Thiosemicarbazones as Co-ordinating Agents. Part 3.† Synthesis, Spectroscopic Characterization, and *X*-Ray Structure of Methyl Pyruvate Thiosemicarbazone Hemihydrate, Chloro(ethyl pyruvate thiosemicarbazonato)copper(II) (Green Form), and Chloro(pyruvic acid thiosemicarbazonato)copper(II) Dihydrate (Blue Form)‡

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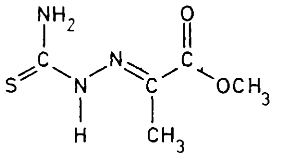
Three new compounds, methyl pyruvate thiosemicarbazone hemihydrate Hmpt·$0.5H_2O$ (**1**), chloro(ethyl pyruvate thiosemicarbazonato)copper(II), [{Cu^{II}(ept)Cl}$_2$] (**2**), and chloro(pyruvic acid thiosemicarbazonato)copper(II) dihydrate, {[Cu^{II}(Hpt)Cl]·$2H_2O$}$_n$ (**3**), have been synthesized and characterized using single-crystal *X*-ray diffraction methods. The following results were obtained: (**1**); space group *C*2/*c*, a = 12.406(1), b = 10.838(1), c = 12.845(1) Å, β = 97.79(1)°, Z = 8, R 0.040, R' 0.048. (**2**), $P2_1/n$, a = 11.785(1), b = 8.202(1), c = 11.057(1) Å, β = 95.70(1)°, Z = 4, R 0.042, R' 0.045. (**3**); $P2_1/c$, a = 8.496(1), b = 18.046(2), c = 7.184(1) Å, β = 109.90(1)°, Z = 4, R 0.031, R' 0.033. In (**1**) the compound is in the fully extended conformation showing an *E* configuration about both the C(2)–N(3) and C(1)–N(2) bonds, but a *Z* configuration about C(2)–C(3) [with respect to donating centres S, N(3), and O(1)]. In (**2**) the organic molecule is hydrolyzed and transesterificated to form chloro(ethyl pyruvate thiosemicarbazonato)copper(II) (green form) (dimeric), while in (**3**) it is hydrolyzed only to form chloro(pyruvic acid thiosemicarbazonato)-copper(II) dihydrate (blue form) (polymeric). The main vibrational bands are also reported and discussed.

Thiosemicarbazones are a large group of organic derivatives whose biological activities are a function of the parent aldehyde or ketone.[1] The solution chemistry and the *X*-ray structure of pyridoxal thiosemicarbazone (H_2L, a nitrogen heterocyclic derivative), spectroscopic properties of its metal complexes, and *X*-ray structure of Mn^{II} and Cu^{II} complexes have recently been studied.[2,3]

The present paper deals with the synthesis, spectroscopic properties, and the structural analysis of an aliphatic thiosemicarbazone, namely methyl pyruvate thiosemicarbazone (Hmpt),



Hmpt

and of the complexes obtained by its reaction with Cu^{II} salts, for comparison with the chelating ability, the steric configuration, and electronic properties of the related nitrogen heterocyclic thiosemicarbazones.

Experimental

Measurements.—Elemental analyses (C, H, N, and S) were performed with a Perkin-Elmer model 240 automatic analyser. I.r. spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. Mass spectra were run on a Varian CH-5 spectrometer [70 eV (*ca.* 1.12×10^{-17} J)].

Preparations.—A mixture of methyl pyruvate (2.04 g, 20 mmol) and thiosemicarbazide (1 : 1 molar ratio) in methanol (50 cm^3) was refluxed under N_2 for *ca.* 2 h. By cooling the light yellow solution an off-white precipitate of the Hmpt ligand (methyl pyruvate thiosemicarbazone) appeared [*m/e* (%): 175 (32.7), 143 (5.8), 116 (100.0), 99 (4.8), 75 (24.0)]. This was filtered off and washed with diethyl ether. Recrystallization of Hmpt from absolute ethanol gave the same product as obtained from methanol solution, as shown by i.r. spectra and melting point (m.p. = 138 °C) (Found: C, 32.9; H, 5.5; N, 22.6; S, 17.3. $C_5H_9N_3O_2S{\cdot}0.5H_2O$ requires C, 32.6; H, 5.5; N, 22.8; S, 17.4%).

The ligand (50 mg) was heated slightly (45 °C) in absolute EtOH (60 cm^3) until dissolution was complete and then was allowed to cool. To this solution under stirring, $CuCl_2{\cdot}2H_2O$ (92.5 mg) (ratio Hmpt: metal = 1:2) dissolved in EtOH (20 cm^3) was added. The green mixture, rather diluted, has a pH of *ca.* 3. Crystals of [{Cu(ept)Cl}$_2$] (Hept = ethyl pyruvate thiosemicarbazone) (green, decomp. > 170 °C) (Found: C, 24.6; H, 3.4; N, 14.8. $C_6H_{10}ClCuN_3O_2S$ requires C, 25.1; H, 3.5; N, 14.6%) and {[Cu(Hpt)Cl]·$2H_2O$}$_n$ (H_2pt = pyruvic acid thiosemicarbazone) (blue, decomp. > 215 °C) (Found: C, 17.4; H, 2.9; N, 14.7. $C_4H_{10}ClCuN_3O_4S$ requires C, 16.7; H, 3.2; N, 14.2%) were obtained by slow evaporation of the solvent. These compounds arise from Cu^{II} complexation with the trans-esterification and hydrolysis products formed as a consequence of the reaction conditions, as shown in the Scheme.

X-Ray Analysis.—Crystal data, a summary of data collection, and details of structure refinement are given in Table 1.

The structures were solved by direct methods using the SHELX 76 system of computer programs[4] for compound (**1**),

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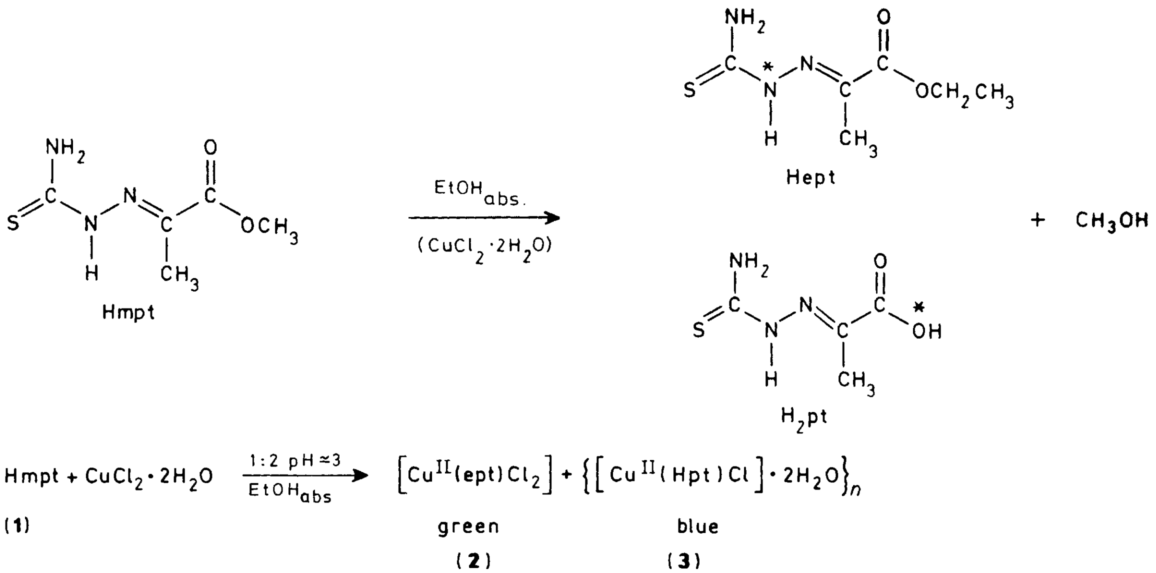
† Part 1 is ref. 2 and Part 2 is ref. 3.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. * Identifies the deprotonation sites

Table 1. Experimental data for the crystallographic analyses*

Compound	Hmpt·$0.5H_2O$, (**1**)	[{Cu(ept)Cl}$_2$], (**2**)	{[Cu(Hpt)Cl]·$2H_2O$}$_n$, (**3**)
Formula	$C_5H_{10}N_3O_{2.5}S$	$C_6H_{10}ClCuN_3O_2S$	$C_4H_{10}ClCuN_3O_4S$
M	184.2	287.2	295.2
Space group	$C2/c$	$P2_1/n$	$P2_1/c$
a/Å	12.406(1)	11.785(1)	8.496(1)
b/Å	10.838(1)	8.202(1)	18.046(2)
c/Å	12.845(1)	11.057(1)	7.184(1)
β/°	97.79(1)	95.70(1)	109.90(1)
U/Å^3	1 711.2(3)	1 063.5(2)	1 035.7(2)
Z	8	4	4
D_m/Mg m^{-3}	1.42	1.78	1.87
D_c/Mg m^{-3}	1.43	1.79	1.89
F(000)	776	580	596
Crystal size/mm	0.10 × 0.10 × 0.33	0.08 × 0.02 × 0.33	0.11 × 0.07 × 0.59
μ/mm^{-1}	3.08	6.92	7.26
θ range/°	2.5—70	2—60	2.5—70
h range	$\overline{15}$—14	$\overline{13}$—13	$\overline{10}$—9
k range	0—13	0—9	0—22
l range	0—15	0—12	0—8
Standard reflection	3 1 2	−5 1 0	2 3 1
Intensity variation	none	none	none
No. of measured reflections	1 788	1 811	2 183
Conditions for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Max./min. height in final difference synthesis/e Å^{-3}	0.11, −0.15	0.39, −0.21	0.27, −0.18
No. of refined parameters	143	167	167
No. of unique reflections	1 226	1 061	1 551
R	0.040	0.042	0.031
R'	0.048	0.045	0.033

* Data common to all three compounds: Cu-K_α radiation (λ = 1.541 79 Å); Siemens-AED diffractometer; T = 293 ± 1 K; unit weights are used.

MULTAN[5,6] for compound (**2**), and three-dimensional Patterson analysis for compound (**3**). Refinements were carried out by full-matrix least-squares cycles. The hydrogen atoms, located on a difference map, were all refined isotropically, except H(3) of water for (**1**).

The final atomic fractional co-ordinates are given in Table 2 for (**1**), (**2**), and (**3**). 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 structure drawings.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

I.r. Spectra.—The main vibrational bands (cm^{-1}) of Hmpt·$0.5H_2O$ (**1**), [{Cu(ept)Cl}$_2$] (**2**), and {[Cu(Hpt)Cl]·$2H_2O$}$_n$ (**3**) are reported in Table 3.

Table 2. Atomic fractional co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s.) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Compound (**1**)			
S	−1 437(1)	1 993(1)	1 498(1)
O(1)	2 188(2)	1 234(3)	−1 659(2)
O(2)	3 572(2)	472(3)	−532(2)
O(3)	0(−)	2 071(5)	7 500(−)
N(1)	−998(2)	2 141(4)	−469(2)
N(2)	393(2)	1 482(3)	760(2)
N(3)	1 012(2)	1 382(3)	−39(2)
C(1)	−657(2)	1 870(3)	527(3)
C(2)	1 994(3)	990(3)	177(3)
C(3)	2 567(3)	921(3)	−783(3)
C(4)	4 214(3)	313(5)	−1 392(3)
C(5)	2 575(3)	629(5)	1 232(3)
Compound (**2**)			
Cu	4 995(1)	7 096(1)	10 018(1)
Cl	4 776(2)	5 496(2)	11 616(2)
S	3 157(2)	7 701(3)	9 475(2)
O(1)	6 744(4)	7 143(7)	10 292(5)
O(2)	8 227(4)	8 272(7)	9 453(5)
N(1)	2 561(7)	9 756(12)	7 712(8)
N(2)	4 481(5)	9 506(8)	8 080(6)
N(3)	5 310(5)	8 746(7)	8 793(5)
C(1)	3 448(6)	9 073(10)	8 340(7)
C(2)	6 375(6)	8 996(10)	8 650(7)
C(3)	7 126(6)	8 067(10)	9 519(7)
C(4)	9 001(7)	7 374(14)	10 335(9)
C(5)	10 173(9)	7 553(17)	9 938(15)
C(6)	6 809(9)	10 097(17)	7 720(10)
Compound (**3**)			
Cu	4 236(1)	2 835(−)	1 428(1)
Cl	2 480(1)	2 052(1)	−666(1)
S	6 028(1)	1 946(1)	3 193(1)
O(1)	3 270(5)	4 985(2)	1 033(6)
O(2)	3 065(3)	3 778(2)	380(4)
O(3)	9 459(5)	757(2)	6 259(7)
O(4)	10 365(5)	3 875(2)	6 784(6)
N(1)	9 007(4)	2 291(2)	5 710(5)
N(2)	7 420(4)	3 280(2)	4 240(5)
N(3)	5 935(4)	3 535(2)	2 981(5)
C(1)	7 601(4)	2 536(2)	4 468(5)
C(2)	5 567(5)	4 231(2)	2 774(6)
C(3)	3 825(6)	4 353(3)	1 268(7)
C(4)	6 671(6)	4 843(2)	3 865(8)

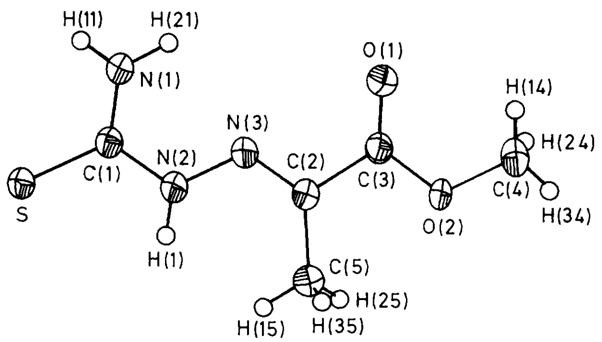


Figure 1. ORTEP view of the molecule of Hmpt with thermal ellipsoids at 50% probability

The bands in the region 3 510—3 150 cm^{-1} are usually attributed to stretching frequencies ν(OH) and ν(NH). It is difficult to assign, specifically, the symmetric and asymmetric vibrations of the amino and imino groups because of numerous hydrogen bonding interactions ($NH_2 \cdots S$, $NH_2 \cdots Cl$, $NH_2 \cdots OH_2$), due also to the presence of unco-ordinated water molecules. However, the narrow bands of medium intensity at 3 510 and 3 460 cm^{-1} present in the spectrum of free Hmpt and in the polymeric complex [(**3**)] respectively may be assigned to ν(OH) from water. The two intense bands arising from the C=N stretching vibrations which occur at 1 625 and 1 610 cm^{-1} in the free ligand undergo slight changes in frequency and intensity caused by complexation. In the spectra of both complexes a considerable shift of the CO frequency (*ca.* 85 cm^{-1}) due to co-ordination at the metal centre is observed. Furthermore other combination bands of –C–C(=O)–O and C=S groups, present in both complexes and in the free ligand, suggest a different degree of interaction with copper due to transesterification and hydrolysis of the ligand. In particular, Hpt in (**3**), in contrast to the other compounds, shows less broad bands in the range 1 300—1 000 cm^{-1} due to complexation. As regards the modes of the C=S group, the more significant ones in order to indicate the sulphur co-ordination are, we think, the bands at *ca.* 900 cm^{-1} which change slightly both in position and intensity.

From the metal–ligand stretching vibrations which are below 400 cm^{-1} it is possible to assign the medium intense band at 320 cm^{-1}, which is present in the complex [{Cu(ept)Cl}$_2$] to ν(Cu–Cl) in agreement with values assigned to analogous bands for other thiosemicarbazones.[11]

Crystal and Molecular Structures.—The structure of (**1**) consists of methyl pyruvate thiosemicarbazone (Hmpt) and water molecules. The compound shows an *E* configuration about both the C(2)–N(3) and C(1)–N(2) bonds, as found in pyridoxal thiosemicarbazone,[2] but the carbonylic oxygen O(1) is *cis* to N(3) and N(1) (Figure 1). So the water molecule, situated on a two-fold axis, hydrogen bonds, tetrahedrally, two thiosemicarbazone molecules *via* the N(1) and O(1) atoms. As in the pyridoxal derivative dimer-like molecules are formed by N–H $\cdots$ S hydrogen bonds across symmetry centres. The Hmpt molecule, though non-planar as a whole, divides up into three planar fragments: the thiosemicarbazide moiety, the N(3)C(2)-C(5)C(3), and C(2)C(3)O(1)O(2) groups. The dihedral angles between these planes are 1.1 and 2.4° respectively. In Table 4 the bond lengths and angles are reported.

As already observed two different chloro complexes were obtained by the reaction of $CuCl_2$ with Hmpt in absolute ethanol (see Scheme). The structure of (**2**), the green product which contains the ethyl pyruvate thiosemicarbazone (ept), is presented in Figure 2. The complex is dimeric and has a crystallographic centre of inversion. The co-ordination geometry about the five-co-ordinate (4 + 1) Cu^{II} ion is square pyramidal. The carbonylic oxygen [O(1)], imine nitrogen [N(3)], sulphur of the Schiff base, and the chlorine atom comprise the basal plane, whereas the apical position is occupied by the Cl′ ($1 - x$, $1 - y$, $2 - z$) of the centrosymmetric group. The basal plane shows a very slight tetrahedral distortion; Cu is 0.13 Å out of the plane, towards the chlorine atom at the apex of the pyramid (Figure 2). The Cu $\cdots$ Cu distance is 3.439(1) Å. In the complex of copper(II) with pyridoxal thiosemicarbazone[3] a dimeric structure is also present, but the chlorine atom is not co-ordinated to the metal and the apical position is occupied instead by S, which serves as the bridging element. The Cu $\cdots$ Cu distance [3.549(2) Å] is greater than that found in the present work. The bond lengths in the basal plane (Table 5) agree well with those generally found in square-planar copper(II) complexes.[3,12–21] The Cu–Cl′ apical bond length [2.819(2) Å] falls within the range of 2.70—3.19 Å found in other metal–chloride bridged systems.[16,22]

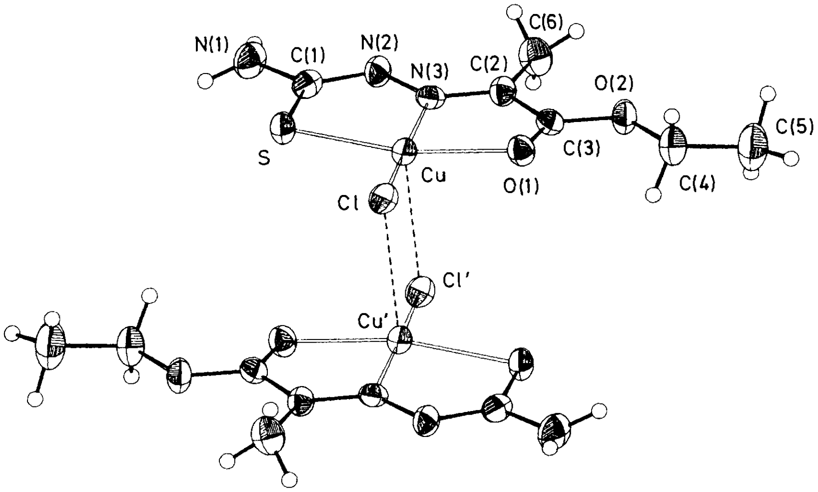


Figure 2. ORTEP drawing of the centrosymmetric [{Cu^{II}(ept)Cl}$_2$], (**2**), dimer with thermal ellipsoids at 40% probability

Table 3. Selected vibrational bands (cm^{-1}) of Hmpt and its copper complex derivatives

	ν(NH), ν(OH)	ν(CH)	ν(C=O)	ν(C=N)	ν(NCS)	ν(NCS), C–C(=O)–O system	ν(C=S)	ν(NCS)	ν(NH), ν(NCS)
Hmpt·0.5H_2O	3 510m, 3 290m,br, 3 230ms, 3 150ms	2 990vw, 2 950w	1 720vs	1 625s, 1 610s	1 435s	1 290vs,br, 1 280 (sh), 1 260vs, 1 210m, 1 165m,br, 1 105vs,br, 1 040 (sh), 1 030 (sh), 1 000w	965m, 860ms	745ms	695ms
[{Cu(ept)Cl}$_2$]	3 440mw, 3 410mw, 3 340ms, 3 300m, 3 180mw, 3 150mw	2 980mw, 2 930w	1 630s	1 605vs, 1 560s	1 400s	1 305vs,br, 1 230m, 1 170vs, 1 150 (sh), 1 105m, 1 005m	900w, 850mw	760m, 750ms	680m
{[Cu(Hpt)Cl]·2H_2O}$_n$	3 460m, 3 390m, 3 290ms,br, 3 260 (sh), 3 220 (sh), 3 180m	3 030w,br	1 650 (sh), 1 640vs,br, 1 630 (sh)	1 610s	1 435ms	1 225s, 1 175m, 1 000w	870m	770ms, 740 (sh)	690m

Table 4. Bond distances (Å) and angles (°) for (**1**)

S–C(1)	1.684(4)	N(2)–N(3)	1.367(4)
O(1)–C(3)	1.208(4)	N(2)–C(1)	1.363(4)
O(2)–C(3)	1.337(4)	N(3)–C(2)	1.285(4)
O(2)–C(4)	1.457(5)	C(2)–C(3)	1.506(6)
N(1)–C(1)	1.325(5)	C(2)–C(5)	1.498(5)
C(3)–O(2)–C(4)	116.6(3)	N(3)–C(2)–C(5)	127.4(3)
N(3)–N(2)–C(1)	118.5(3)	N(3)–C(2)–C(3)	112.2(3)
N(2)–N(3)–C(2)	118.5(3)	C(3)–C(2)–C(5)	120.3(3)
N(1)–C(1)–N(2)	116.8(3)	O(2)–C(3)–C(2)	110.4(3)
S–C(1)–N(2)	119.3(3)	O(1)–C(3)–C(2)	125.6(3)
S–C(1)–N(1)	123.9(2)	O(1)–C(3)–O(2)	124.0(3)

In compound (**3**), the blue product which contains the pyruvic acid thiosemicarbazone (Hpt) as ligand, the Cu^{II} ion has an approximate square-planar environment (Figure 3). The sulphur atom, the imine nitrogen N(3), the carboxylate oxygen O(2) of the Schiff base, and the chlorine atom constitute the square base. In this plane the Cu–N and Cu–Cl distances (Table 6) agree well with those found in (**2**), while the Cu–O(2)(carboxylate) [1.986(3) Å] bond is significantly shorter than Cu–O(1)(carbonylic) [2.054(5) Å] in (**2**). This shortening is probably due to the negative charge present on the carboxylate oxygen. The Cu–S distance is greater than that in (**2**) and the C–S bond is shorter. The tetrahedrally distorted co-ordination completes a very elongated square bipyramid by two long interactions [2.957(1); 3.207(1) Å] between Cu and Cl″ ($x, \frac{1}{2} - y, z + \frac{1}{2}$) and S′($x, \frac{1}{2} - y, z - \frac{1}{2}$) atoms respectively of two centrosymmetrically related molecules. So, chains of co-ordination polyhedra run zig-zag along the crystallographic *c* axis (Figure 3). The Cu^{II} atom deviates by 0.04 Å from the mean plane containing the co-ordinated atoms, toward the apical chlorine. The Cu ··· Cu distance is 3.790(1) Å. The packing is governed by hydrogen-bonded links *via* lattice water molecules (Table 7).

In both compounds (**2**) and (**3**) the ligand is anionic

Table 5. Bond distances (Å) and angles (°) for (**2**)

Cu-Cl	2.236(2)	N(1)-C(1)	1.321(11)
Cu-S	2.245(3)	N(2)-N(3)	1.346(8)
Cu-O(1)	2.054(5)	N(2)-C(1)	1.327(10)
Cu-N(3)	1.975(6)	N(3)-C(2)	1.297(9)
S-C(1)	1.745(8)	C(2)-C(3)	1.455(11)
O(1)-C(3)	1.258(10)	C(2)-C(6)	1.496(15)
O(2)-C(3)	1.318(9)	C(4)-C(5)	1.496(15)
O(2)-C(4)	1.465(11)	Cu-Cl'	2.819(2)
O(1)-Cu-N(3)	80.4(2)	Cu-N(3)-C(2)	116.2(4)
S-Cu-N(3)	84.7(2)	N(1)-C(1)-N(2)	117.9(7)
S-Cu-O(1)	164.3(2)	S-C(1)-N(2)	125.4(6)
Cl-Cu-N(3)	171.0(2)	S-C(1)-N(1)	116.7(6)
Cl-Cu-O(1)	95.0(2)	N(3)-C(2)-C(6)	125.5(7)
Cl-Cu-S	99.0(1)	N(3)-C(2)-C(3)	111.7(6)
Cu-S-C(1)	94.7(3)	C(3)-C(2)-C(6)	122.9(7)
Cu-O(1)-C(3)	109.4(4)	O(2)-C(3)-C(2)	115.7(6)
C(3)-O(2)-C(4)	116.8(6)	O(1)-C(3)-C(2)	121.9(6)
N(3)-N(2)-C(1)	112.2(6)	O(1)-C(3)-O(2)	122.4(6)
Cu-N(3)-N(2)	122.9(4)	O(2)-C(4)-C(5)	106.7(9)
N(2)-N(3)-C(2)	120.7(6)		

Table 6. Bond distances (Å) and angles (°) for (**3**)

Cu-Cl	2.226(1)	N(1)-C(1)	1.301(4)
Cu-S	2.277(2)	N(2)-N(3)	1.358(4)
Cu-O(2)	1.986(3)	N(2)-C(1)	1.355(5)
Cu-N(3)	1.956(3)	N(3)-C(2)	1.291(5)
S-C(1)	1.710(3)	C(2)-C(3)	1.523(6)
O(1)-C(3)	1.224(7)	C(2)-C(4)	1.488(5)
O(2)-C(3)	1.273(6)		
O(2)-Cu-N(3)	80.8(1)	Cu-N(3)-C(2)	117.4(3)
S-Cu-N(3)	85.1(1)	N(1)-C(1)-N(2)	117.4(3)
S-Cu-O(2)	165.6(1)	S-C(1)-N(2)	121.1(3)
Cl-Cu-N(3)	171.7(1)	S-C(1)-N(1)	121.6(3)
Cl-Cu-O(2)	98.8(1)	N(3)-C(2)-C(4)	125.2(4)
Cl-Cu-S	95.5(1)	N(3)-C(2)-C(3)	111.2(3)
Cu-S-C(1)	96.4(1)	C(3)-C(2)-C(4)	123.6(4)
Cu-O(2)-C(3)	113.9(2)	O(2)-C(3)-C(2)	116.3(4)
N(3)-N(2)-C(1)	117.2(3)	O(1)-C(3)-C(2)	117.9(5)
Cu-N(3)-N(2)	119.9(2)	O(1)-C(3)-O(2)	125.8(5)
N(2)-N(3)-C(2)	122.7(3)		

terdentate with an *E*, *Z*, *Z* configuration [with respect to donating centres S, N(3), and O(1), or O(2) for (**3**)]. This results from a rotation of 180° about C(1)-N(2) with respect to the free ligand. In both complexes two five-membered chelate rings are present. In (**2**) these are nearly planar with deviations ranging between 0.001 and 0.049 Å, in (**3**) the deviations are in the range 0.003—0.070 Å. In compound (**2**) the chelate rings are characterized by a fold across the lines N(3) • • • O(1) and N(3) • • • S to give an 'envelope' conformation as appears from puckering parameters [q_2 = 0.064(7), $\varphi = -175.7(6.6)$; q_2 = 0.052(5) Å,

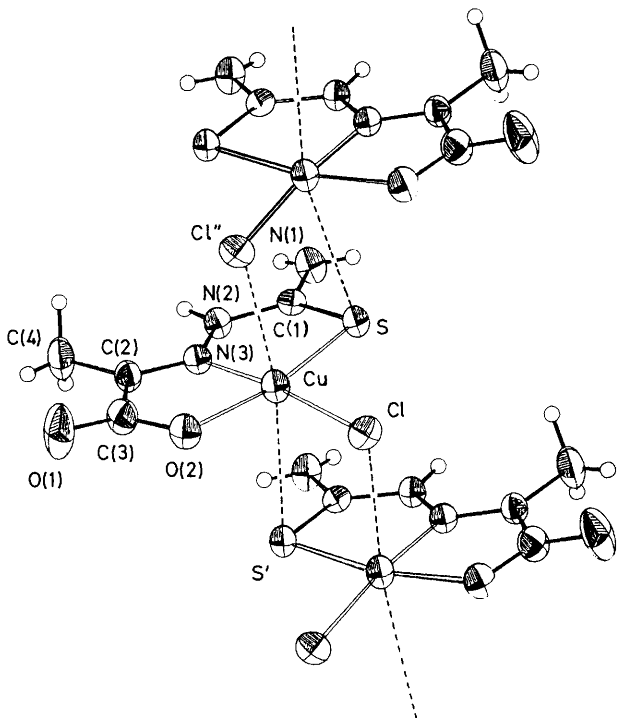


Figure 3. ORTEP drawing of the polymeric $[Cu^{II}(Hpt)]_n$ chain with thermal ellipsoids at 50% probability

Table 7. Hydrogen bonds (Å) in compounds (**1**), (**2**), and (**3**)

Bond D–H • • • A[a]	Position of A	D–H	H • • • A	D • • • A	Angles (°), D–H • • • A
Compound (**1**)					
O(3)–H(3) • • • O(1)	$x, y, 1 + z$	1.10(–)[b]	2.04(–)[b]	2.926(3)	135(–)[b]
N(1)–H(21) • • • N(3)	x, y, z	0.95(5)	2.35(4)	2.613(4)	95(3)
N(1)–H(21) • • • O(3)	$x, y, z - 1$	0.95(5)	2.11(5)	3.036(3)	162(4)
N(1)–H(11) • • • S	$-x - \frac{1}{2}, \frac{1}{2} - y, -z$	0.83(4)	2.60(4)	3.408(3)	167(4)
Compound (**2**)					
N(1)–H(11) • • • S	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$	0.75(9)	2.77(9)	3.463(9)	155(9)
N(1)–H(21) • • • Cl	$x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$	0.87(9)	2.61(9)	3.391(8)	149(8)
N(1)–H(21) • • • O(1)	$x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$	0.87(9)	2.76(9)	3.163(10)	110(7)
Compound (**3**)					
N(1)–H(11) • • • O(4)	x, y, z	0.80(4)	2.41(4)	3.081(5)	142(4)
N(1)–H(11) • • • Cl	$1 + x, y, 1 + z$	0.80(4)	2.79(3)	3.231(3)	117(3)
N(1)–H(21) • • • O(3)	x, y, z	0.76(4)	2.04(4)	2.804(5)	173(4)
N(2)–H(1) • • • O(4)	x, y, z	0.82(3)	2.00(3)	2.764(5)	153(3)
O(3)–H(2) • • • O(1)	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	0.90(5)	1.84(5)	2.726(5)	170(5)
O(4)–H(4) • • • O(2)	$1 + x, y, 1 + z$	0.88(4)	1.96(4)	2.817(4)	164(5)
O(4)–H(5) • • • Cl	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	0.99(6)	2.46(5)	3.359(5)	150(4)

[a] Donor–hydrogen • • • acceptor, D–H is at *x*, *y*, *z* and A is in the position given. [b] The H(3) hydrogen atom has not been refined.

Table 8. Comparison of bond lengths in the thiosemicarbazone moiety

	S–C(1)	C(1)–N(1)	C(1)–N(2)	N(2)–N(3)	C(2)–N(3)	C(2)–C(3)	Ref.
Hmpt·$0.5H_2O$	1.684(4)	1.325(5)	1.363(4)	1.367(4)	1.285(4)	1.506(6)	This work
$\{[Cu(Hpt)Cl]\cdot 2H_2O\}_n$	1.710(3)	1.301(4)	1.355(5)	1.358(4)	1.291(5)	1.523(6)	This work
$[\{Cu(ept)Cl\}_2]$	1.745(8)	1.321(11)	1.327(10)	1.346(8)	1.297(9)	1.455(11)	This work
$H_2L\cdot 3H_2O$	1.70(1)	1.33(1)	1.35(1)	1.40(1)	1.30(1)	1.45(1)	2
$[Mn(H_2L)(OH_2)Cl]Cl$	1.71(1)	1.30(1)	1.33(1)	1.36(1)	1.26(1)	1.46(1)	3
$[Cu(HL)(OH_2)]Cl\cdot H_2O$	1.719(7)	1.333(8)	1.324(8)	1.368(7)	1.298(8)	1.435(8)	3

$\varphi = -173.4(8.2)°$ respectively].[23] In compound (**3**) the Cu-SC(1)N(2)N(3) ring shows an 'envelope' conformation as in compound (**2**) [$q_2 = 0.064(3)$ Å, $\varphi = -2.8\ (3.1)°$] while CuN(3)C(2)C(3)O(2) shows a 'twist' conformation with a two-fold axis passing through the C(2) atom [$q_2 = 0.069(4)$ Å, $\varphi = 154.2(3.4)°$].[23]

In compound (**2**) the ligand is nearly planar, the largest deviation from the best plane being 0.04 Å for C(6), while in compound (**3**) the organic molecule considerably deviates from planarity. In fact the thiourea moiety and the pyruvic group are planar, but the dihedral angle between them is 10.5(2)°. This deviation from planarity can be justified by considering that the hydrazinic N(2) is not deprotonated in (**3**), whereas it is deprotonated in (**2**), where a larger charge delocalization is observed. The comparison of bond lengths in the thiosemicarbazone moiety is shown in Table 8 for some compounds. It can be seen, with regard to free ligands, that the charge delocalization is larger in the heterocyclic derivative as previously observed.[2] In the complexes the deprotonation on the hydrazinic nitrogen is instead more important, since it is believed that it is this deprotonation which allows a larger planarity and therefore the facile electron transfer through the extended conjugated system.

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