Thiosemicarbazones as Co-ordinating Agents. Part 2.* Synthesis, Spectroscopic Characterization, and *X*-Ray Structure of Aquachloro(pyridoxal thiosemicarbazone)manganese(II) Chloride and Aqua(pyridoxal thiosemicarbazonato)copper(II) Chloride Monohydrate†

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The chelating behaviour of neutral (H_2L) and deprotonated pyridoxal thiosemicarbazone has been investigated in two new complexes, $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**) and $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**). Both crystal structures have been determined using single-crystal *X*-ray diffraction methods. Compound (**1**) crystallizes in space group $P2_1/n$, with a = 13.902(4), b = 9.316(1), c = 11.982(3) Å, β = 107.61(2)° and Z = 4; compound (**2**) crystallizes in space group $P\bar{1}$, with a = 9.732(2), b = 9.491(3), c = 7.894(2) Å, α = 95.73(3), β = 101.65(3), γ = 79.30(2)°, and Z = 2. The structures were solved by the heavy-atom method and refined to R values of 0.057 and 0.044 respectively. The co-ordination geometry about the manganese(II) ion, in the monomer (**1**), is based on an uncommon distorted square pyramid, with H_2L together with the H_2O molecule forming the equatorial plane and the Cl atom occupying the axial position. The Cu^{II} ion, in compound (**2**), has a square-planar geometry with phenolic oxygen, imine nitrogen, sulphur, and a water molecule as the basal donors. A sulphur atom of a centrosymmetrically related molecule, occupying the axial position, serves as a bridging element to form a dimeric structure. Both compounds are paramagnetic and their effective magnetic moments are 4.37 for (**1**) and 1.81 for (**2**). The main vibrational bands are also reported and discussed.

As part of a programme concerning the behaviour of mono- and di-(thiosemicarbazone) compounds related to their chelating power and subsequent biological antitumoral activity,[1-3] we have recently undertaken the study of several transition-metal complexes with thiosemicarbazones[4] to extend the knowledge in this research field, particularly with regard to behaviour of the ligands and stereochemistry of complex co-ordination.

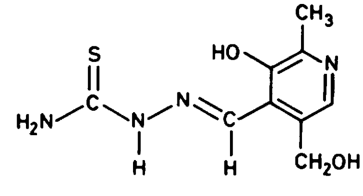
In the present paper we have considered the chelating properties of pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde) thiosemicarbazone (H_2L) and report the synthesis, i.r. spectra, and *X*-ray structural study of the complexes $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**) and $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**).

Experimental

Measurements.—Elemental (C, H, and N) analyses were carried out on a Perkin-Elmer model 240 automatic instrument. I.r. spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. The magnetic susceptibility was measured at 303 K by the Gouy balance technique using $[Ni(en)_3]S_2O_3$ as calibrant. Diamagnetic corrections were made by employing Pascal's constants.[5]

Preparations.—Pyridoxal thiosemicarbazone (H_2L) was prepared by treating thiosemicarbazide with pyridoxal, in its neutral form, in absolute ethanol using the published procedure.[4]

Complex $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**) was prepared by mixing a boiling chloroform–methanol (1:1 v/v) solution of H_2L with a methanol solution of the metal chloride (1:1 molar ratio). The solution was stirred for *ca.* 1 h and then allowed to stand and slowly evaporate until a crystalline brown product was isolated (decomp. >228 °C) (Found: C, 28.3; H, 3.8; N, 14.9. $C_9H_{14}Cl_2MnN_4O_3S$ requires C, 28.1; H, 3.7; N, 14.6%).



H_2L

Complex $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**) was obtained by the reaction of equimolar amounts of H_2L and copper(II) chloride dihydrate in aqueous solution at 80 °C. Even if a 2:1 or 3:1 metal–ligand molar ratio was used, in all cases a dark green solution (*ca.* pH 4) was formed, which after slow evaporation gave green prismatic crystals (decomp. >222 °C) (Found: C, 28.5; H, 3.9; N, 14.9. $C_9H_{15}ClCuN_4O_4S$ requires C, 28.9; H, 4.0; N, 15.0%).

X-Ray Analysis.—The relevant data concerning the crystal-structure analyses are summarized in Table 1.

For both compounds, three-dimensional Patterson maps were computed and the positions of the Mn and Cu atoms determined. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms and the disordered distribution of the alcoholic group in (**1**). Refinements were carried out by full-matrix least-squares cycles using the SHELX-76 system of computer programs.[6] The hydrogen atoms, located on a difference map, were all refined isotropically, except H(38), H(3), H(1) for (**1**) and H(13), H(23), H(21) for (**2**) because their refinement led to a worsening of their bonding geometries.

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* Part 1 is ref. 4.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Experimental data for the crystallographic analyses

Compound	$[Mn(H_2L)(OH_2)Cl]Cl$	$[Cu(HL)(OH_2)]Cl{\cdot}H_2O$
Formula	$C_9H_{14}Cl_2MnN_4O_3S$	$C_9H_{15}ClCuN_4O_4S$
M	384.1	374.3
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.902(4)	9.732(2)
b/Å	9.316(1)	9.491(3)
c/Å	11.982(3)	7.894(2)
α/°	90.0	95.73(3)
β/°	107.61(2)	101.65(3)
γ/°	90.0	79.30(2)
U/Å^3	1 479(1)	700.2(3)
Z	4	2
D_m/Mg m^{-3}	1.75	1.80
D_c/Mg m^{-3}	1.73	1.78
Radiation	Mo-K_α	Cu-K_α
λ/Å	0.710 69	1.541 79
F(000)	780	382
Temp./K	293(1)	293(1)
Crystal size/mm	0.20 × 0.39 × 0.75	0.05 × 0.09 × 0.19
Diffractometer	Siemens-AED	Siemens-AED
μ/mm^{-1}	1.37	5.54
θ range/°	2.5—30	2.5—70
h range	$\bar{18}$—18	$\bar{11}$—11
k range	0—11	$\bar{11}$—11
l range	0—10	0—9
Standard reflections	250	131
Intensity variation	None	None
No. of measured reflections	2 969	2 666
Conditions for obs. reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Max./min. height in final difference synthesis	0.31, $0.\overline{25}$	0.32, $0.\overline{32}$
No. of refined parameters	223	228
No. of unique reflections	1 372	1 736
R	0.0567	0.0439
R'	0.0649	0.0512

Table 2. Atomic fractional co-ordinates (× 10^4) for $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**)

Atom	X/a	Y/b	Z/c
Mn	8 901(1)	828(2)	1 341(1)
Cl(1)	7 449(2)	764(4)	2 039(3)
Cl(2)	8 494(3)	−5 256(3)	−906(3)
S	8 294(3)	547(3)	−815(3)
O(1)	10 073(6)	580(7)	2 790(7)
O(2)	9 260(8)	3 015(8)	1 264(7)
O(3)	9 688(10)	−5 120(14)	3 148(13)
O(31)	10 872(32)	−5 287(41)	4 673(40)
O(32)	10 693(31)	−5 256(37)	2 924(34)
N(1)	7 962(9)	−1 959(12)	−1 854(9)
N(2)	8 832(7)	−2 086(9)	47(7)
N(3)	9 257(7)	−1 515(9)	1 131(7)
N(4)	11 448(7)	−1 250(10)	5 301(8)
C(1)	8 364(8)	−1 282(11)	−874(8)
C(2)	9 769(9)	−2 368(12)	1 898(10)
C(3)	10 321(8)	−1 967(11)	3 098(9)
C(4)	10 735(9)	−3 034(11)	3 922(10)
C(5)	11 279(9)	−2 661(12)	5 004(10)
C(6)	11 086(8)	−174(12)	4 579(10)
C(7)	10 457(8)	−488(12)	3 426(9)
C(8)	11 321(12)	1 311(14)	4 978(12)
C(9)	10 598(12)	−4 648(13)	3 654(13)

Table 3. Atomic fractional co-ordinates (× 10^4) for $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**)

Atom	X/a	Y/b	Z/c
Cu	4 786(1)	−458(1)	7 045(1)
Cl	1 823(2)	−3 265(2)	3 759(2)
S	2 941(2)	596(2)	5 177(2)
O(1)	6 256(5)	−1 363(5)	8 706(6)
O(2)	9 543(5)	3 097(6)	12 891(7)
O(3)	4 317(5)	−2 364(5)	6 405(6)
O(4)	5 513(6)	−4 820(6)	7 704(8)
N(1)	2 336(6)	3 406(6)	5 117(8)
N(2)	4 244(6)	2 652(6)	7 157(7)
N(3)	5 125(5)	1 471(6)	7 856(6)
N(4)	9 378(6)	−1 160(6)	11 743(7)
C(1)	3 221(7)	2 310(7)	5 888(8)
C(2)	6 150(7)	1 775(7)	9 089(8)
C(3)	7 236(6)	721(7)	9 979(8)
C(4)	8 362(6)	1 240(7)	11 200(8)
C(5)	9 397(7)	251(7)	12 022(9)
C(6)	8 361(7)	−1 730(8)	10 645(8)
C(7)	7 232(7)	−755(7)	9 734(8)
C(8)	8 436(8)	−3 289(7)	10 412(9)
C(9)	8 412(7)	2 812(8)	11 527(9)
Cu′	5 214(1)	458(1)	2 955(1)
S′	7 059(2)	−596(2)	4 823(2)

The final positional parameters for the non-hydrogen atoms are given in Tables 2 and 3 for (**1**) and (**2**) respectively. Atomic scattering factors were taken from ref. 7.

All calculations were performed on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) and on the GOULD-SEL 77/22 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma) using the PARST[8] program for the geometrical description of the structure, and ORTEP[9] and PLUTO[10] for the structural drawings.

Results and Discussion

Magnetic Properties.—Both compounds (**1**) and (**2**) are paramagnetic and their effective magnetic moments are 4.37 for (**1**) and 1.81 for (**2**). The value of the copper complex falls in the range usually found for magnetically dilute copper(II) ions[5] and there will be negligible spin–spin coupling characteristic of dinuclear structures.

In the manganese complex the magnetic moment is lower than the 'spin-only' value. Since intramolecular interaction between neighbouring paramagnetic manganese atoms can be excluded, owing to the monomeric nature of the complex, the lowering of the magnetic moment may arise from other sources such as low-symmetry ligand fields and spin–orbit coupling. On the other hand, the observed $\mu_{eff.}$ value indicates the presence of three unpaired electrons ($S = \frac{3}{2}$), which agrees with values previously found in other five-co-ordinated manganese(II) complexes.[11,12]

I.r. Spectra.—A comparison of the main vibrational bands of H_2L, $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**), and $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**) (see Table 4) leads to the following observations. (*i*) The hydrate nature of the complexes is well evidenced by the presence of single, medium intensity absorptions at 3 430 cm^{-1}. (*ii*) In the copper complex, the bands arising from the NH_2 stretching modes, which occur at 3 390 and 3 250 cm^{-1} in the spectrum of free H_2L, are shifted to lower frequency values, while in the manganese complex they are replaced by a single band at 3 230 cm^{-1}. (*iii*) In the manganese complex the ν(N–H) band is shifted to a lower frequency ($\Delta\nu \simeq$ 30 cm^{-1})

Table 4. Selected vibrational bands (cm^{-1}) of H_2L and metal complexes

	$\nu(NH_2)$ $\nu(OH)^a$	$\nu(NH)$	$\nu(NH^+)$ $\nu(OH)^b$	$\nu(C=N)^c$ $\nu(C=C)$	Ring(I)	$\nu(C=N)^d$	Ring(I)	$\delta(OH)^b$	$\delta(NCS)$	$\nu(C=S)$	$\delta(CH)$
H_2L	3 390m 3 250m	3 160m	2 860 (sh)	1 600s	1 570mw	1 540s	1 505 (sh) 1 498s 1 465m 1 430m 1 415m	1 375vs	1 250s 1 220m 1 090s 1 035vs	920m	825ms 815 (sh)
$[Cu(HL)(OH_2)]Cl{\cdot}H_2O$	3 430m 3 320s 3 180m		2 880m 2 850m br	1 670 (sh) 1 640 (sh) 1 610s	1 565ms	1 555 (sh)	1 495s 1 465vs 1 455 (sh) 1 420m br	1 380ms	1 240 (sh) 1 230m 1 205m 1 150ms 1 085m 1 035ms	915mw	835m
$[Mn(H_2L)(OH_2)Cl]Cl$	3 430mw 3 230m	3 130m	2 880m br	1 620s	1 580m	1 560m	1 500s 1 460mw 1 440m 1 410ms	1 375ms	1 245mw 1 210ms 1 160ms 1 075mw 1 025ms	930mw	840mw

[a] Water and hydroxymethyl OH. [b] Alcoholic OH. [c] Ring and chain C=N. [d] Chain C=N.

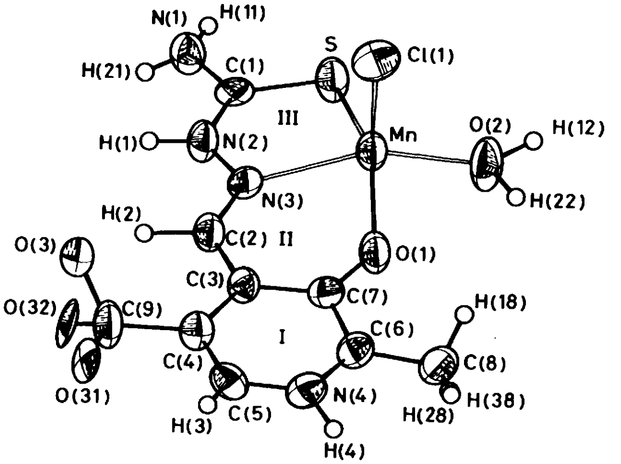

Figure 1. Molecular structure of the complex cation in $[Mn(H_2L)(OH_2)Cl]Cl$ (**1**)

Table 5. Bond distances (Å) and angles (°) for (**1**)

Mn–Cl(1)	2.408(4)	N(2)–C(1)	1.330(12)
Mn–S	2.477(4)	N(3)–C(2)	1.260(13)
Mn–O(1)	2.002(7)	N(4)–C(5)	1.363(15)
Mn–O(2)	2.106(8)	N(4)–C(6)	1.320(14)
Mn–N(3)	2.269(9)	C(2)–C(3)	1.458(14)
S–C(1)	1.709(11)	C(3)–C(4)	1.396(14)
O(1)–C(7)	1.269(13)	C(3)–C(7)	1.430(15)
O(3)–C(9)	1.302(19)	C(4)–C(5)	1.334(15)
O(31)–C(9)	1.307(46)	C(4)–C(9)	1.537(16)
O(32)–C(9)	1.083(45)	C(6)–C(7)	1.424(14)
N(1)–C(1)	1.301(14)	C(6)–C(8)	1.468(17)
N(2)–N(3)	1.362(11)		

O(2)–Mn–N(3)	149.7(3)	S–C(1)–N(1)	120.4(8)
O(1)–Mn–N(3)	80.7(2)	N(3)–C(2)–C(3)	124.7(10)
O(1)–Mn–O(2)	90.5(3)	C(2)–C(3)–C(7)	120.3(9)
S–Mn–N(3)	78.4(2)	C(2)–C(3)–C(4)	119.7(9)
S–Mn–O(2)	93.8(2)	C(4)–C(3)–C(7)	120.0(9)
S–Mn–O(1)	145.4(2)	C(3)–C(4)–C(9)	123.4(10)
Cl(1)–Mn–N(3)	104.4(2)	C(3)–C(4)–C(5)	119.5(9)
Cl(1)–Mn–O(2)	105.9(2)	C(5)–C(4)–C(9)	117.1(10)
Cl(1)–Mn–O(1)	104.1(2)	N(4)–C(5)–C(4)	120.5(10)
Cl(1)–Mn–S	107.6(1)	N(4)–C(6)–C(8)	119.9(10)
Mn–S–C(1)	98.2(3)	N(4)–C(6)–C(7)	118.7(10)
Mn–O(1)–C(7)	134.1(7)	C(7)–C(6)–C(8)	121.4(10)
N(3)–N(2)–C(1)	122.3(8)	C(3)–C(7)–C(6)	117.1(9)
Mn–N(3)–N(2)	115.8(6)	O(1)–C(7)–C(6)	116.4(9)
N(2)–N(3)–C(2)	115.8(8)	O(1)–C(7)–C(3)	126.4(9)
Mn–N(3)–C(2)	128.3(7)	O(32)–C(9)–C(4)	130.0(23)
C(5)–N(4)–C(6)	124.0(9)	O(31)–C(9)–C(4)	105.5(20)
N(1)–C(1)–N(2)	116.4(9)	O(3)–C(9)–C(4)	118.0(13)
S–C(1)–N(2)	123.2(7)		

compared to the free ligand, while in the copper derivative this band disappears as a consequence of the deprotonation of H_2L upon co-ordination. (*iv*) The neutral or deprotonated forms of H_2L in (**1**) and (**2**) respectively only exhibit small differences in the 1 600—700 cm^{-1} region, in agreement with similar SNO tridentate ligand behaviour. In particular, the band at 920 cm^{-1}, which is mainly due to ν(CS), is scarcely influenced by the participation of the sulphur atom in the metal co-ordination.[13,14] Slightly more remarkable shifts are observed for the bands arising from the C=N stretching vibrations (1 600—1 200 cm^{-1}); these shifts agree well with the involvement of the imine nitrogen atom in the co-ordination.[15,16] (*v*) Finally, a medium band at 340 cm^{-1} can be attributed to the ν(Cu–S) stretching mode, in agreement with other metal chelates containing sulphur donors, which usually display ν(M–S) within the range 400—300 cm^{-1}.[17]

Crystal and Molecular Structures.—The molecular structure of compound (**1**) consists of discrete $[Mn(H_2L)(OH_2)Cl]^+$ cations and Cl^- anions. As can be seen from the structure of the cation (Figure 1) and from the values of the bond distances and angles of the co-ordination polyhedron (Table 5), the Mn^{II} ion, five-co-ordinated, has an uncommon approximate square-pyramidal geometry. The phenolic oxygen [O(1)], imine nitrogen [N(3)], sulphur of the Schiff base, and a water molecule [O(2)] constitute the square base (IV), while the chlorine atom occupies the axial site. The basal plane shows a very slight tetrahedral distortion; Mn is 0.59 Å out of the same plane towards the chlorine atom at the apex of the pyramid (Figure 2) and the Mn–Cl bond is nearly perpendicular to the same plane [angle formed by Mn–Cl and normal to the plane = 176.3(1)°]. The Mn–S distance [2.477(4) Å] is longer than the sum of the covalent radii of Mn (1.38 Å) and S (1.04 Å) but is also longer than other terminal Mn–S bonds (2.37—2.46 Å) found in complexes with sulphur-containing chelating ligands.[18] The

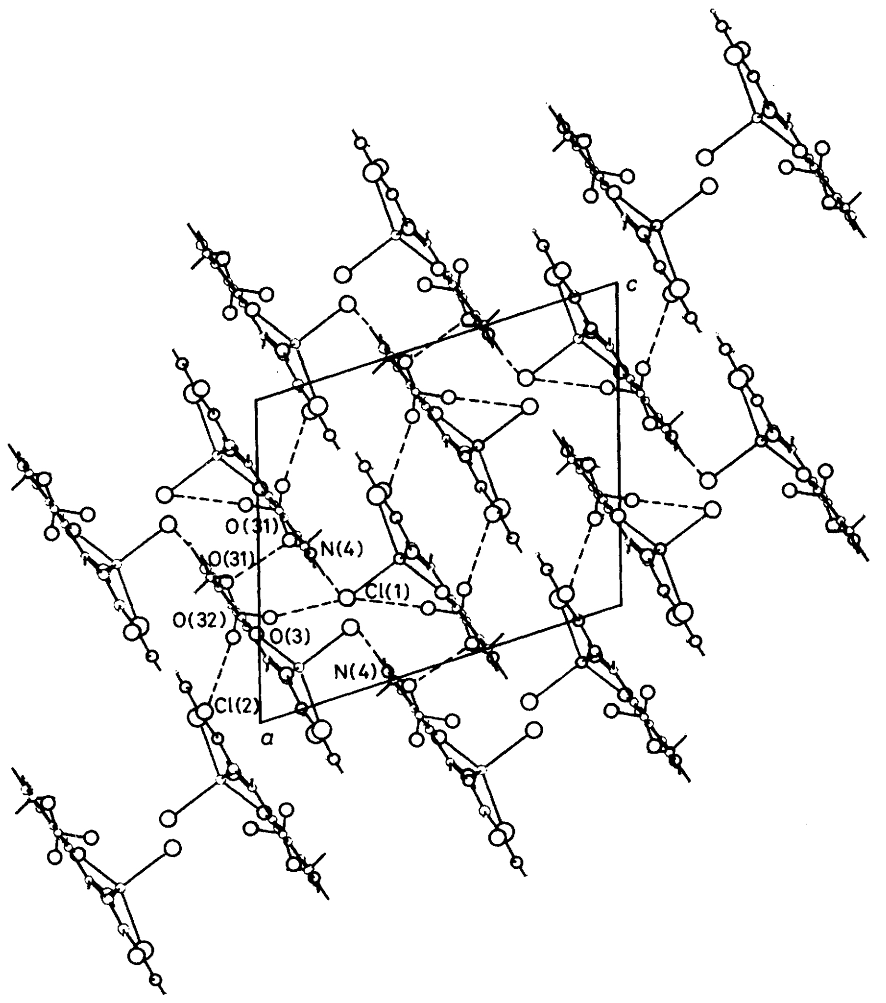

Figure 2. The packing arrangement of (**1**), showing the large out-of-plane displacement of the metal ions

chemistry of manganese complexes with sulphur donor ligands is much less understood than that for oxygen- or nitrogen-donor ligand complexes. Comparisons among other Mn–S distances are very difficult because of differences in co-ordination number and ligand properties.

The value of the Mn–N bond distance [2.269(9) Å] compares fairly well with those found in analogous compounds.[19,20] The axial Mn–Cl bond [2.408(4) Å] is similar to an equatorial distance (2.392 Å) found in a dichloro five-co-ordinate manganese complex,[21] where instead the axial chlorine atom, in a trigonal-bipyramidal geometry, forms a much longer bond (2.525 Å) to the metal. In chloro(*N*-methyl-5,10,15,20-tetraphenylporphyrinato)manganese(II),[22] the Mn–Cl axial bond is shorter (2.295 Å) than that in (**1**). The Mn–O(1)(phenolic) bond is significantly shorter than Mn–O(2)(water). This shortening is probably determined by the negative charge present on the phenolic oxygen, due to the loss of the proton which transfers to N(4).

In compound (**2**) (Figure 3) the Cu atom co-ordinates, in an approximate square-planar environment, a water molecule [O(3)], sulphur, a nitrogen atom [N(3)] from the hydrazinic chain, and the phenolic oxygen [O(1)] of the pyridoxal group. The tetrahedrally distorted co-ordination completes a very elongated square pyramid by a long interaction [3.066(2) Å] between the copper and a sulphur (S′) of a centrosymmetrically related molecule. The copper atom is displaced 0.08 Å from the basal plane (IV) towards S′, which serves as a bridging element to form a dimeric structure (Figure 3). Therefore the molecular structure of (**2**) consists of centrosymmetric dimeric cations and Cl^- anions. Uncommonly the chlorine atom is not co-ordinated to copper. The Cu $\cdots$ Cu distance is 3.549(2) Å. The Cu–N(3) [1.943(6) Å] and Cu–O(3)(water) [1.941(5) Å] distances (Table 6) agree well with those generally found in square-planar copper(II) complexes, while the Cu–O(1)(phenolic) distance [1.875(4) Å], as in compound (**1**), is significantly shorter. The Cu–S [2.226(2) Å] distance, in the co-ordination plane, is similar to that found in other thiosemicarbazone copper(II) compounds.[3,23,24] The Cu–S′ apical bond length [3.066(2) Å], shorter than the value [3.454(3) Å] given by Bushnell and Tsang,[23] is nearly perpendicular to the square plane [N(3)CuS′ 87.4(2), O(3)CuS′ 98.5(2), O(1)CuS′ 86.2(2), and SCuS′ 97.4(1)°]. This finding, according to Taylor *et al.*,[3] may have important implications in understanding the biological activity of the chelate.

In both (**1**) and (**2**) the pyridoxal thiosemicarbazone is tridentate *via* the SNO donating centres; in (**1**) it behaves as neutral (H_2L), while in (**2**) as a monodeprotonated molecule (HL^-). The co-ordinated ligand consists of three rings, one heterocyclic and two chelate. The heterocyclic ring (I) in (**1**) is nearly planar [the largest deviation from the best plane being

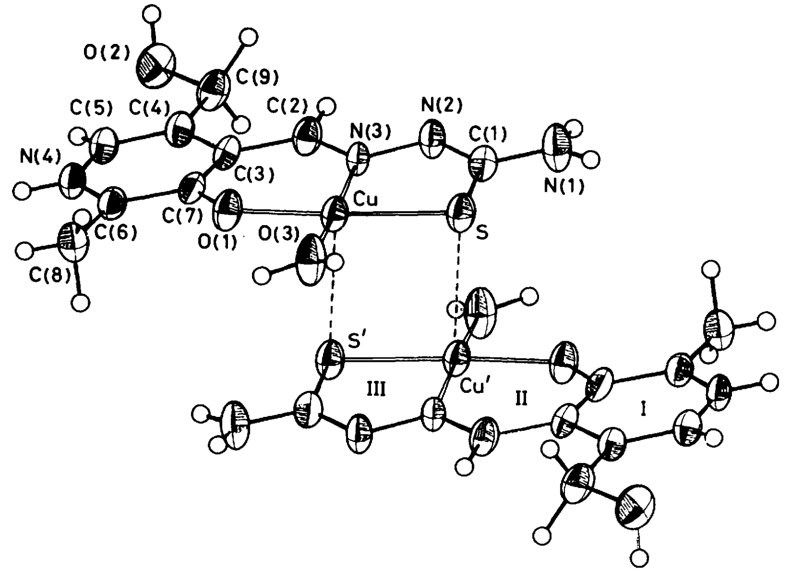

Figure 3. Molecular structure of a centrosymmetric dimeric cation in $[Cu(HL)(OH_2)]Cl{\cdot}H_2O$ (**2**)

Table 6. Bond distances (Å) and angles (°) for (**2**)

Cu-S	2.226(2)	N(4)-C(5)	1.338(9)
Cu-O(1)	1.875(4)	N(4)-C(6)	1.335(9)
Cu-O(3)	1.941(5)	C(2)-C(3)	1.435(8)
Cu-N(3)	1.943(6)	C(3)-C(4)	1.432(8)
S-C(1)	1.719(7)	C(3)-C(7)	1.396(9)
O(1)-C(7)	1.301(8)	C(4)-C(5)	1.350(8)
O(2)-C(9)	1.421(8)	C(4)-C(9)	1.497(10)
N(1)-C(1)	1.333(8)	C(6)-C(7)	1.420(9)
N(2)-N(3)	1.368(7)	C(6)-C(8)	1.463(10)
N(2)-C(1)	1.324(8)	Cu-S'	3.066(2)
N(3)-C(2)	1.298(8)		
O(3)-Cu-N(3)	174.1(2)	N(3)-C(2)-C(3)	124.3(6)
O(1)-Cu-N(3)	94.5(2)	C(2)-C(3)-C(7)	123.6(5)
O(1)-Cu-O(3)	85.4(2)	C(2)-C(3)-C(4)	117.1(5)
S-Cu-N(3)	86.3(1)	C(4)-C(3)-C(7)	119.3(5)
S-Cu-O(3)	93.5(1)	C(3)-C(4)-C(9)	121.6(5)
S-Cu-O(1)	176.3(1)	C(3)-C(4)-C(5)	117.3(6)
Cu-S-C(1)	94.3(2)	C(5)-C(4)-C(9)	121.1(5)
Cu-O(1)-C(7)	126.1(4)	N(4)-C(5)-C(4)	122.1(6)
N(3)-N(2)-C(1)	112.6(5)	N(4)-C(6)-C(8)	120.5(6)
Cu-N(3)-N(2)	121.0(4)	N(4)-C(6)-C(7)	116.8(6)
N(2)-N(3)-C(2)	113.9(5)	C(7)-C(6)-C(8)	122.7(6)
Cu-N(3)-C(2)	125.0(4)	C(3)-C(7)-C(6)	120.1(6)
C(5)-N(4)-C(6)	124.3(6)	O(1)-C(7)-C(6)	114.4(6)
N(1)-C(1)-N(2)	116.1(6)	O(1)-C(7)-C(3)	125.5(6)
S-C(1)-N(2)	125.7(5)	O(2)-C(9)-C(4)	112.3(5)
S-C(1)-N(1)	118.1(5)		

Table 7. Selected dihedral angles (°) and hydrogen bonds (Å)

Compound (**1**)[a]			
(I)—(II)	14.6	N(1) ··· Cl(2)	3.28(1)
(I)—(III)	17.5	N(2) ··· Cl(2)	3.15(1)
(II)—(III)	22.7	N(1) ··· Cl(2^{i})	3.24(1)
(I)—(IV)	2.0	N(4) ··· Cl(1^{ii})	3.12(1)
(II)—(IV)	14.9	O(2) ··· O(32^{iii})	2.85(4)
(III)—(IV)	15.5	O(2) ··· Cl(2^{iii})	2.97(1)
		O(2) ··· O(3^{iii})	2.77(2)
Compound (**2**)[b]			
(I)—(II)	5.7	O(3) ··· O(4)	2.61(1)
(I)—(III)	5.5	O(3) ··· Cl	3.06(1)
(II)—(III)	1.8	N(1) ··· Cl^{i}	3.35(1)
(I)—(IV)	6.4	O(2) ··· Cl^{ii}	3.17(1)
(II)—(IV)	1.9	N(4) ··· Cl^{iii}	3.09(1)
(III)—(IV)	3.7	O(4) ··· N(2^{iv})	2.85(1)
		O(4) ··· Cl^{v}	3.23(1)
		N(1) ··· O(2^{vi})	2.97(1)

[a] i = $\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; ii = $2 - x, -y, 1 - z$; iii = $x, 1 + y, z$.
[b] i = $x, 1 + y, z$; ii = $1 - x, -y, 2 - z$; iii = $1 + x, y, 1 + z$; iv = $x, y - 1, z$; v = $1 - x, -1 - y, 1 - z$; vi = $x - 1, y, z - 1$.

0.03 Å for C(7)] with a slightly flattened 'boat' conformation. The chelate rings are non-planar, the six-membered ring (II) showing a boat distortion, while the five-membered ring (III) is characterized by a bend across the line S ··· N(3) to give a 'envelope' conformation. The dihedral angles between the planes are reported in Table 7. The ligand corresponds to a dipolar ion, owing to the shift of the proton from O(1) to N(4) and can be described as consisting of three systems: the pyridoxal ring (I), the thiourea moiety (V), and the hydrazinic chain (VI). The displacement from coplanarity of these systems is indicated by the dihedral angles (Table 7). The hydrazinic chain C(1)N(2)N(3)C(2) in (**1**) is non-planar and this deviation gives a puckering of the whole ligand. Bond distances and angles in the pyridoxal ring are in agreement with those found in (**2**) and in other compounds containing the same moiety. The bond angle at the protonated pyridinic nitrogen [C(5)N(4)C(6) 124°] is in agreement with other similar compounds.[25] The alcoholic group is disordered and it is statistically distributed in three positions, O(3), O(31), O(32), having 0.60 (not refined, from electron density), 0.18(1), and 0.22(1) occupancy factors respectively.

In the compound (**2**) the six-membered (II) and five-membered (III) chelate rings show 'twist–boat' and 'twist' conformations. Considering the planarity of the organic ligand, the situation is different to that observed in compound (**1**); in fact the whole molecule is nearly planar. This can be ascribed to the deprotonation of the ligand or to the shorter co-ordination distances. The loss of the proton originally bound to N(2) produces a negative charge, which is delocalized in the N(2)-N(3)-C(2) system as indicated by the bond distances, and

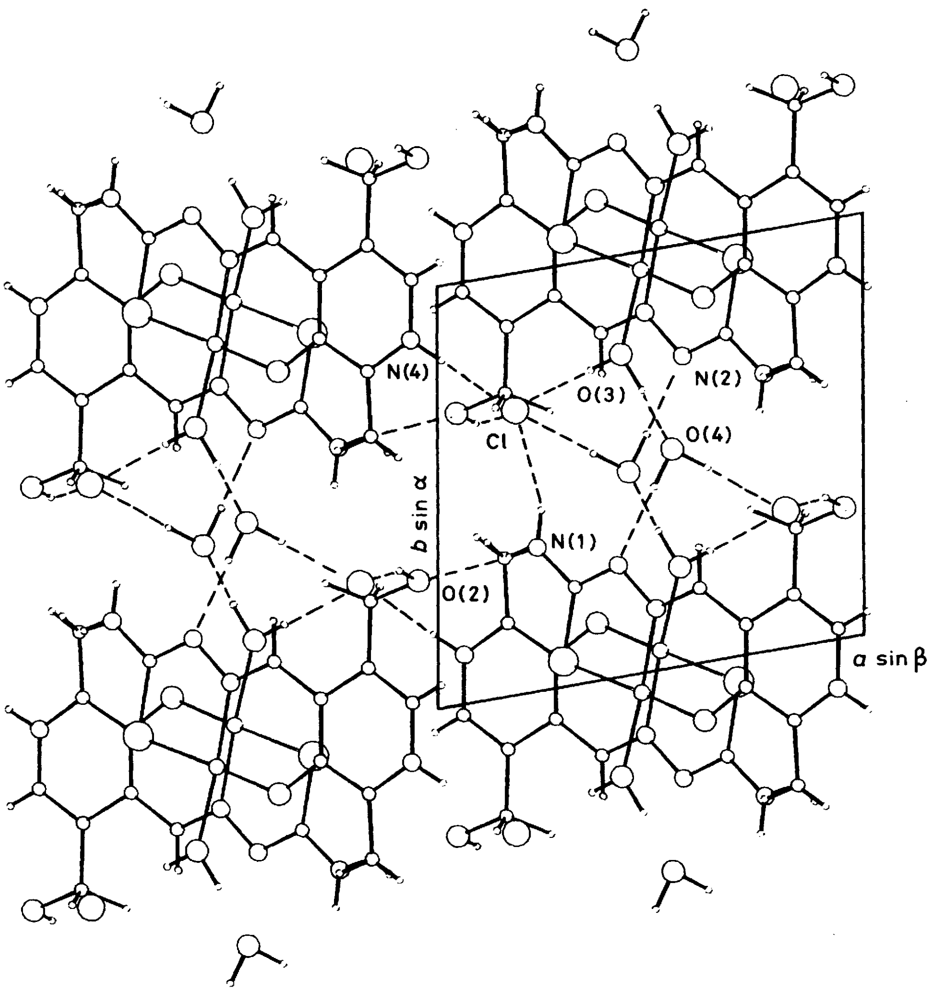

Figure 4. Projection of the structure of (**2**) on the (001) plane

in particular by C(2)–N(3) 1.30(1) Å. In compound (**1**) this distance corresponds fairly well to a double bond [1.26(1) Å]. The dihedral angles between the pyridoxal ring (I), the thiourea moiety (V), and the hydrazinic chain (VI) are reported in Table 7. The S–C distance is nearly the same as that for free H_2L [1.705(9) Å],[4] in contrast to those previously observed.[26–28] The alcoholic group is not disordered.

While the thiosemicarbazone moiety in free H_2L shows an *E* configuration about both the C(2)–N(3) and C(1)–N(2) bonds,[4] (**1**) and (**2**) also show an *E* configuration about C(2)–N(3), but a *Z* configuration about C(1)–N(2); thus the organic molecule acts as tridentate ligand with the ONS donors placed on the same side. In both compounds the unco-ordinated chlorine ions lie in the cavities between the complex cations.

In (**1**) the hydrogen bonds, involving the chloride anions [Cl(2)], the thiourea nitrogens, and a disordered oxygen atom of the alcoholic group, form layers of complexed molecules nearly parallel to the ($\bar{4}$02) planes. These layers are interlinked by other hydrogen bonds involving co-ordinated chlorine [Cl(1)], pyridoxal nitrogen, and alcoholic oxygens (Table 7, Figure 2). Figure 4 illustrates the packing for complex (**2**). The dimers are joined together through Cl • • • H–N, Cl • • • HO, OH_2 • • • N, and NH • • • O hydrogen bonds (Table 7). Centrosymmetrically related dimers, stacked in the *a* direction, are interleaved with layers of chloride anions and water molecules. In both compounds the N–H • • • S hydrogen bonds, which are present in the crystal structure of free H_2L, are not present.

With respect to the relationships between biological activities and molecular structures of the compounds, it can be observed that the planarity of the pyridoxylidene Schiff bases has always been considered to be important in explaining the reactivities either of metal–pyridoxylideneamino acids[29,30] or of thiosemicarbazones. In fact in these last systems the *planar monoanionic tridentate* nature of the molecule appears to be an essential feature for antitumour activity.[31] The planarity of the ligand could allow the facile electron transfer through the extended conjugated system.[30]

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References

1 A. Furst, 'The Chemistry of Chelation in Cancer,' C. C. Thomas, Springfield, Illinois, 1963.
2 S. Padhyé and G. B. Kauffman, *Coord. Chem. Rev.*, 1985, **63**, 127.
3 M. R. Taylor, J. P. Glusker, E. J. Gabe, and J. A. Minkin, *Bioinorg. Chem.*, 1974, **3**, 189.
4 M. Ferrari Belicchi, G. Fava Gasparri, E. Leporati, C. Pelizzi, P. Tarasconi, and G. Tosi, *J. Chem. Soc., Dalton Trans.*, 1986, 2455.

5 J. Lewis and R. G. Wilkins, 'Modern Coordination Chemistry,' Interscience, New York, 1964, p. 406.
6 G. Sheldrick, SHELX-76 System of Computer Programs, University of Cambridge, 1976.
7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
8 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
9 C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
10 W. D. S. Motherwell, PLUTO, University of Cambridge, 1976.
11 L. J. Boucher and V. W. Day, *Inorg. Chem.*, 1977, **16**, 1360.
12 H. Connors, C. A. McAuliffe, and J. Tames, *Rev. Inorg. Chem.*, 1981, **3**, 199.
13 D. M. Wiles and T. Suprunchuk, *Can. J. Chem.*, 1968, **46**, 1865.
14 M. F. Iskander and L. El-Sayed, *J. Inorg. Nucl. Chem.*, 1971, **33**, 4253.
15 R. K. Sharma, R. V. Singh, and J. P. Tandon, *J. Inorg. Nucl. Chem.*, 1980, **42**, 463.
16 S. P. Mital, R. V. Singh, and J. P. Tandon, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3187.
17 S. E. Livingstone and J. E. Oluka, *Transition Met. Chem.*, 1977, **2**, 163.
18 T. Costa, J. R. Dorfman, K. S. Hagen, and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 4091.
19 G. J. Palenik and D. W. Wester, *Inorg. Chem.*, 1978, **17**, 864.
20 C. Pelizzi, G. Pelizzi, G. Predieri, and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349.
21 F. L. Phillips, F. M. Shreeve, and A. C. Skapski, *Acta Crystallogr., Sect. B*, 1976, **32**, 687.
22 O. P. Anderson and D. K. Lavallee, *Inorg. Chem.*, 1977, **16**, 1634.
23 G. W. Bushnell and A. Y. M. Tsang, *Can. J. Chem.*, 1979, **57**, 603.
24 H. G. Petering and G. J. Van Giessen, 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, London, 1966, p. 197.
25 C. S. Singh, *Acta Crystallogr.*, 1965, **19**, 861.
26 M. Matew and G. J. Palenik, *Inorg. Chim. Acta*, 1971, **5**, 349.
27 M. Matew and G. J. Palenik, *J. Am. Chem. Soc.*, 1969, **91**, 6310.
28 A. Corradi Bonamartini, G. Fava Gasparri, M. Ferrari Belicchi, and M. Nardelli, *Acta Crystallogr.*, in the press.
29 S. Capasso, F. Giordano, C. Mattia, L. Mazzarella, and A. Ripamonti, *J. Chem. Soc., Dalton Trans.*, 1974, 2228.
30 S. P. Sudhakara Rao, H. Manohar, and R. Bau, *J. Chem. Soc., Dalton Trans.*, 1985, 2051.
31 G. J. Palenik, D. F. Rendle, and W. S. Carter, *Acta Crystallogr., Sect. B*, 1974, **30**, 2390.

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