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Structural Research on the Stabilization of Oxidation State Two in Thiourea–Copper(II) Complexes. The Crystal and Molecular Structures of *N*,*N*′-Ethylenebis(salicylaldiminato)copper(II)–Thiourea and *N*,*N*′-*o*-Phenylenebis(salicylaldiminato)copper(II)–Thiourea

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The crystal structures of the title compounds have been determined by three-dimensional Patterson, Fourier and least-squares methods on X-ray Cu $K\alpha$ diffraction data. Crystal data are: $[Cu(C_{16}H_{14}N_2O_2)]SC(NH_2)_2$, $a=10\cdot72$ (1), $b=8\cdot76$ (1), $c=9\cdot64$ (1) Å; $\alpha=83\cdot9$ (1), $\beta=80\cdot0$ (1), $\gamma=75\cdot6$ (1)°, $Z=2$, space group $P\bar{1}$; final $R=6\cdot0$ %; $[Cu(C_{20}H_{14}N_2O_2)]SC(NH_2)_2$, $a=11\cdot46$ (1), $b=16\cdot87$ (2), $c=10\cdot94$ (1) Å; $\alpha=74\cdot3$(1), $\beta=85\cdot7$ (1), $\gamma=80\cdot6$ (1)°, $Z=4$, space group $P\bar{1}$; final $R=6\cdot5$ %. In both compounds coordination around Cu is square planar and involves two O and two N atoms from the ligands. In neither complex do the thiourea molecules participate in the coordination to the metal atom but form N–H···O hydrogen bonds with the ligands and N–H···S bonds among themselves. Packing is determined by these hydrogen bonds and also by forces which are probably due to charge-transfer interactions.

Introduction

The structure analyses of the title compounds are part of a systematic study on the stabilization of the oxidation state two for Cu in the presence of reducing agents such as thiourea, I^-, *etc.* In this research it has been found that different situations are possible when the ligands, which in general are polydentate nitrogen and oxygen-containing molecules, are changed. Two different kinds of coordination have been found so far: (*a*) hexacoordination, with elongated tetragonal bipyramids where the reducing ligands (sulphur of thiourea) are at the apices far from the metal atom, as in bis(picolinato)bis(thiourea)copper(II) and bis(picolinato)bis(allylthiourea)copper(II) (Ferrari, Capacchi, Fava, Montenero & Nardelli, 1972); (*b*) pentacoordination with trigonal bipyramids where the reducing ligands (sulphur of thiourea, I^-) are equatorial, as in bis-(2,2′-bipyridyl)thioureacopper(II) perchlorate, *N*,*N*′-tetramethylenebis-(2-pyridinaldimine)thioureacopper-(II) perchlorate (Ferrari, Corradi, Fava, Palmieri, Nardelli & Pelizzi, 1973), bis-(1,10-phenanthroline)-thioureacopper(II) perchlorate monohydrate (Ferrarir, Fava & Montenero, 1975), and iodo-*N*,*N*′-tetramethylenebis(pyridinaldimine)copper(II) iodide (Corradi, Domiano, Fava, Guastini & Nardelli, 1974).

A third situation, quite different from the other two, is found in the title compounds where no interaction at all has been found between copper(II) and the reducing ligand (thiourea), which behaves as 'crystallization-thiourea' binding together the complex molecules through a system of hydrogen bonds.

Experimental

[Cu(salen)]tu [salen = *N*,*N*′-ethylenebis(salicylaldiminato), tu = thiourea] was prepared as previously described (Montenero & Pelizzi, 1972) and [Cu(salof)]tu [salof = *N*,*N*′-*o*-phenylenebis(salicylaldiminato)] was obtained in a similar way from the reaction of *N*,*N*′-*o*-phenylenebis(salicylaldiminato)copper(II) with thiourea in acetonitrile.

Crystal data, determined from rotation and Weissenberg photographs and refined by single-crystal diffractometry (Cu $K\alpha$, $\lambda=1\cdot5418$ Å) are: $[Cu(C_{16}H_{14}N_2O_2)]SC(NH_2)_2$; brown-violet; $a=10\cdot72$ (1), $b=8\cdot76$ (1), $c=9\cdot64$ (1) Å; $\alpha=83\cdot9$ (1), $\beta=80\cdot0$ (1), $\gamma=75\cdot6$ (1)°; $V=862$ Å^3; $Z=2$, $D_m=1\cdot58$, $D_c=1\cdot56$ g cm^{-3}, $\mu=30\cdot6$ cm^{-1}; space group $P\bar{1}$. $[Cu(C_{20}H_{14}N_2O_2)]SC(NH_2)_2$; dark-brown prismatic; $a=11\cdot46$ (1), $b=16\cdot87$ (2), $c=10\cdot94$ (1) Å; $\alpha=74\cdot3$ (1), $\beta=85\cdot7$ (1), $\gamma=80\cdot6$ (1)°; $V=2008$ Å^3; $Z=4$; $D_m=1\cdot52$, $D_c=1\cdot53$ g cm^{-3}; $\mu=27\cdot3$ cm^{-1}; space group $P\bar{1}$.

For both compounds the intensity data were collected on an 'on-line' Siemens AED single-crystal diffractometer, with Cu $K\alpha$ radiation. The $\omega/2\theta$ scan technique ($2\theta_{\max}=120°$) was used. The intensities of 2391, for [Cu(salen)]tu, and 4446, for [Cu(salof)]tu, independent reflexions were measured excluding those with $I<2\sigma(I)$. 1733 reflexions for the first compound and 3269 for the second were used in the successive analyses and refinements.

After Lorentz and polarization corrections had been made, the absolute scale was determined, first by Wilson's (1942) method and then by comparison of the

Table 1. *Final fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10$ Å^2) *for non-hydrogen atoms with estimated standard deviations for* [Cu(salen)]tu

The anisotropic temperature factors are expressed in the form

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3065 (1)	817 (1)	−708 (1)	46 (0)	42 (0)	30 (0)	−8 (0)	−9 (0)	1 (0)
S	−584 (2)	2682 (2)	−5121 (2)	40 (1)	29 (1)	33 (1)	−4 (1)	−15 (1)	1 (1)
O(1)	3523 (5)	−26 (5)	−2501 (4)	47 (3)	33 (2)	22 (2)	−2 (2)	−10 (2)	2 (2)
O(2)	2729 (5)	2888 (5)	−1574 (4)	45 (2)	33 (2)	19 (2)	−5 (2)	−7 (2)	1 (1)
N(1)	3832 (6)	−1162 (7)	268 (5)	47 (3)	38 (3)	22 (2)	−12 (2)	−11 (2)	7 (2)
N(2)	2282 (6)	1461 (7)	1147 (5)	39 (3)	41 (3)	23 (2)	−9 (2)	−4 (2)	4 (2)
N(3)	1197 (6)	673 (7)	−3817 (6)	49 (3)	29 (3)	32 (2)	−4 (2)	−14 (2)	3 (2)
N(4)	1332 (6)	3256 (7)	−4000 (6)	40 (3)	34 (3)	31 (2)	−10 (2)	−8 (2)	0 (2)
C(1)	4299 (7)	−1412 (8)	−2833 (7)	33 (3)	32 (3)	29 (3)	−5 (3)	−7 (2)	1 (2)
C(2)	4585 (8)	−1772 (9)	−4275 (8)	45 (4)	41 (4)	33 (3)	−5 (3)	−4 (3)	−9 (3)
C(3)	5423 (8)	−3183 (10)	−4687 (8)	45 (4)	44 (4)	47 (4)	−9 (3)	−4 (3)	−6 (3)
C(4)	6001 (8)	−4320 (10)	−3701 (9)	47 (4)	43 (4)	53 (4)	−8 (3)	−1 (3)	−4 (3)
C(5)	5692 (8)	−3997 (9)	−2280 (8)	40 (4)	35 (3)	49 (4)	−7 (3)	−9 (3)	−1 (3)
C(6)	4847 (7)	−2569 (8)	−1824 (7)	37 (3)	34 (3)	33 (3)	−9 (3)	−10 (2)	3 (2)
C(7)	4558 (7)	−2394 (8)	−322 (7)	36 (3)	34 (3)	36 (3)	−10 (3)	−8 (2)	6 (2)
C(8)	3585 (8)	−1112 (9)	1826 (7)	58 (4)	47 (4)	21 (3)	−10 (3)	−8 (3)	7 (2)
C(9)	2302 (8)	109 (10)	2223 (7)	56 (4)	50 (4)	26 (3)	−14 (3)	−1 (3)	8 (3)
C(10)	1769 (7)	2886 (9)	1511 (7)	38 (4)	49 (4)	28 (3)	−11 (3)	−2 (2)	−3 (3)
C(11)	1685 (7)	4258 (8)	538 (7)	34 (3)	40 (3)	26 (3)	−7 (3)	−4 (2)	−4 (2)
C(12)	1115 (8)	5761 (10)	1119 (8)	43 (4)	49 (4)	39 (3)	−8 (3)	−3 (3)	−12 (3)
C(13)	1021 (8)	7141 (9)	289 (9)	46 (4)	42 (4)	50 (4)	−8 (3)	−10 (3)	−11 (3)
C(14)	1510 (8)	7097 (9)	−1153 (8)	43 (4)	40 (4)	45 (4)	−9 (3)	−8 (3)	−3 (3)
C(15)	2088 (7)	5672 (8)	−1744 (7)	40 (4)	36 (3)	36 (3)	−10 (3)	−9 (3)	0 (2)
C(16)	2177 (7)	4224 (8)	−925 (7)	32 (3)	35 (3)	27 (3)	−7 (2)	−10 (2)	−3 (2)
C(17)	724 (7)	2171 (8)	−4252 (6)	36 (3)	29 (3)	20 (2)	−5 (2)	−2 (2)	−1 (2)

observed and the calculated structure amplitudes. The crystals used were considered small enough for no correction to be made for absorption, the mean radii being 0·05 mm for both [Cu(salen)]tu and [Cu(salof)]tu.

Structure analysis and refinement

For both compounds, the structures were determined by the heavy-atom method and refined by block-diagonal isotropic and anisotropic least-squares analysis. The function $\sum w|\Delta F|^2$ was minimized, with weights derived from the $\langle|\Delta F|\rangle$ *vs* $|F_o|$ distribution, until R was 0·07 for both complexes. At this point final difference-Fourier syntheses were used to locate all the H atoms, whose coordinates were then isotropically refined. The final values of the conventional R index are 0·060 for [Cu(salen)]tu and 0·065 for [Cu(salof)]tu.

Table 2. *Final fractional coordinates* ($\times 10^3$) *and thermal parameters* ($\times 10$ Å^2) *for hydrogen atoms with estimated standard deviations for* [Cu(salen)]tu

	x	y	z	B
H(2)	428 (6)	−93 (7)	−502 (6)	41 (13)
H(3)	567 (6)	−347 (7)	−534 (6)	66 (17)
H(4)	669 (6)	−534 (7)	−391 (6)	53 (16)
H(5)	617 (6)	−500 (7)	−158 (6)	54 (15)
H(7)	469 (5)	−355 (6)	51 (6)	42 (13)
H(8)	442 (6)	−65 (7)	210 (6)	50 (15)
H(8′)	325 (6)	−217 (7)	250 (6)	64 (17)
H(9)	152 (6)	−61 (7)	210 (6)	43 (14)
H(9′)	163 (6)	28 (7)	319 (6)	59 (16)
H(10)	108 (5)	335 (7)	245 (6)	44 (14)
H(12)	33 (6)	566 (7)	200 (6)	66 (18)
H(13)	50 (6)	800 (7)	50 (6)	61 (19)
H(14)	168 (6)	799 (7)	−189 (6)	51 (15)
H(15)	239 (5)	566 (7)	−277 (6)	45 (14)
H(18)	88 (5)	−20 (7)	604 (6)	38 (13)
H(19)	194 (6)	40 (7)	647 (6)	38 (13)
H(20)	98 (5)	443 (6)	573 (6)	35 (12)
H(21)	212 (5)	304 (6)	632 (6)	43 (13)

The final positional and thermal parameters with their estimated standard deviations are given in Tables 1 and 2 for the first compound and in Tables 3 and 4 for the second. The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the H atoms.

All the calculations were performed on the C.D.C. 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, using programs written by Immirzi (1967).*

Discussion

Bond distances and angles for [Cu(salen)]tu and [Cu(salof)]tu are listed in Tables 5 and 6 respectively. The projections of the two structures in the planes of the thiourea molecule are shown in Figs. 1 and 2. In [Cu(salof)]tu there are two crystallographically independent molecules of both [Cu(salof)] and thiourea,

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* Structure factor tables are available from the authors on request and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31285 (29 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

while in [Cu(salen)]tu there is only one crystallographically independent molecule of each species.

In both compounds coordination around the Cu atom is square-planar and involves two O and two N atoms from the salen or the salof ligands. The coordination planes show slight tetrahedral distortions: Cu(salen)tu [N(1) −0·28, N(2) +0·13, O(2) −0·18, O(1) +0·33 Å], Cu(salof)tu [molecule *A*: N(1) +0·06, N(2) −0·06, O(2) +0·06, O(1) −0·06 Å; molecule *B*: N(1) +0·16, N(2) −0·16, O(2) +0·15, O(1) −0·15

Table 3. *Final fractional coordinates* (× 10⁴) *and thermal parameters* (× 10 Å²) *for non-hydrogen atoms with estimated standard deviations for* [Cu(salof)]tu

The anisotropic temperature factors are expressed in the form

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(*A*)	312 (1)	126 (1)	−2194 (1)	39 (0)	38 (1)	37 (1)	−2 (0)	−1 (0)	−12 (0)
S(*A*)	4455 (2)	1291 (2)	3790 (2)	39 (1)	42 (1)	45 (1)	3 (1)	8 (1)	−1 (1)
O(*A*1)	1091 (5)	−740 (3)	−2889 (5)	33 (3)	37 (3)	38 (3)	−1 (2)	0 (2)	−13 (2)
O(*A*2)	1805 (5)	185 (3)	−1602 (5)	32 (2)	42 (3)	40 (3)	−2 (2)	0 (2)	−19 (2)
N(*A*1)	−1221 (5)	116 (4)	−2829 (6)	26 (3)	29 (3)	31 (3)	−2 (2)	0 (2)	−4 (2)
N(*A*2)	−564 (5)	942 (4)	−1354 (6)	31 (3)	32 (3)	28 (3)	−7 (2)	2 (2)	−4 (3)
N(*A*3)	6280 (7)	150 (5)	3530 (7)	45 (4)	42 (4)	47 (4)	3 (3)	4 (3)	−3 (3)
N(*A*4)	6239(7)	1431 (5)	2119 (7)	49 (4)	52 (4)	42 (4)	−1 (3)	7 (3)	0 (3)
C(*A*1)	654 (7)	−1051 (5)	−3689 (7)	37 (4)	24 (3)	29 (4)	−3 (3)	3 (3)	−4 (3)
C(*A*2)	1436 (8)	−1603 (5)	−4274 (8)	57 (5)	28 (4)	31 (4)	−4 (3)	6 (4)	−4 (3)
C(*A*3)	1052 (9)	−1941 (5)	−5145 (9)	72 (6)	27 (4)	39 (5)	−10 (4)	4 (4)	−7 (4)
C(*A*4)	−157 (9)	−1782 (6)	−5450 (9)	73 (6)	37 (4)	38 (5)	−13 (4)	−3 (4)	−6 (4)
C(*A*5)	−933 (9)	−1262 (6)	−4900 (9)	71 (6)	35 (4)	40 (5)	−13 (4)	−4 (4)	−6 (4)
C(*A*6)	−535 (8)	−884 (5)	−4028 (8)	53 (4)	22 (3)	26 (4)	−10 (3)	−1 (3)	−2 (3)
C(*A*7)	−1425 (8)	−317 (5)	−3561 (8)	46 (4)	33 (4)	29 (4)	−11 (3)	0 (3)	−6 (3)
C(*A*8)	−2131 (7)	687 (5)	−2408 (8)	33 (4)	30 (4)	36 (4)	0 (3)	−1 (3)	−1 (3)
C(*A*9)	−3327 (7)	818 (6)	−2782 (9)	29 (4)	52 (5)	46 (5)	−1 (3)	−3 (4)	−9 (4)
C(*A*10)	−4120 (8)	1404 (6)	−2333 (10)	40 (5)	56 (5)	64 (6)	4 (4)	−2 (4)	−12 (4)
C(*A*11)	−3774 (8)	1822 (7)	−1549 (10)	41 (5)	57 (5)	64 (6)	8 (4)	3 (4)	−18 (5)
C(*A*12)	−2587 (8)	1717 (6)	−1184 (9)	43 (4)	48 (5)	47 (5)	5 (4)	1 (4)	−13 (4)
C(*A*13)	−1788 (7)	1119 (5)	−1640 (8)	31 (4)	34 (4)	31 (4)	2 (3)	0 (3)	−4 (3)
C(*A*14)	−90 (7)	1268 (5)	−608 (8)	33 (4)	27 (4)	31 (4)	−5 (3)	5 (3)	−6 (3)
C(*A*15)	1138 (7)	1139 (5)	−326 (7)	40 (4)	24 (3)	22 (4)	−8 (3)	0 (3)	−3 (3)
C(*A*16)	1449 (8)	1576 (5)	502 (8)	50 (5)	37 (4)	30 (4)	−11 (3)	−4 (3)	−7 (3)
C(*A*17)	2599 (8)	1519 (6)	809 (9)	57 (5)	40 (4)	34 (4)	−14 (4)	−5 (4)	−5 (4)
C(*A*18)	3487 (8)	1011 (6)	303 (9)	52 (5)	40 (4)	42 (5)	−15 (4)	−10 (4)	−1 (4)
C(*A*19)	3211 (8)	578 (6)	−525 (9)	40 (4)	46 (4)	38 (5)	−2 (3)	−10 (4)	−11 (4)
C(*A*20)	2026 (8)	621 (5)	−843 (8)	46 (4)	30 (4)	36 (4)	−7 (3)	−2 (3)	−7 (3)
C(*A*21)	5728 (7)	947 (5)	3120 (8)	34 (4)	42 (4)	31 (4)	−1 (3)	−1 (3)	−6 (3)
Cu(*B*)	299 (1)	4762 (1)	2996 (1)	34 (0)	37 (0)	33 (1)	−4 (0)	0 (0)	−8 (0)
S(*B*)	5196 (2)	3547 (2)	531 (2)	43 (1)	41 (1)	43 (1)	0 (1)	11 (1)	−9 (1)
O(*B*1)	1137 (5)	5467 (3)	1715 (5)	35 (2)	32 (2)	27 (3)	−4 (2)	−2 (2)	−2 (2)
O(*B*2)	1764 (4)	4289 (3)	3791 (5)	30 (2)	39 (3)	28 (3)	−4 (2)	2 (2)	−2 (2)
N(*B*1)	−1203 (5)	5098 (4)	2144 (6)	17 (2)	33 (3)	28 (3)	−5 (2)	3 (2)	−10 (2)
N(*B*2)	−660 (5)	4219 (4)	4459 (6)	26 (3)	25 (3)	32 (3)	−4 (2)	1 (2)	−9 (2)
N(*B*3)	3555 (6)	3366 (4)	2391 (6)	34 (3)	39 (3)	29 (3)	−4 (3)	3 (3)	−5 (3)
N(*B*4)	3572 (6)	4693 (4)	1165 (7)	31 (3)	31 (3)	48 (4)	−1 (2)	−2 (3)	−7 (3)
C(*B*1)	739 (7)	5900 (5)	594 (7)	29 (3)	27 (3)	28 (4)	4 (3)	−4 (3)	−10 (3)
C(*B*2)	1523 (8)	6354 (5)	−283 (8)	43 (4)	32 (4)	30 (4)	0 (3)	−1 (3)	−4 (3)
C(*B*3)	1196 (8)	6796 (5)	−1491 (8)	46 (4)	30 (4)	33 (4)	1 (3)	2 (3)	−5 (3)
C(*B*4)	36 (8)	6830 (5)	−1888 (8)	49 (5)	34 (4)	36 (4)	2 (3)	0 (4)	−12 (3)
C(*B*5)	−769 (8)	6411 (5)	−1050 (8)	51 (4)	27 (4)	24 (4)	2 (3)	−1 (3)	−11 (3)
C(*B*6)	−415 (7)	5949 (5)	197 (7)	38 (4)	27 (3)	17 (3)	−1 (3)	−1 (3)	−7 (3)
C(*B*7)	−1343 (7)	5560 (5)	993 (8)	32 (4)	30 (4)	30 (4)	−2 (3)	3 (3)	−11 (3)
C(*B*8)	−2157 (6)	4799 (5)	2943 (7)	24 (3)	34 (4)	32 (4)	−5 (3)	1 (3)	−12 (3)
C(*B*9)	−3327 (7)	4932 (6)	2546 (8)	32 (4)	54 (5)	33 (4)	−5 (3)	0 (3)	−17 (4)
C(*B*10)	−4199 (8)	4618 (7)	3431 (10)	39 (4)	64 (6)	52 (5)	−7 (4)	−2 (4)	−19 (4)
C(*B*11)	−3911 (8)	4184 (6)	4703 (10)	34 (4)	62 (5)	54 (5)	−11 (4)	0 (4)	−13 (4)
C(*B*12)	−2738 (8)	4051 (6)	5058 (9)	38 (4)	43 (4)	42 (5)	−7 (3)	1 (4)	−11 (4)
C(*B*13)	−1862 (7)	4345 (5)	4178 (7)	28 (3)	28 (3)	30 (4)	−5 (3)	1 (3)	−10 (3)
C(*B*14)	−254 (7)	3821 (5)	5569 (8)	33 (4)	28 (3)	34 (4)	−5 (3)	−1 (3)	−11 (3)
C(*B*15)	965 (7)	3626 (4)	5868 (7)	36 (4)	23 (3)	19 (3)	−2 (3)	−2 (3)	−6 (3)
C(*B*16)	1249 (7)	3159 (5)	7123 (8)	45 (4)	28 (4)	30 (4)	−6 (3)	−2 (3)	−5 (3)
C(*B*17)	2411 (8)	2909 (5)	7510 (8)	53 (5)	35 (4)	30 (4)	−4 (3)	−8 (4)	−4 (3)
C(*B*18)	3333 (8)	3144 (6)	6630 (9)	46 (5)	43 (4)	39 (5)	1 (4)	−7 (4)	−6 (4)
C(*B*19)	3108 (8)	3605 (6)	5387 (8)	37 (4)	49 (5)	29 (4)	−2 (3)	−8 (3)	−5 (4)
C(*B*20)	1911 (7)	3845 (5)	4991 (7)	34 (4)	31 (4)	27 (4)	−2 (3)	−2 (3)	−7 (3)
C(*B*21)	4045 (7)	3880 (5)	1423 (8)	30 (4)	39 (4)	36 (4)	−1 (3)	−4 (3)	−12 (3)

Table 4. *Final fractional coordinates* (× 10³) *and thermal parameters* (× 10 Å²) *for hydrogen atoms with estimated standard deviations for* [Cu(salof)]tu

	x	*y*	*z*	*B*
H(*A*2)	234 (7)	−170 (6)	−400 (7)	39 (13)
H(*A*3)	150 (8)	−250 (5)	−550 (7)	46 (13)
H(*A*4)	−33 (8)	−217 (6)	−617 (7)	49 (13)
H(*A*5)	−167 (7)	−117 (6)	−533 (8)	49 (14)
H(*A*7)	−217 (7)	−30 (6)	−364 (7)	36 (13)
H(*A*9)	−350 (7)	55 (6)	−334 (7)	42 (16)
H(*A*10)	−500 (7)	162 (5)	−267 (7)	53 (16)
H(*A*11)	−450 (7)	225 (6)	−117 (7)	54 (14)
H(*A*12)	−230 (7)	205 (5)	−67 (8)	46 (13)
H(*A*14)	−43 (7)	162 (6)	1 (7)	31 (16)
H(*A*16)	77 (7)	208 (5)	67 (7)	39 (14)
H(*A*17)	277 (7)	172 (6)	167 (7)	44 (17)
H(*A*18)	433 (7)	80 (5)	90 (8)	45 (15)
H(*A*19)	384 (7)	17 (5)	−67 (7)	41 (13)
H(*A*22)	600 (7)	−38 (5)	400 (7)	44 (15)
H(*A*23)	700 (7)	17 (6)	300 (7)	44 (13)
H(*A*24)	567 (7)	192 (5)	167 (7)	48 (14)
H(*A*25)	683 (7)	137 (5)	133 (7)	48 (13)
H(*B*2)	243 (7)	617 (6)	0 (7)	35 (14)
H(*B*3)	177 (7)	710 (6)	−200 (8)	37 (12)
H(*B*4)	−33 (7)	730 (5)	−267 (7)	40 (13)
H(*B*5)	−163 (7)	650 (6)	−133 (8)	34 (14)
H(*B*7)	−233 (8)	567 (5)	77 (6)	31 (14)
H(*B*9)	−350 (7)	526 (6)	167 (7)	40 (15)
H(*B*10)	−500 (7)	483 (6)	283 (7)	52 (14)
H(*B*11)	−443 (7)	403 (6)	516 (7)	50 (18)
H(*B*12)	−247 (7)	377 (5)	583 (7)	41 (13)
H(*B*14)	−83 (7)	355 (5)	627 (7)	32 (14)
H(*B*16)	50 (7)	293 (6)	767 (7)	34 (16)
H(*B*17)	250 (7)	236 (5)	833 (7)	39 (15)
H(*B*18)	433 (7)	308 (5)	700 (7)	43 (13)
H(*B*19)	400 (7)	383 (5)	483 (7)	38 (15)
H(*B*22)	367 (7)	284 (5)	283 (7)	34 (12)
H(*B*23)	290 (7)	350 (6)	283 (7)	34 (18)
H(*B*24)	363 (7)	500 (5)	33 (7)	37 (14)
H(*B*25)	287 (7)	513 (5)	150 (7)	37 (14)

Å]. The Cu atom is 0·03 Å out of the mean coordination plane in both compounds. Bond distances and angles in the coordination sphere agree well with those usually found in square planar copper(II) complexes for which the Cu–N and Cu–O distances are in the ranges 1·914–2·003 and 1·878–1·990 Å respectively.

In neither structure do the thiourea molecules participate in the coordination to the metal atom, but form hydrogen bonds N–H···O with the ligands and N–H···S among themselves. The geometry of these molecules is practically the same as that found for thiourea itself (Kunchur & Truter, 1958) (Figs. 1 and 2). If the main vibrational bands are compared for thiourea when it is uncoordinated and in Cu(II) complexes (Table 7), it can be seen that only the frequency due mainly to the C=S stretching mode (715–730 cm⁻¹) seems to be influenced by the situation of thiourea in the complex; the more strongly the sulphur is bonded to the metal atom the lower is the frequency.

Bond distances and angles for the tetradentate ligands in both complexes are in agreement with those generally found in similar compounds. The presence of thiourea in [Cu(salen)]tu does not seem to influence significantly the geometry of the metal complex as compared with Cu(salen) (Hall & Waters, 1960). From

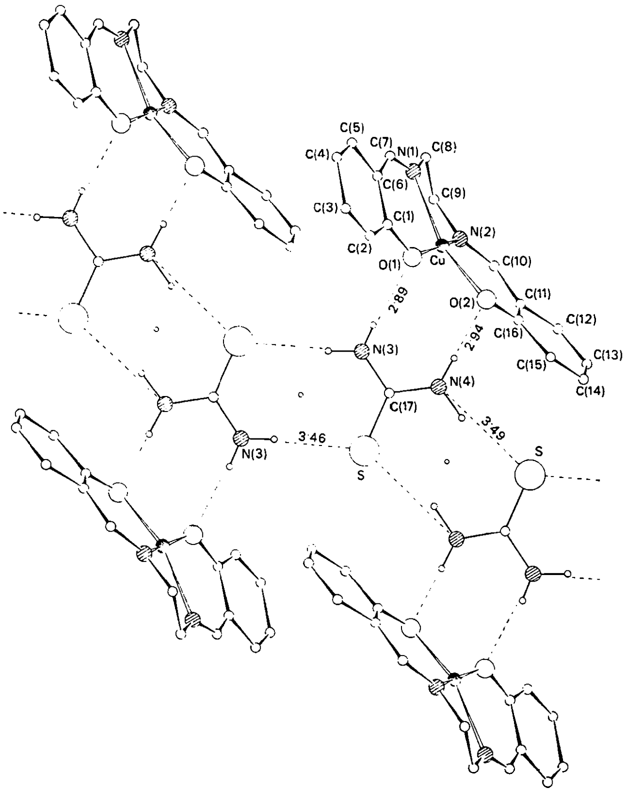

Fig. 1. Projection of [Cu(salen)]tu in the plane of thiourea.

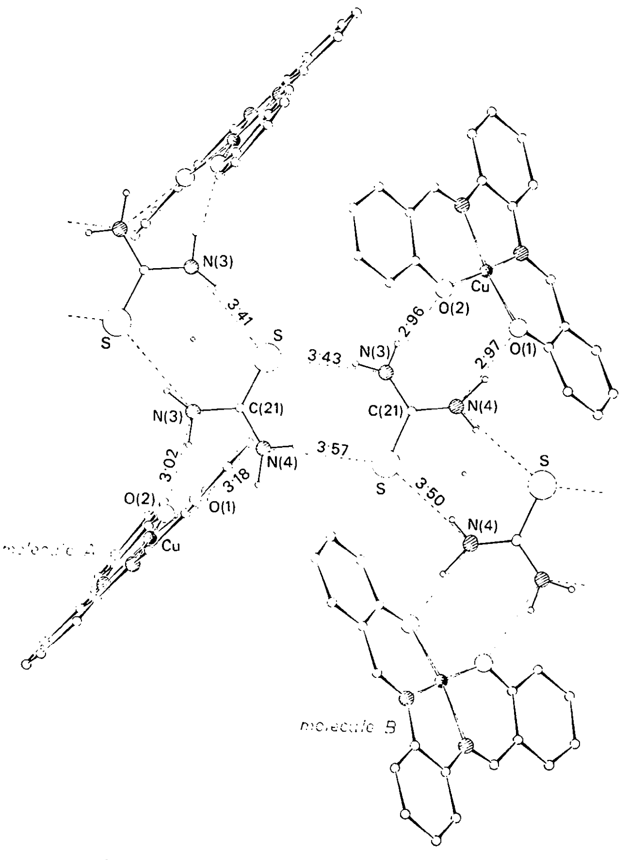

Fig. 2. Projection of [Cu(salof)]tu in the plane of thiourea.

the torsion angles given in Table 8 it can be seen that the salof ligand shows only small distortions from complete planarity, while the salen ligand is more distorted from planarity owing to the presence of the ethylene C(8)–C(9) bridge which is in a *gauche* conformation. It is probable that this distortion is responsible for the different packing observed in both compounds (Figs. 3 and 4).

Table 5. *Bond distances and angles with e.s.d.'s for* [Cu(salen)]tu

The coordination polyhedron			
Cu–O(1)	1·890 (5) Å	O(1)–Cu–O(2)	90·3 (0·2)°
Cu–O(2)	1·891 (5)	O(1)–Cu–N(1)	93·5 (0·2)
Cu–N(1)	1·945 (6)	O(2)–Cu–N(2)	94·6 (0·2)
Cu–N(2)	1·918 (6)	N(1)–Cu–N(2)	84·8 (0·2)
The organic ligand			
O(1)–C(1)	1·33 (1) Å	O(2)—C(16)	1·34 (1) Å
C(1)–C(2)	1·42 (1)	C(16)–C(15)	1·41 (1)
C(2)–C(3)	1·39 (1)	C(15)–C(14)	1·38 (1)
C(3)–C(4)	1·41 (1)	C(14)–C(13)	1·40 (1)
C(4)–C(5)	1·39 (1)	C(13)–C(12)	1·37 (1)
C(5)–C(6)	1·41 (1)	C(12)–C(11)	1·44 (1)
C(6)–C(1)	1·42 (1)	C(11)–C(16)	1·42 (1)
C(6)–C(7)	1·44 (1)	C(11)–C(10)	1·44 (1)
C(7)–N(1)	1·29 (1)	C(10)–N(2)	1·29 (1)
N(1)–C(8)	1·48 (1)	N(2)—C(9)	1·49 (1)
C(8)–C(9)	1·53 (1)		
C(2)–H(2)	1·01 (6)	C(15)–H(15)	0·99 (6)
C(3)–H(3)	0·68 (6)	C(14)–H(14)	1·03 (6)
C(4)–H(4)	1·02 (6)	C(13)–H(13)	0·84 (6)
C(5)–H(5)	1·12 (6)	C(12)–H(12)	1·10 (6)
C(7)–H(7)	1·22 (5)	C(10)–H(10)	1·10 (6)
C(8)–H(8)	1·15 (7)	C(9)—H(9)	1·19 (7)
C(8)–H(8′)	1·17 (6)	C(9)—H(9′)	1·07 (6)
O(1)–C(1)–C(2)	118·4 (0·6)°	O(2)—C(16)–C(15)	118·1 (0·6)°
O(1)–C(1)–C(6)	123·5 (0·6)	O(2)—C(16)–C(11)	123·4 (0·6)
C(1)–C(2)–C(3)	120·8 (0·7)	C(16)–C(15)–C(14)	121·3 (0·7)
C(2)–C(3)–C(4)	121·6 (0·7)	C(15)–C(14)–C(13)	120·5 (0·7)
C(3)–C(4)–C(5)	117·9 (0·8)	C(14)–C(13)–C(12)	119·7 (0·8)
C(4)–C(5)–C(6)	122·0 (0·7)	C(13)–C(12)–C(11)	121·4 (0·7)
C(5)–C(6)–C(1)	119·6 (0·6)	C(12)–C(11)–C(16)	118·6 (0·6)
C(6)–C(1)–C(2)	118·1 (0·6)	C(11)–C(16)–C(15)	118·5 (0·6)
C(5)–C(6)–C(7)	117·0 (0·6)	C(12)–C(11)–C(10)	116·8 (0·6)
C(1)–C(6)–C(7)	123·4 (0·7)	C(10)–C(11)–C(16)	124·6 (0·7)
C(6)–C(7)–N(1)	125·1 (0·7)	C(11)–C(10)–N(2)	123·8 (0·6)
C(7)–N(1)–C(8)	120·7 (0·6)	C(10)–N(2)—C(9)	120·0 (0·6)
N(1)–C(8)–C(9)	107·8 (0·6)	N(2)—C(9)—C(8)	106·9 (0·6)
C(1)–C(2)–H(2)	119·3 (3·4)	C(16)–C(15)–H(15)	119·3 (3·5)
H(2)–C(2)–C(3)	119·3 (3·4)	H(15)–C(15)–C(14)	119·3 (3·5)
C(2)–C(3)–H(3)	131·9 (5·3)	C(15)–C(14)–H(14)	108·2 (3·4)
H(3)–C(3)–C(4)	106·5 (5·3)	H(14)–C(14)–C(13)	130·3 (3·4)
C(3)–C(4)–H(4)	127·0 (3·5)	C(14)–C(13)–H(13)	113·1 (4·3)
H(4)–C(4)–C(5)	114·9 (3·5)	H(13)–C(13)–C(12)	124·6 (4·3)
C(4)–C(5)–H(5)	112·1 (3·1)	C(13)–C(12)–H(12)	119·1 (3·3)
H(5)–C(5)–C(6)	125·8 (3·1)	H(12)–C(12)–C(11)	110·7 (3·3)
C(6)–C(7)–H(7)	120·6 (2·7)	C(11)–C(10)–H(10)	102·5 (3·1)
H(7)–C(7)–N(1)	111·6 (2·7)	H(10)–C(10)–N(2)	131·6 (3·2)
N(1)–C(8)–H(8)	105·3 (2·9)	N(2)—C(9)—H(9)	111·3 (2·9)
N(1)–C(8)–H(8′)	118·3 (2·9)	N(2)—C(9)—H(9′)	118·7 (3·4)
H(8)–C(8)–H(8′)	120·4 (4·2)	H(9)—C(9)—H(9′)	76·8 (4·3)
C(9)–C(8)–H(8′)	95·4 (3·0)	H(9′)–C(9)—C(8)	131·9 (3·3)
C(9)–C(8)–H(8)	108·4 (3·1)	H(9)—C(9)—C(8)	101·1 (3·0)
Thiourea molecule			
S——C(17)	1·70 (1) Å	S——C(17)–N(3)	121·2 (0·5)°
N(3)–C(17)	1·33 (1)	S——C(17)–N(4)	121·1 (0·5)
N(4)–C(17)	1·34 (1)	N(3)—C(17)–N(4)	117·6 (0·6)
N(3)–H(18)	0·94 (7)	C(17)–N(3)—H(18)	125·7 (3·6)
N(3)–H(19)	0·86 (6)	H(18)–N(3)—H(19)	112·5 (5·4)
N(4)–H(20)	1·02 (5)	C(17)–N(3)—H(19)	120·5 (4·1)
N(4)–H(21)	0·91 (6)	C(17)–N(4)—H(20)	120·4 (3·1)
		H(20)–N(4)—H(21)	114·0 (4·8)
		C(17)–N(4)—H(21)	125·3 (3·6)

Table 6. *Bond distances and angles with e.s.d.'s for the two crystallographically independent molecules of* [Cu(salof)]tu

	Molecule *A*	Molecule *B*
The coordination polyhedra		
Cu–O(1)	1·893 (6) Å	1·889 (6) Å
Cu–O(2)	1·902 (6)	1·902 (6)
Cu–N(1)	1·942 (7)	1·946 (6)
Cu–N(2)	1·960 (7)	1·970 (6)
O(1)–Cu–O(2)	87·4 (0·2)°	88·1 (0·2)°
O(1)–Cu–N(1)	94·1 (0·3)	95·0 (0·2)
O(2)–Cu–N(2)	94·3 (0·3)	94·0 (0·2)
N(1)–Cu–N(2)	84·3 (0·3)	84·2 (0·2)
The organic ligands		
O(1)—C(1)	1·30 (1) Å	1·32 (1) Å
C(1)—C(2)	1·43 (1)	1·42 (1)
C(2)—C(3)	1·37 (2)	1·38 (1)
C(3)—C(4)	1·42 (2)	1·42 (1)
C(4)—C(5)	1·37 (1)	1·39 (1)
C(5)—C(6)	1·42 (1)	1·43 (1)
C(6)—C(7)	1·44 (1)	1·45 (1)
C(7)—N(1)	1·28 (1)	1·29 (1)
N(1)—C(8)	1·44 (1)	1·42 (1)
C(8)—C(9)	1·43 (1)	1·40 (1)
C(9)—C(10)	1·40 (1)	1·40 (1)
C(10)–C(11)	1·36 (2)	1·42 (1)
C(11)–C(12)	1·42 (1)	1·39 (1)
C(12)–C(13)	1·42 (1)	1·39 (1)
C(13)–N(2)	1·43 (1)	1·40 (1)
N(2)—C(14)	1·29 (1)	1·30 (1)
C(14)–C(15)	1·43 (1)	1·42 (1)
C(15)–C(16)	1·41 (1)	1·42 (1)
C(16)–C(17)	1·37 (1)	1·39 (1)
C(17)–C(18)	1·40 (1)	1·41 (1)
C(18)–C(19)	1·39 (2)	1·39 (1)
C(19)–C(20)	1·41 (1)	1·43 (1)
C(20)–O(2)	1·31 (1)	1·33 (1)
C(2)—H(2)	1·07 (6)	1·08 (6)
C(3)—H(3)	1·15 (11)	0·95 (8)
C(4)—H(4)	1·19 (10)	1·05 (8)
C(5)—H(5)	0·97 (7)	1·04 (7)
C(7)—H(7)	0·86 (6)	1·15 (6)
C(9)—H(9)	0·90 (10)	0·99 (7)
C(10)–H(10)	1·07 (7)	1·12 (6)
C(11)–H(11)	1·14 (9)	0·78 (7)
C(12)–H(12)	1·00 (10)	0·90 (7)
C(14)–H(14)	1·03 (9)	1·03 (7)
C(16)–H(16)	1·10 (10)	1·07 (7)
C(17)–H(17)	1·12 (9)	1·10 (9)
C(18)–H(18)	1·16 (7)	1·22 (7)
C(19)–H(19)	0·95 (9)	1·21 (7)
O(1)—C(1)—C(2)	118·1 (0·7)°	118·2 (0·7)°
O(1)—C(1)—C(6)	124·9 (0·7)	124·7 (0·7)
C(1)—C(2)—C(3)	121·7 (0·8)	122·0 (0·8)
C(2)—C(3)—C(4)	120·4 (0·9)	120·3 (0·8)
C(3)—C(4)—C(5)	119·5 (0·9)	119·5 (0·8)
C(4)—C(5)—C(6)	120·6 (0·9)	119·5 (0·8)
C(5)—C(6)—C(1)	120·8 (0·8)	121·4 (0·7)
C(6)—C(1)—C(2)	117·0 (0·7)	117·1 (0·7)
C(5)—C(6)—C(7)	115·3 (0·8)	114·3 (0·7)
C(1)—C(6)—C(7)	123·9 (0·7)	124·3 (0·7)
C(6)—C(7)—N(1)	124·4 (0·8)	124·3 (0·7)
C(7)—N(1)—C(8)	122·5 (0·7)	122·8 (0·6)
N(1)—C(8)—C(13)	116·4 (0·7)	115·5 (0·6)
N(1)—C(8)—C(9)	122·6 (0·8)	123·7 (0·7)
C(8)—C(9)—C(10)	117·1 (0·9)	118·4 (0·8)
C(9)—C(10)–C(11)	121·6 (0·9)	120·9 (0·8)
C(10)–C(11)–C(12)	122·5 (1·0)	119·1 (0·9)
C(11)–C(12)–C(13)	115·5 (0·9)	120·3 (0·8)
C(12)–C(13)–C(8)	122·3 (0·8)	120·3 (0·7)
C(13)–C(8)—C(9)	120·9 (0·8)	120·9 (0·7)
C(12)–C(13)–N(2)	122·2 (0·8)	123·5 (0·7)
C(8)—C(13)–N(2)	115·4 (0·7)	116·2 (0·7)
C(13)–N(2)—C(14)	124·1 (0·7)	123·3 (0·7)
N(2)—C(14)–C(15)	126·5 (0·7)	125·0 (0·7)
C(14)–C(15)–C(20)	124·0 (0·7)	124·7 (0·7)
C(14)–C(15)–C(16)	116·2 (0·7)	117·3 (0·7)
C(15)–C(16)–C(17)	121·2 (0·8)	122·3 (0·8)
C(16)–C(17)–C(18)	119·5 (0·9)	118·7 (0·8)
C(17)–C(18)–C(19)	120·6 (0·9)	121·6 (0·8)
C(18)–C(19)–C(20)	120·7 (0·8)	119·3 (0·8)
C(19)–C(20)–C(15)	118·0 (0·8)	120·1 (0·7)
C(20)–C(15)–C(16)	119·9 (0·7)	118·0 (0·7)
C(19)–C(20)–O(2)	118·5 (0·8)	115·9 (0·7)
C(15)–C(20)–O(2)	123·5 (0·7)	124·0 (0·7)
C(1)—C(2)—H(2)	114·2 (5·3)	111·9 (4·3)
H(2)—C(2)—C(3)	124·0 (5·2)	123·8 (3·7)
C(2)—C(3)—H(3)	128·8 (3·6)	116·2 (4·1)
H(3)—C(3)—C(4)	108·4 (3·8)	123·3 (4·1)
C(3)—C(4)—H(4)	110·6 (3·6)	122·1 (4·8)
H(4)—C(4)—C(5)	129·9 (3·6)	115·6 (4·1)
C(4)—C(5)—H(5)	106·1 (5·7)	117·6 (4·4)
H(5)—C(5)—C(6)	132·5 (6·2)	122·5 (4·1)
H(7)—C(7)—C(6)	122·9 (6·7)	126·6 (3·7)
H(7)—C(7)—N(1)	111·9 (6·2)	108·8 (3·5)
C(8)—C(9)—H(9)	117·8 (4·7)	118·4 (4·1)
H(9)—C(9)—C(10)	124·9 (4·8)	123·2 (4·1)
C(9)—C(10)–H(10)	123·0 (5·4)	100·4 (3·7)
H(10)–C(10)–C(11)	114·9 (5·7)	138·6 (3·7)
C(10)–C(11)–H(11)	116·5 (4·2)	117·0 (4·9)
H(11)–C(11)–C(12)	121·0 (4·1)	123·9 (4·9)
C(11)–C(12)–H(12)	123·9 (4·4)	125·3 (4·5)
H(12)–C(12)–C(13)	120·6 (4·3)	114·3 (4·4)
H(14)–C(14)–N(2)	133·3 (3·8)	118·7 (3·5)
H(14)–C(14)–C(15)	99·9 (3·6)	115·8 (3·6)
C(15)–C(16)–H(16)	115·5 (4·3)	112·9 (3·6)
H(16)–C(16)–C(17)	121·2 (4·7)	124·0 (3·9)
C(16)–C(17)–H(17)	117·6 (3·7)	112·4 (3·8)
H(17)–C(17)–C(18)	120·2 (4·1)	124·5 (3·8)
C(17)–C(18)–H(18)	113·4 (4·5)	119·9 (3·1)
H(18)–C(18)–C(19)	122·2 (5·4)	117·2 (3·5)
C(18)–C(19)–H(19)	113·6 (4·8)	111·3 (3·1)
H(19)–C(19)–C(20)	123·9 (5·3)	128·8 (3·3)
Thiourea molecules		
S——C(21)	1·67 (1) Å	1·69 (1) Å
N(3)–C(21)	1·36 (1)	1·33 (1)
N(4)–C(21)	1·34 (1)	1·35 (1)
N(3)–H(22)	1·00 (10)	0·89 (10)
N(3)–H(23)	0·97 (6)	0·89 (7)
N(4)–H(24)	1·00 (8)	0·92 (6)
N(4)–H(25)	1·07 (6)	1·11 (8)
S——C(21)–N(3)	122·0 (0·7)°	122·6 (0·7)°
S——C(21)–N(4)	121·9 (0·7)	120·8 (0·6)
N(3)—C(21)–N(4)	116·0 (0·8)	116·6 (0·7)
C(21)–N(3)—H(22)	133·4 (4·1)	139·6 (4·3)
H(22)–N(3)—H(23)	122·5 (8·0)	94·5 (7·7)
C(21)–N(3)—H(23)	101·3 (6·0)	125·9 (6·4)
C(21)–N(4)—H(24)	112·0 (3·7)	116·6 (6·0)
H(24)–N(4)—H(25)	98·8 (5·4)	97·9 (6·4)
C(21)–N(4)—H(25)	138·9 (5·6)	141·8 (4·3)

In both complexes there are no contacts between Cu and the O atoms belonging to adjacent molecules that can complete the coordination to elongated tetragonal pyramid or bipyramid, as is frequently observed in similar cases. This is in agreement with the observations of Hall & Waters that in the copper(II)–Schiff base complexes the tendency to form Cu–O contacts of this kind decreases when the O atoms are engaged in hydrogen bonding (Baker, Hall & Waters, 1970; Hall, Waters & Wright, 1973). This is just the case for the present compounds where both O atoms of each ligand form hydrogen bonds of the type O··· H–N with the thiourea molecules. These hydrogen bonds, however, do not seem to influence the Cu–O distance in the coordination plane in contrast to the suggestion of Calligaris, Nardin & Randaccio (1972) that this metal–oxygen distance is significantly lengthened when oxygen is involved in other interactions such as hydrogen bonds. Nevertheless this lack of influence is in agreement with what was found by Randaccio (1974) in bis-[*N*,*N*′-ethylenebis(salicylideneiminato)cobalt(II)]bistetrahydrofuransodium(I) tetraphenylborate, and by Milburn, Truter & Vickery (1974) in bis-[*N*,*N*′-ethylenebis(salicylideneiminato)copper(II)] perchloratosodium-*p*-xylene, where no lengthening is observed for the metal–oxygen distance in the coordination plane when oxygen is involved in additional interactions.

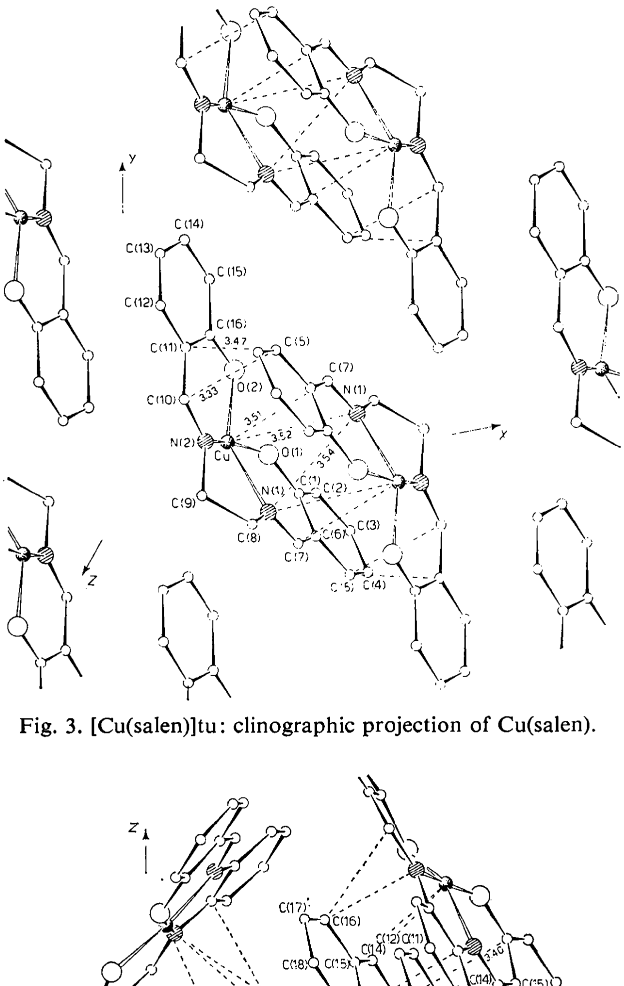

Fig. 3. [Cu(salen)]tu: clinographic projection of Cu(salen).

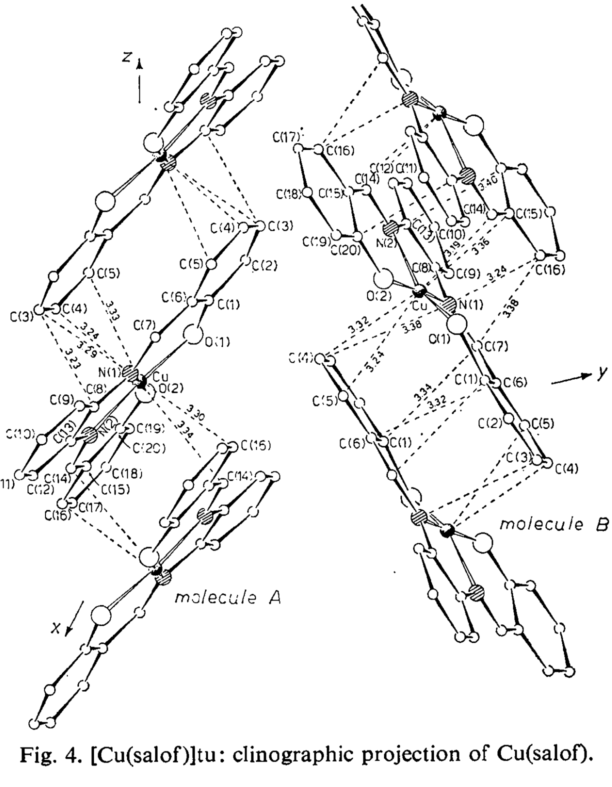

Fig. 4. [Cu(salof)]tu: clinographic projection of Cu(salof).

Table 7. *Main vibrational bands* (cm^{-1}) *for thiourea and* Cu···S *distances* (Å) *in copper*(II) *complexes*

Compound	$\delta(NH_2)$, $\nu(NCN)$	$\nu(CS)$, $\nu(NCN)$	Cu···S
tu	1412	730	–
[Cu(pic)$_2$tu$_2$]	1412	738	2·94
[Cu(pic)$_2$alltu$_2$]	1418	738	2·93
[Cu(bipy)$_2$tu] (ClO$_4$)$_2$	1425	715	2·37
[Cu(pib)tu] (ClO$_4$)$_2$	1405	720	2·34
[Cu(fen)$_2$tu] (ClO$_4$)$_2$	1415	720	2·41
[Cu(salen)]tu	1400	735	>4
[Cu(salof)]tu	1405	735	>4

pic = picolinate; alltu = allylthiourea; bipy = 2,2′-bipiridyl; pib = *N*,*N*′-tetramethylenebis-(2-piridinaldimine); fen = *o*-phenanthroline.

In [Cu(salen)]tu the complex molecules are joined in centrosymmetric dimers held together by forces which can probably be interpreted as due to charge-transfer interactions as indicated by the distances between the pairs of molecules which are in the range 3·3–3·5 Å and by the presence of a band at 363 nm in the electronic spectrum of the compound (the *d–d* band occurs at 565 nm).

In [Cu(salof)]tu, packing of the complex molecules is favoured by their nearly complete planarity. In fact, these molecules are packed in stacks running along the *z* axis and there are two crystallographically non-equivalent stacks. The molecules can therefore approach each other more directly (3·19–3·40 Å) owing to their planarity. The electronic band which could be assigned to a charge-transfer transition is now shifted to a longer wavelength (420 nm; the *d–d* band occurs at 570 nm).

The thiourea molecules are joined together by ribbons of N–H···S hydrogen-bond interactions running along the *y* axis in [Cu(salen)]tu and along the [0$\bar{1}$1] axis in [Cu(salof)]tu. These ribbons join together the molecular dimers in [Cu(salen)]tu and the stacks in [Cu(salof)]tu through N–H···O hydrogen bonds as shown in Figs. 1 and 2. All the other packing distances

Table 8. *The torsion angles for salof and salen ligands*

Salof ligand	Molecule *A*	Molecule *B*
C(5)—C(6)—C(7)—N(1)	175·9°	178·3°
C(6)—C(7)—N(1)—C(8)	178·6	173·2
C(7)—N(1)—C(8)—C(13)	179·2	176·8
C(12)-C(13)-N(2)—C(14)	175·9	179·5
C(13)-N(2)—C(14)-C(15)	177·4	175·1
N(2)—C(14)-C(15)-C(16)	178·9	177·7

Salen ligand			
C(5)-C(6)-C(7)-N(1)	178·5°	C(8)-C(9)—N(2)—C(10)	144·4°
C(6)-C(7)-N(1)-C(8)	179·3	C(9)-N(2)—C(10)-C(11)	178·8
C(7)-N(1)-C(8)-C(9)	156·3	N(2)-C(10)-C(11)-C(12)	178·5
N(1)-C(8)-C(9)-N(2)	140·5		

are consistent with van der Waals contacts in both structures (Tables 9 and 10).

Table 9. *Contacts less than* 3·6 Å *for* [Cu(salen)]tu

(i)	$1-x, \bar{y}, \bar{z}$	(v)	$x, y, 1+z$
(ii)	$\bar{x}, 1-y, 1-z$	(vi)	$1-x, \bar{y}, \bar{z}-1$
(iii)	$\bar{x}, \bar{y}, 1-z$	(vii)	$\bar{x}, 1-y, \bar{z}$
(iv)	$x, y, z-1$		

Cu—N(1^{i})	3·52 (1) Å	N(4)—C(4^{i})	3·56 (1) Å
Cu—C(7^{i})	3·51 (1)	N(4)—C(16^{v})	3·49 (1)
S—N(4^{ii})	3·49 (1)	N(4)—C(3^{i})	3·48 (1)
S—N(3^{iii})	3·46 (1)	N(4)—C(12^{ii})	3·49 (1)
O(1)-N(3^{iv})	2·89 (1)	C(2)—C(2^{vi})	3·52 (1)
O(1)-N(4^{iv})	3·58 (1)	C(5)—C(11^{i})	3·47 (1)
O(2)-N(4^{iv})	2·94 (1)	C(5)—C(10^{i})	3·33 (1)
N(1)-N(1^{i})	3·54 (1)	C(10)-C(14^{vii})	3·59 (1)
N(4)-C(15^{v})	3·51 (1)	C(12)-C(16^{vii})	3·56 (1)

Table 10. *Contacts less than* 3·4 Å *for* [Cu(salof)]tu

(i)	$\bar{x}, \bar{y}, \bar{z}$	(iv)	$\bar{x}, 1-y, \bar{z}$
(ii)	$\bar{x}, \bar{y}, \bar{z}-1$	(v)	$\bar{x}, 1-y, 1-z$
(iii)	$1-x, \bar{y}, \bar{z}$	(vi)	$x, 1+y, z$

Molecule *A*		Molecule *B*	
Cu—C(14^{i})	3·34 (1) Å	Cu—C(14^{v})	3·19 (1) Å
Cu—C(4^{ii})	3·24 (1)	Cu—C(4^{iv})	3·32 (1)
Cu—C(5^{ii})	3·33 (1)	Cu—C(5^{iv})	3·24 (1)
O(1)-N(3^{iii})	3·29 (1)	Cu—C(15^{v})	3·36 (1)
O(1)-N(4^{iii})	3·18 (1)	O(1)-N(4)	2·97 (1)
O(2)-N(3^{iii})	3·02 (1)	O(2)-N(3)	2·96 (1)
O(2)-N(4^{iii})	3·38 (1)	N(1)-C(4^{iv})	3·38 (1)
N(1)-C(3^{ii})	3·29 (1)	N(1)-C(16^{v})	3·24 (1)
N(1)-C(16^{i})	3·30 (1)	C(1)-C(7^{iv})	3·34 (1)
C(3)-C(8^{ii})	3·23 (1)	C(6)-C(6^{iv})	3·32 (1)
		C(7)-C(16^{v})	3·38 (1)

Contacts less than 3·6 Å between *A* and *B* molecules

C(*A*3)—C(*B*14^{i})	3·59 (1) Å	C(*A*16)-C(*B*4^{iv})	3·57 (1) Å
C(*A*4)—C(*B*14^{i})	3·43 (1)	C(*B*3)—C(*A*2^{vi})	3·51 (1)
C(*A*4)—C(*B*15^{i})	3·54 (1)	C(*B*4)—C(*A*16^{iv})	3·57 (1)
C(*A*16)-C(*B*5^{iv})	3·56 (1)	C(*B*14)-C(*A*3^{i})	3·59 (1)
S(*B*)—N(*A*4)	3·57 (1)	S(*A*)—N(*B*3)	3·43 (1)

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