted in a simplified bonding description.

While the thiosemicarbazone moiety in free HL shows an *E* configuration about both C(2)–N(3) and C(1)–N(2), the copper(II) complexes have the *E* configuration about C(2)–N(3) but a *Z* configuration about C(1)–N(2) with the donors placed on the same side. The data in Table 2 show that all the bond distances in the side chain are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire moiety. Examination of the structural data for thiosemicarbazones and their copper(II) complexes,[44,45] as well as other related systems,[46–51] has shown that the N(1)–C(1) and C(1)–S(1) bonds in L^- are longer than those in the neutral form HL (1.34 *vs.* 1.31 Å and 1.73 *vs.* 1.71 Å on

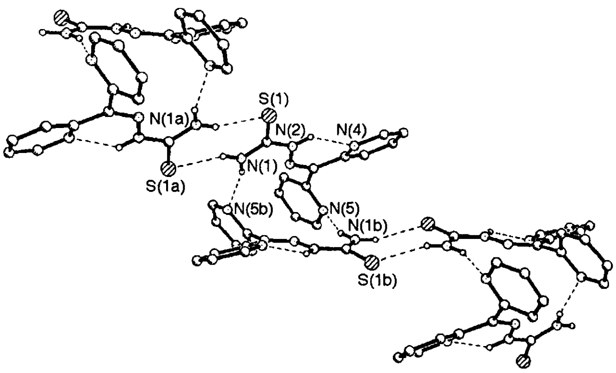

Fig. 2 Hydrogen-bonding scheme showing an infinite chain in the crystal structure of HL. Symmetry codes: a $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; b $1 - x, y, \frac{3}{2} - z$

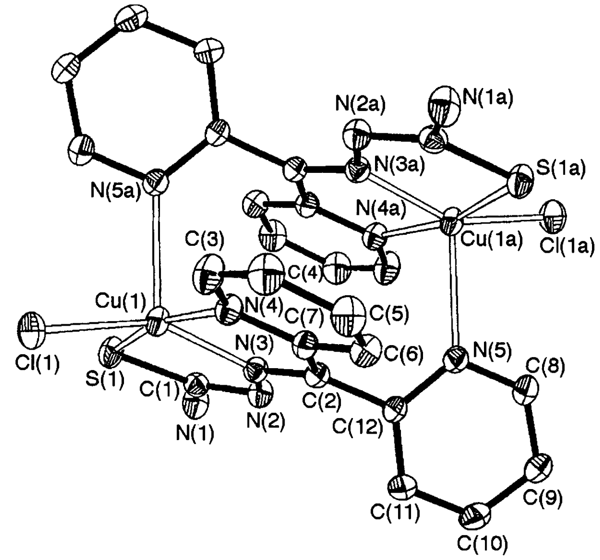

Fig. 3 Molecular structure and atom numbering of $[(CuLCl)_2]\cdot2dmf$ **1**. Thermal ellipsoids are drawn at the 30% probability level

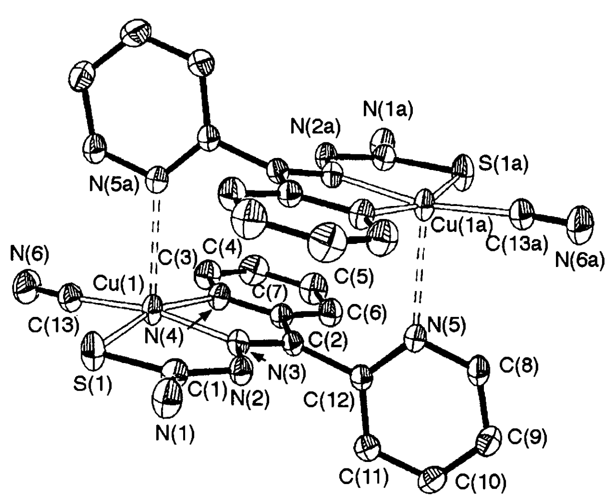

Fig. 4 Molecular structure and atom numbering of $[\{CuL(CN)\}_2]\cdot2MeOH$ **2**. Thermal ellipsoids are drawn at the 30% probability level. The weak metal–axial ligand interaction is represented by broken double lines

Table 1 Crystal data for compound HL and complexes **1** and **2**

	HL	**1**	**2**
Formula	$C_{12}H_{11}N_5S$	$C_{30}H_{34}Cl_2Cu_2N_{12}O_2S_2$	$C_{28}H_{28}Cu_2N_{12}O_2S_2$
M	257.3	956.8	755.8
Colour/habit	Colourless prism	Black needle	Black prism
Size/mm	0.26 × 0.28 × 0.35	0.12 × 0.18 × 0.61	0.13 × 0.24 × 0.35
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a/Å	22.134(2)	9.977(1)	8.325(1)
b/Å	9.034(1)	9.185(1)	9.371(1)
c/Å	15.663(1)	20.540(1)	10.984(1)
α/°			68.88(1)
β/°	126.12(2)	101.31(1)	80.02(1)
γ/°			86.31(1)
U/Å^3	2530.8(13)	1845.3(9)	787.3(4)
Z	8	2	1
D_c/g cm^{-3}	1.351	1.542	1.594
μ	0.245	1.457	1.532
$F(000)$	1072	876	386
Reflections collected	2680	6223	2775
Unique reflections	1956	3500	2775
Observed reflections [$I > 3\sigma(I)$]	1598	3006	2605
R, R'	0.048, 0.050	0.041, 0.064	0.046, 0.060
w^{-1}	$\sigma^2(F)$	$\sigma^2(F) + 0.0006F^2$	$\sigma^2(F) + 0.0001F^2$
Goodness of fit	1.42	1.25	1.39
$\Delta\rho_{max}, \Delta\rho_{min}$/e Å^3	0.17, −0.18	0.36, −0.42	0.46, −0.71

Table 2 Selected bond lengths (Å) and angles (°) for compounds HL, **1** and **2**

	HL	**1**		**2**	
Cu(1)–S(1)		2.243(1)		2.275(1)	
Cu(1)–N(3)		2.008(2)		1.989(2)	
Cu(1)–N(4)		2.003(3)		2.029(2)	
Cu(1)–Cl(1)/C(13)		2.286(1)		1.965(2)	
Cu(1)–N(5a)		2.369(3)		2.565(3)	
S(1)–C(1)	1.682(2)	1.742(3)		1.737(2)	
N(1)–C(1)	1.323(4)	1.334(4)		1.337(3)	
N(2)–N(3)	1.354(3)	1.362(4)		1.364(3)	
N(2)–C(1)	1.365(3)	1.336(5)		1.327(2)	
N(3)–C(2)	1.301(3)	1.297(4)		1.291(2)	
N(4)–C(3)	1.345(4)	1.337(5)		1.322(3)	
N(4)–C(7)	1.347(3)	1.356(4)		1.349(2)	
N(5)–C(8)	1.343(3)	1.339(4)		1.341(3)	
N(5)–C(12)	1.344(2)	1.343(4)		1.395(3)	
C(2)–C(7)	1.482(4)	1.475(4)		1.473(3)	
C(2)–C(12)	1.495(3)	1.495(4)		1.496(3)	
		Cl(1)–Cu(1)–S(1)	96.2(1)	S(1)–Cu(1)–N(3)	83.4(1)
		Cl(1)–Cu(1)–N(3)	150.9(1)	S(1)–Cu(1)–N(4)	162.8(1)
		S(1)–Cu(1)–N(3)	83.9(1)	N(3)–Cu(1)–N(4)	81.0(1)
		Cl(1)–Cu(1)–N(4)	96.2(1)	S(1)–Cu(1)–C(13)	97.1(1)
		S(1)–Cu(1)–N(4)	164.2(1)	N(3)–Cu(1)–C(13)	167.5(1)
		N(3)–Cu(1)–N(4)	80.5(1)	N(4)–Cu(1)–C(13)	96.6(1)
N(3)–N(2)–C(1)	119.6(2)		111.4(2)		112.2(2)
N(2)–N(3)–C(2)	119.9(2)		120.9(2)		121.0(2)
S(1)–C(1)–N(1)	124.6(2)		116.8(3)		117.1(1)
S(1)–C(1)–N(2)	118.5(2)		125.3(2)		125.0(2)
N(1)–C(1)–N(2)	116.8(2)		117.9(3)		117.9(2)
N(3)–C(2)–C(7)	128.1(2)		114.7(2)		115.9(2)
N(3)–C(2)–C(12)	113.0(2)		125.1(3)		124.8(2)
C(7)–C(2)–C(12)	118.8(2)		120.2(3)		118.8(2)

Symmetry code: a $1 - x, -y, 2 - z$ for complex **1** and $-x, -y, 1 - z$ for **2**.

average, respectively), whereas the N(2)–C(1) bond is shorter than that in HL (1.35 *vs.* 1.33 Å on average). Thus the data in Table 2 confirm the importance of the resonance structures for HL and L^- depicted above and show that the electronic flexibility of the thiosemicarbazone system allows it to gain or lose a proton without significantly altering its ligating properties.

The analogous conformation of complexes **1** and **2** is stabilized by favourable π–π interaction between the planar chelating portions of symmetry-related L ligands in the dimeric molecule. In **1** the strongest overlap occurs between N_2-chelate ring V (see Fig. 3 and Table 3 for atoms defining this and other rings) and its counterpart Va and between basal pyridine ring I and *NS*-chelate ring IV; the centre-to-centre distance is 3.38 Å for the first pair of rings and 3.26 Å for the second. The π–π overlap in **2** is comparatively weak, the most significant interaction being that between the pair of rings V and Va at a centre-to-centre separation of 3.81 Å (Fig. 4 and Table 3).

There exist hydrogen-bonding interactions in compound **1** between N(1) and the oxygen atom of the dimethylformamide

Table 3 Least-squares planes, mean deviations of atoms from individual planes, and dihedral angles between pairs of planes

Compound	Atoms defining plane	Mean deviation/Å	Dihedral angle/°				
			I	II	III	IV	V
HL	I N(4), C(3), C(4), C(5), C(6), C(7)	0.003					
	II N(5), C(8), C(9), C(10), C(11), C(12)	0.009	65.8				
	III S(1), C(1), C(2), N(1), N(2), N(3)	0.024	21.6	60.0			
1	I N(4), C(3), C(4), C(5), C(6), C(7)	0.009					
	II N(5), C(8), C(9), C(10), C(11), C(12)	0.013	66.7				
	III S(1), C(1), C(2), N(1), N(2), N(3)	0.030	8.4	75.9			
	IV Cu(1), S(1), C(1), N(2), N(3)	0.030	8.0	62.8	3.3		
	V Cu(1), N(3), C(2), C(7), N(4)	0.019	4.7	64.1	4.8	3.4	
	VI Cl(1), S(1), N(3), N(4)	0.203					
2	I N(4), C(3), C(4), C(5), C(6), C(7)	0.004					
	II N(5), C(8), C(9), C(10), C(11), C(12)	0.003	91.6				
	III S(1), C(1), C(2), N(1), N(2), N(3)	0.026	7.0	91.3			
	IV Cu(1), S(1), C(1), N(2), N(3)	0.029	1.7	93.0	6.2		
	V Cu(1), N(3), C(2), C(7), N(4)	0.013	0.6	91.6	6.4	1.5	
	VI C(13), S(1), N(3), N(4)	0.024	8.9	93.8	3.1	7.6	8.4

solvent molecule. The contact distances are N(1)···O(1) 2.857(3) and N(1)···O(1b) $(2 - x, 1 - y, 2 - z)$ 3.015(3) Å, and the angles around the hydrogen atom are N(1)–H(1A)···O(1) 158.2 and N(1)–H(1b)···O(1b) 138.3°, respectively. In **2** intermolecular hydrogen bonds are also found between N(1) and N(2b) $(-x, 1 - y, 1 - z)$ at 3.005(3) Å, and between N(6) of the CN^- group to O(1) of the MeOH molecule at 2.903(3) Å. The bond angles around the hydrogen atoms are N(1)–H(1b)···N(2) 170.8 and O(1)–H(1c)···N(6) 179.7°.

Acknowledgements

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