

## Structural Research on the Stabilization of Oxidation State Two in Thiourea–Copper(II) Complexes. The Crystal and Molecular Structures of *N,N'*-Tetramethylenebis-(2-pyridinaldimine)thiourecopper(II) Perchlorate and Bis-(2,2'-bipyridyl)thiourecopper(II) Perchlorate

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The crystal structures have been determined by three-dimensional Patterson–Fourier and least-squares methods on X-ray Cu  $K\alpha$  diffraction data. Crystal data are:  $\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_4)[\text{SC}(\text{NH}_2)_2](\text{ClO}_4)_2$ ,  $a = 9.91$  (1),  $b = 11.42$  (1),  $c = 21.72$  (1) Å;  $\beta = 98.5$  (2)°,  $Z = 4$ , space group  $P2_1/c$ ; final  $R = 8.7\%$ ;  $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2[\text{SC}(\text{NH}_2)_2](\text{ClO}_4)_2$ ,  $a = 11.05$  (1),  $b = 20.16$  (2),  $c = 12.13$  (1) Å,  $Z = 4$ , space group  $P2_12_12_1$ ; final  $R = 7.2\%$ . In both compounds coordination around the metal is trigonal bipyramidal and involves four nitrogen atoms from the organic ligand and a sulphur atom from thiourea. In both complexes one of the two perchlorate groups is disordered. Packing is determined by N–H...O hydrogen bonds which the  $\text{NH}_2$  thiourea groups form with the perchlorate oxygen atoms and by van der Waals contacts.

### Introduction

The investigation of the crystal structures of *N,N'*-tetramethylenebis-(2-pyridinaldimine)thiourecopper(II) perchlorate,  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$  (pib = *N,N'*-tetramethylenebis-(2-pyridinaldimine), tu = thiourea), and of bis-(2,2'-bipyridyl)thiourecopper(II) perchlorate,  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$  (bipy = 2,2'-bipyridyl), was undertaken as a part of a research programme on the stabilization of the oxidation state two for copper in complexes with reducing ligands such as thiourea, iodine, etc. (Belicchi Ferrari, Calzolari Capacchi, Gasparri Fava, Montenero & Nardelli, 1972). The reducing properties of thiourea are inhibited when copper is chelated by  $\pi$ -donor ligands e.g. 1,10-phenanthroline, bis-(salicylaldehyde)ethylenedimine. The compounds described in the present paper have been prepared by Montenero & Pelizzi (1972), who have also discussed their electronic spectra and magnetic properties.

### Experimental

Crystal data, determined from rotation and Weissenberg photographs and refined on an automated single crystal diffractometer (Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å), are as follows.

*N,N'*-Tetramethylenebis-(2-pyridinaldimine)thiourecopper(II) perchlorate,  $\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_4)[\text{SC}(\text{NH}_2)_2](\text{ClO}_4)_2$ , green prismatic crystals, biaxial, with unit-cell parameters:  $a = 9.91$  (1),  $b = 11.42$  (1),  $c = 21.72$  (1) Å;  $\beta = 98.5$  (2)°;  $V = 2402$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 1.68$ ,  $D_c = 1.67$  g cm<sup>-3</sup>;  $\mu = 46.3$  cm<sup>-1</sup>; space group  $P2_1/c$ . Bis-(2,2'-bipyridyl)thiourecopper(II) perchlorate,  $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2[\text{SC}(\text{NH}_2)_2](\text{ClO}_4)_2$ ,

green, needle-like crystals, with unit-cell parameters:  $a = 11.05$  (1),  $b = 20.16$  (2),  $c = 12.13$  (1) Å;  $V = 2700$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 1.60$ ,  $D_c = 1.59$  g cm<sup>-3</sup>;  $\mu = 41.6$  cm<sup>-1</sup>, space group  $P2_12_12_1$ .

For both compounds the intensity data were collected on a single-crystal automated Siemens diffractometer on line with a Siemens 304/P computer, using nickel-filtered Cu  $K\alpha$  radiation and the  $\omega/2\theta$  scan technique ( $2\theta_{\text{max}} = 140^\circ$ ). In this way 4442 independent reflexions were measured for  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$  and 2901 for  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ ; excluding those with  $I < 2\sigma(I)$ , 2656 reflexions for the first compound and 1938 for the second remained for the successive analysis and refinement. After the usual Lorentz and polarization corrections, the intensities were put on absolute scale by Wilson's (1942) method. No correction for absorption was made [mean radius 0.05 mm for  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$  and for  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ ].

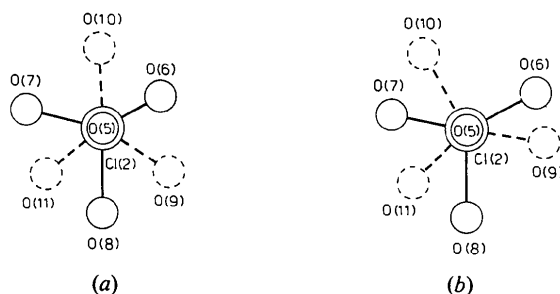


Fig. 1. Orthogonal projections along the Cl(2)–O(5) bond in the disordered perchlorate anions. (a)  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ , (b)  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ .

## Determination of the structure and refinement

For both structures the copper atom was easily located from three-dimensional Patterson calculations: the positions of the lighter non-hydrogen atoms were determined by the heavy-atom method in successive Fourier syntheses, excepting the oxygen atoms of a perchlorate ion as they were disordered in both compounds. The structures were then refined by block-diagonal isotropic and anisotropic least-squares calculations, excluding from the refinement the disordered oxygen atoms. The function  $\sum w|\Delta F|^2$  was minimized using weighting coefficients, derived from the  $\langle |\Delta F| \rangle$  vs  $|F_o|$  distribution, for Cu(bipy)<sub>2</sub>tu(ClO<sub>4</sub>)<sub>2</sub> and unit weights for Cu(pib)tu(ClO<sub>4</sub>)<sub>2</sub>; the *R* values improved to 0.13 and to 0.11 respectively. At this point the three-dimensional difference syntheses revealed for both complexes many peaks around Cl(2) which could be well explained assuming for the perchlorate anion two different orientations, arising from rotation about the

Cl(2)–O(5) bond (Fig. 1). The populations for the two orientations were estimated from the difference synthesis and refined by least-squares calculations. By these means, the *R* values gradually decreased and the shapes of the perchlorate groups improved. At the end of the refinement the *R* indices were 8.7% for Cu(pib)tu(ClO<sub>4</sub>)<sub>2</sub> and 7.2% for Cu(bipy)<sub>2</sub>tu(ClO<sub>4</sub>)<sub>2</sub>.

In Tables 1 and 2 positional and thermal parameters with their e.s.d.'s are given for the two structures. The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968). All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) using the programs of Immirzi (1967).\*

\* The structure factor tables have been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30115. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1N2, England.

Table 1. Final atomic fractional coordinates ( $\times 10^4$ ), *m*\* (population), thermal parameters ( $\times 10 \text{ \AA}^2$ ) and their standard deviations for Cu(pib)tu(ClO<sub>4</sub>)<sub>2</sub>

The anisotropic temperature factors are expressed in the form:  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hla^*c^* \cos \beta^*)]$ . Standard deviations are in parentheses.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>m</i> *	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Cu	2128 (1)	3036 (1)	3025 (1)		57 (1)	59 (1)	49 (1)	-1 (1)	10 (1)	-1 (1)
Cl(1)	1817 (2)	6543 (2)	616 (1)		53 (1)	66 (1)	45 (1)	-12 (1)	4 (1)	4 (1)
Cl(2)	4217 (2)	2166 (2)	842 (1)		55 (1)	62 (1)	57 (1)	-7 (1)	2 (1)	-4 (1)
S	2372 (3)	1044 (2)	3278 (1)		89 (2)	50 (1)	52 (1)	4 (1)	22 (1)	2 (1)
O(1)	2201 (12)	7568 (10)	431 (6)		165 (9)	121 (7)	173 (9)	-13 (7)	-16 (7)	83 (7)
O(2)	980 (11)	5934 (14)	227 (5)		119 (7)	320 (16)	145 (8)	-99 (9)	56 (6)	-135 (10)
O(3)	3005 (10)	5896 (9)	726 (5)		106 (6)	122 (7)	183 (9)	13 (6)	44 (6)	25 (7)
O(4)	1362 (10)	6642 (9)	1171 (4)		153 (7)	127 (7)	68 (4)	9 (6)	38 (4)	-22 (4)
N(1)	615 (7)	2784 (6)	2336 (3)		53 (3)	47 (3)	41 (3)	0 (3)	14 (2)	-9 (2)
N(2)	978 (7)	4156 (6)	3548 (3)		51 (3)	40 (3)	43 (3)	-5 (3)	12 (2)	-1 (2)
N(3)	3622 (7)	3596 (6)	3676 (3)		50 (3)	58 (4)	47 (3)	7 (3)	6 (3)	4 (3)
N(4)	2853 (6)	4010 (6)	2352 (3)		45 (3)	46 (3)	47 (3)	-1 (3)	9 (2)	-1 (3)
N(5)	1862 (8)	1464 (8)	4420 (3)		76 (5)	87 (5)	55 (4)	0 (4)	28 (3)	3 (4)
N(6)	3747 (11)	424 (13)	4351 (5)		93 (6)	206 (12)	79 (6)	67 (7)	22 (5)	24 (7)
C(1)	-559 (9)	2191 (9)	2355 (4)		63 (5)	64 (5)	53 (4)	-12 (4)	15 (4)	-18 (4)
C(2)	-1651 (9)	2241 (9)	1887 (4)		58 (5)	70 (6)	65 (5)	-5 (4)	14 (4)	-24 (4)
C(3)	-1546 (10)	2888 (9)	1348 (5)		61 (5)	61 (5)	72 (5)	1 (4)	0 (4)	-22 (4)
C(4)	-282 (9)	3478 (8)	1313 (4)		65 (5)	56 (5)	54 (4)	12 (4)	-2 (4)	-11 (4)
C(5)	741 (8)	3394 (7)	1817 (3)		52 (4)	38 (4)	46 (4)	5 (3)	5 (3)	-9 (3)
C(6)	2017 (9)	4035 (7)	1831 (4)		63 (5)	45 (4)	47 (4)	2 (4)	14 (3)	-3 (3)
C(7)	4123 (9)	4716 (8)	2420 (4)		51 (5)	57 (5)	77 (6)	-13 (4)	9 (4)	11 (4)
C(8)	5400 (9)	3953 (10)	2577 (5)		51 (5)	84 (7)	90 (6)	4 (5)	24 (5)	2 (5)
C(9)	5451 (11)	3075 (13)	3066 (13)		64 (6)	129 (10)	104 (8)	37 (7)	30 (5)	15 (7)
C(10)	5062 (9)	3291 (11)	3703 (4)		42 (4)	117 (8)	60 (5)	26 (5)	-2 (3)	-12 (5)
C(11)	3288 (9)	4291 (7)	4084 (4)		66 (5)	47 (4)	41 (4)	5 (4)	10 (3)	5 (3)
C(12)	1848 (8)	4611 (7)	4038 (3)		59 (4)	40 (4)	34 (3)	0 (3)	13 (3)	2 (3)
C(13)	1380 (10)	5419 (8)	4443 (4)		77 (5)	45 (4)	46 (4)	-5 (4)	20 (4)	0 (3)
C(14)	4 (11)	5735 (8)	4333 (4)		87 (6)	52 (5)	69 (5)	1 (4)	43 (5)	8 (4)
C(15)	-888 (10)	5270 (8)	3828 (4)		61 (5)	55 (5)	72 (5)	-3 (4)	29 (4)	-2 (4)
C(16)	-330 (9)	4456 (8)	3459 (4)		51 (4)	52 (4)	65 (5)	1 (4)	21 (4)	-5 (4)
C(17)	2704 (10)	997 (9)	4079 (4)		64 (5)	73 (6)	63 (5)	19 (5)	15 (4)	16 (4)
O(5)	4489 (10)	1775 (9)	1416 (5)	1.00	129 (3)					
O(6)	5161 (21)	2631 (19)	641 (10)	0.49	139 (6)					
O(7)	2949 (17)	2724 (15)	754 (8)	0.46	88 (4)					
O(8)	3830 (18)	1128 (16)	488 (8)	0.48	97 (4)					
O(9)	5004 (20)	1615 (18)	421 (9)	0.51	124 (5)					
O(10)	4346 (13)	3382 (12)	826 (6)	0.54	76 (3)					
O(11)	3000 (18)	1859 (17)	513 (8)	0.52	114 (5)					

## Discussion

The orthogonal projections of the complex cations in the two structures are shown in Figs. 2 and 3. In both compounds the coordination polyhedron is a trigonal-bipyramid where four nitrogen atoms from the organic molecules and a sulphur atom from thiourea are involved. Two nitrogen atoms, N(2), N(4), and one sulphur atom occupy the trigonal plane, while N(3) and N(1) are on the axial positions. The copper atom lies in the trigonal plane in the case of  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ , while it is displaced by 0.03 Å out of the equatorial plane in  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ .

Trigonal bipyramidal geometry is not common in the case of Cu(II) complexes, particularly when they contain ligands with reducing properties; only iodobis-(2,2'-bipyridyl)copper(II) iodide (Barclay, Hoskins & Kennard, 1963) is known besides those discussed in the present paper.

These compounds are mixed-ligand complexes, with ligands having strong  $\pi$ -conjugation properties such as 2,2'-bipyridyl and *N,N'*-tetramethylenebis-(2-pyridinildimine), indicating that the presence of these ligands is required to stabilize copper(II), as has already been shown for Cu(II)-thiourea complexes (Belicchi, Calzolari, Gasparri, Montenero & Nardelli, 1972). In the latter, coordination is tetragonally distorted octahedral and the equatorial ligands are such as to give rise to  $\pi$ -conjugation with metal, while the sulphur atoms of the thiourea molecules are far enough from the metal [2.943 Å in bis(picolinato)bis(thiourea)copper(II) and 2.927 Å in bis(picolinato)bis(allylthiourea)copper(II)] to justify the lack of reducing effects.

In the complexes described in the present paper, the situation is different, not only in so far as the coordination is concerned, but also because the distance of the thiourea-sulphur from the metal is of the same order of magnitude as that found in Cu(I)-thiourea

Table 2. Final fractional coordinates ( $\times 10^4$ ),  $m^*$  (population), thermal parameters ( $\times 10 \text{ \AA}^2$ ) and their standard deviations for  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$

The anisotropic temperature factors are expressed in the form:  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2})]$ .

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$m^*$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cu	2068 (1)	169 (1)	1563 (1)		52 (0)	50 (0)	54 (0)	-2 (0)	5 (0)	-6 (0)
Cl(1)	2150 (3)	2812 (1)	8979 (2)		68 (1)	49 (1)	76 (1)	-5 (1)	10 (1)	-1 (1)
Cl(2)	1774 (2)	3712 (1)	4092 (2)		44 (1)	44 (1)	63 (1)	-2 (1)	-11 (1)	-7 (1)
S	1381 (2)	383 (1)	-253 (2)		61 (1)	67 (1)	41 (1)	1 (1)	-2 (1)	-9 (1)
O(1)	2548 (9)	3371 (4)	8570 (10)		82 (5)	74 (4)	164 (8)	-12 (4)	-11 (5)	36 (5)
O(2)	2579 (16)	2921 (9)	1.0033 (12)		163 (12)	249 (16)	131 (8)	-88 (13)	28 (9)	-4 (11)
O(3)	2432 (12)	2212 (5)	8653 (12)		125 (8)	83 (5)	194 (10)	23 (5)	3 (8)	-56 (7)
O(4)	883 (10)	2822 (5)	8951 (12)		92 (6)	89 (5)	198 (11)	-20 (5)	21 (8)	1 (7)
N(1)	2779 (7)	-691 (3)	1131 (6)		44 (3)	44 (3)	60 (4)	0 (3)	8 (3)	-6 (3)
N(2)	3857 (6)	303 (3)	2095 (6)		44 (3)	53 (3)	39 (3)	-4 (3)	-2 (3)	5 (3)
N(3)	1354 (7)	998 (3)	2161 (6)		53 (3)	45 (3)	37 (3)	-2 (3)	-3 (3)	-8 (2)
N(4)	1005 (6)	-225 (3)	2838 (6)		38 (3)	44 (3)	45 (3)	-5 (2)	-2 (2)	3 (3)
N(5)	-849 (8)	599 (4)	480 (8)		50 (4)	57 (4)	78 (5)	1 (3)	-5 (4)	-6 (3)
N(6)	-6 (10)	1449 (3)	-531 (7)		98 (6)	31 (3)	66 (4)	-4 (3)	-6 (4)	-1 (3)
C(1)	2119 (11)	-1168 (5)	562 (9)		72 (5)	50 (4)	64 (5)	-14 (4)	5 (5)	-8 (4)
C(2)	2615 (11)	-1792 (5)	403 (9)		74 (6)	56 (4)	70 (5)	-10 (4)	24 (5)	-10 (4)
C(3)	3773 (12)	-1935 (5)	767 (10)		87 (7)	49 (4)	77 (6)	7 (5)	17 (6)	4 (4)
C(4)	4468 (9)	-1432 (5)	1330 (9)		52 (4)	74 (5)	62 (5)	8 (4)	7 (4)	6 (4)
C(5)	3928 (8)	-813 (4)	1501 (8)		50 (4)	45 (3)	55 (4)	0 (3)	11 (4)	-5 (4)
C(6)	4491 (8)	-252 (5)	1991 (7)		48 (4)	64 (4)	38 (3)	-6 (4)	8 (3)	15 (3)
C(7)	5723 (8)	-271 (5)	2360 (8)		47 (4)	80 (6)	54 (4)	-4 (4)	13 (4)	12 (4)
C(8)	6186 (9)	296 (7)	2812 (9)		48 (4)	112 (8)	56 (5)	-17 (5)	-5 (4)	18 (6)
C(9)	5535 (10)	866 (6)	2908 (9)		61 (5)	84 (6)	52 (4)	-21 (5)	5 (4)	-4 (5)
C(10)	4343 (11)	875 (5)	2542 (7)		79 (6)	70 (5)	36 (4)	-24 (5)	-5 (4)	-3 (4)
C(11)	1581 (11)	1603 (4)	1801 (8)		89 (6)	33 (3)	53 (4)	-4 (4)	-15 (4)	1 (3)
C(12)	1030 (11)	2171 (5)	2145 (8)		81 (6)	56 (4)	45 (4)	11 (4)	-7 (4)	-7 (4)
C(13)	133 (14)	2094 (5)	2871 (10)		105 (8)	48 (4)	77 (6)	21 (5)	-19 (6)	-13 (4)
C(14)	-179 (10)	1453 (5)	3311 (9)		65 (5)	72 (5)	55 (5)	15 (4)	-8 (4)	-9 (4)
C(15)	492 (8)	914 (4)	2945 (7)		47 (4)	56 (4)	38 (3)	2 (3)	-11 (3)	-13 (3)
C(16)	333 (7)	242 (4)	3351 (7)		38 (3)	49 (3)	39 (3)	-2 (3)	-4 (3)	-4 (3)
C(17)	-453 (8)	77 (5)	4205 (8)		52 (4)	68 (5)	43 (4)	-5 (4)	-5 (3)	-13 (4)
C(18)	-513 (10)	-587 (7)	4547 (9)		53 (5)	110 (8)	55 (5)	-21 (5)	-9 (4)	-9 (5)
C(19)	206 (11)	-1066 (5)	4043 (8)		74 (6)	72 (5)	41 (4)	-20 (5)	-7 (4)	-8 (4)
C(20)	949 (9)	-866 (5)	3186 (8)		45 (4)	61 (4)	57 (5)	-11 (3)	-4 (3)	-2 (4)
C(21)	74 (11)	829 (5)	-53 (8)		77 (6)	55 (4)	50 (4)	2 (4)	-16 (4)	-8 (4)
O(5)	678 (8)	3396 (4)	4465 (7)	1.00	84 (2)					
O(6)	2455 (12)	3323 (6)	3319 (10)	0.44	50 (2)					
O(7)	2398 (17)	4031 (8)	4933 (14)	0.57	97 (4)					
O(8)	1325 (15)	4317 (7)	3548 (14)	0.54	83 (4)					
O(9)	2085 (17)	3615 (8)	2936 (16)	0.56	98 (4)					
O(10)	2522 (19)	3444 (10)	4973 (17)	0.43	86 (5)					
O(11)	1948 (17)	4398 (9)	4293 (15)	0.46	80 (4)					

complexes (Okaya & Knobler, 1964; Calzolari Capacchi, Cavalca, Fava Gasparri & Ferrari, 1969). This fact suggests that the electron density in the region between metal and sulphur is equal in both types of compounds, in the case of Cu(II)-complexes the electronic charge being supplied by the chelating ligands through a  $\pi$ -donor effect. The unusual coordination polyhedron probably arises as a consequence of steric interference.

It is interesting to observe that in both compounds the Cu-N distances are not equal, the axial bonds

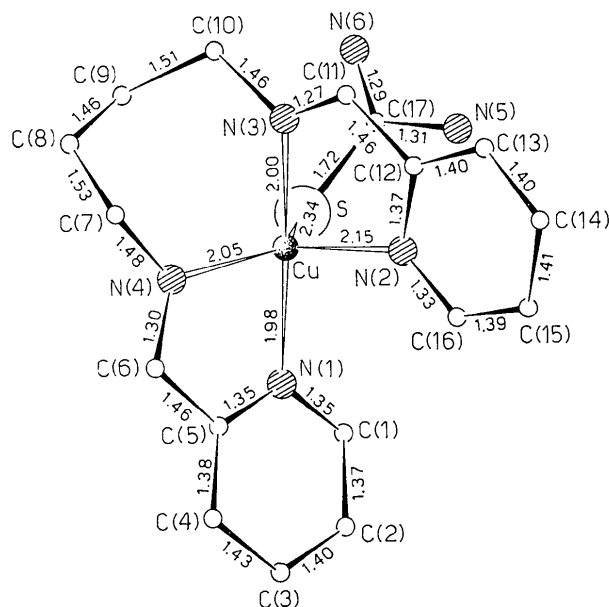


Fig. 2.  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ . Projection of the cation on (010).

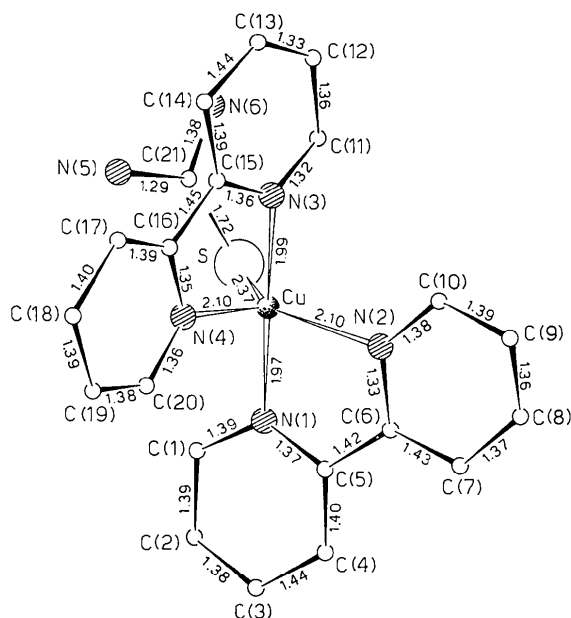


Fig. 3.  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ . Projection of the cation on (001).

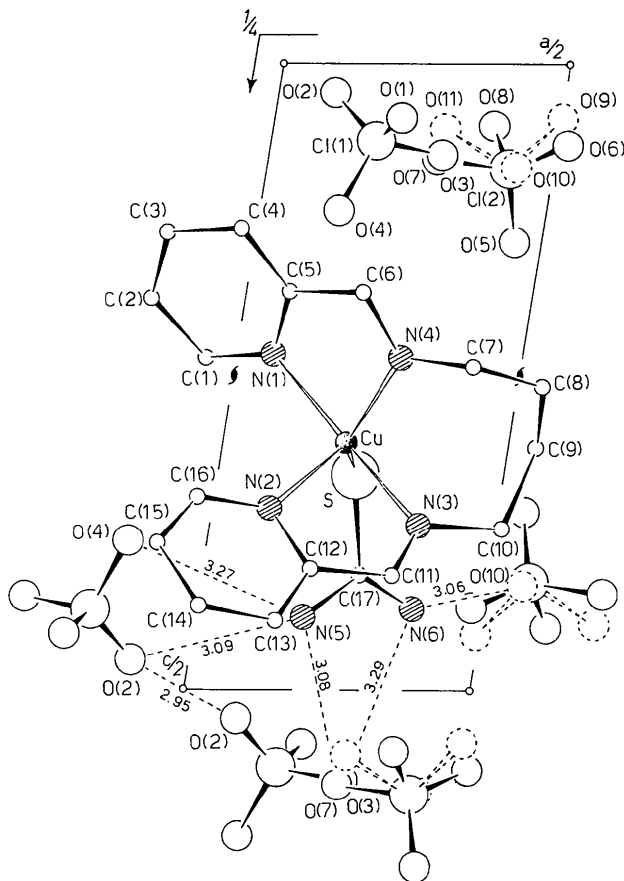


Fig. 4.  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ . Projection of the structure on (010).

being significantly shorter than the equatorial ones [1.977, 1.995 Å and 2.147, 2.050 Å in  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ ; 1.974, 1.985 Å and 2.097, 2.098 Å in  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ ] as was found in hexamminechromium(III) pentachlorocuprate(II) (Raymond, Meek & Ibers, 1968) and as predicted by Gillespie (1963) on the basis of the electron-pair repulsion model.

Bond distances and angles for  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$  are listed in Tables 3 and 4 respectively. For both compounds the geometry of the thiourea ligand corresponds well with that found in the uncoordinated molecule (Kunchur & Truter, 1958).

In  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$  the tetradentate ligand makes one seven-membered [ $\text{CuN}(4)\text{C}(7)\text{C}(8)\text{C}(9)\text{C}(10)\text{N}(3)$ ], and two five-membered [ $\text{CuN}(1)\text{C}(5)\text{C}(6)\text{N}(4)$  and  $\text{CuN}(2)\text{C}(12)\text{C}(11)\text{N}(3)$ ] chelation rings. These last rings are not planar, as the copper atom lies out from the least-squares planes N(1)C(5)C(6)N(4) and N(2)C(12)C(11)N(3) by 0.03 and 0.09 Å respectively. The equations of these planes are:

$$\begin{aligned} \text{N}(1)\text{C}(5)\text{C}(6)\text{N}(4) \\ 0.4992X - 0.7949Y - 0.3447Z = -4.3352 \\ \text{N}(2)\text{C}(12)\text{C}(11)\text{N}(3) \\ 0.2528X + 0.7851Y - 0.5655Z = -0.6291 \end{aligned}$$

In the same compound N(3) and N(4) are trigonal, as

the bonds N(3)–C(11) = 1.27 Å and N(4)–C(6) = 1.30 Å are mainly double in character; the two pyridine rings are planar and their bond distances agree well with the values usually found for these systems. Relevant distortions from the expected tetrahedral values are found in the chain C(7)C(8)C(9)C(10).

In Cu(bipy)<sub>2</sub>tu(ClO<sub>4</sub>)<sub>2</sub> the pyridine rings are planar, but in each ligand molecule they do not lie in the same plane but are slightly twisted about the 2,2'-carbon bond. The internal rotation angles are 3.5 and 4.6° for the molecules defined by N(1) and N(2) and by N(3) and N(4) respectively.

Table 3. Bond distances and angles with e.s.d.'s for Cu(pib)tu(ClO<sub>4</sub>)<sub>2</sub>

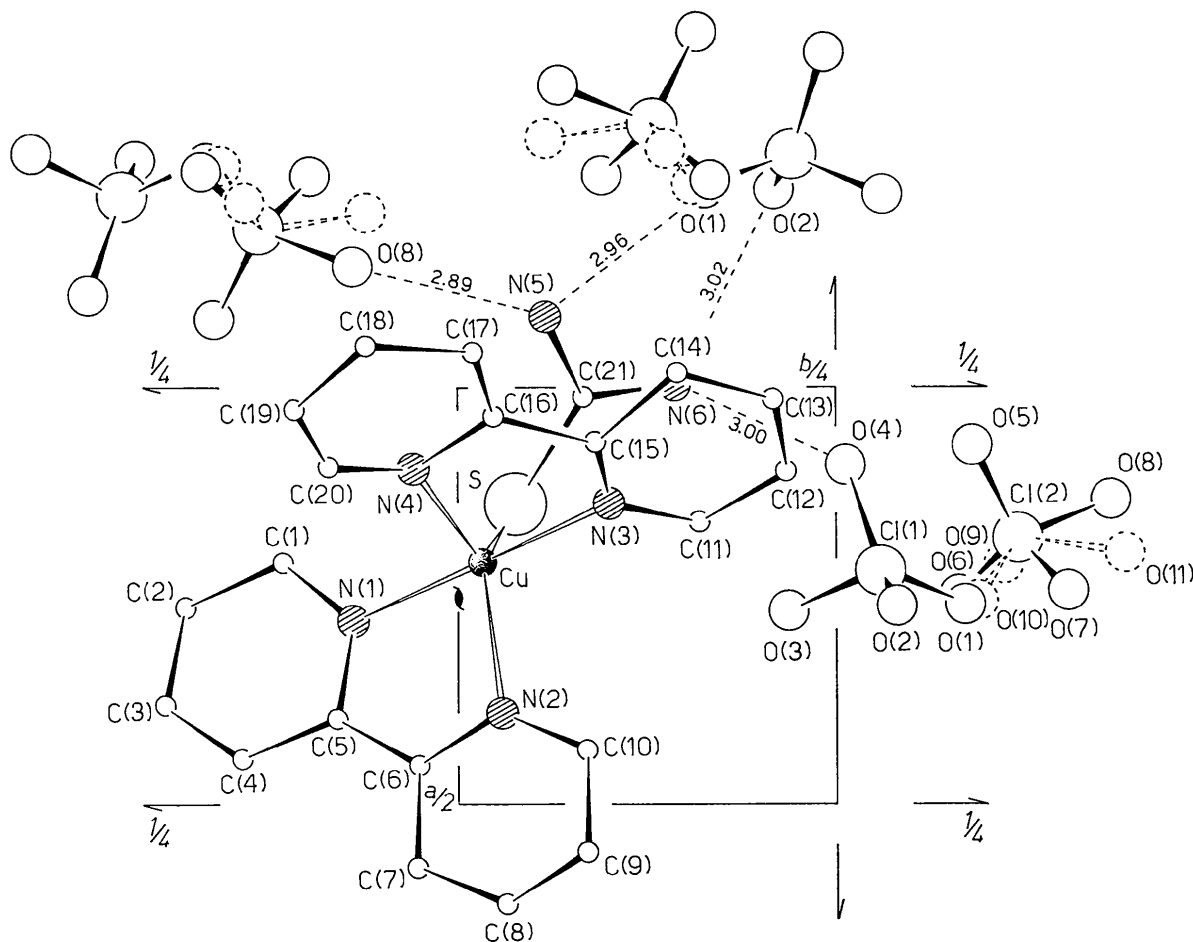
The coordination polyhedron			
Cu—N(1)	1.977 (7) Å	N(1)—Cu—N(2)	94.9 (0.5)°
Cu—N(2)	2.147 (7)	N(1)—Cu—N(4)	81.1 (0.6)
Cu—N(3)	1.995 (7)	N(1)—Cu—S	94.4 (0.4)
Cu—N(4)	2.050 (16)	N(1)—Cu—N(3)	169.6 (5.0)
Cu—S	2.344 (3)	N(2)—Cu—N(3)	80.2 (0.4)
		N(2)—Cu—N(4)	108.9 (1.1)
		N(2)—Cu—S	119.9 (0.5)
		N(3)—Cu—N(4)	91.7 (0.9)
		N(3)—Cu—S	96.0 (0.4)
		N(4)—Cu—S	131.2 (1.2)
<i>N,N'</i> -Tetramethylenebis(pyridinaldimine) ligand			
N(1)—C(1)	1.35 (1) Å	N(2)—C(16)	1.33 (1) Å
C(1)—C(2)	1.37 (1)	C(16)—C(15)	1.39 (1)
C(2)—C(3)	1.40 (1)	C(15)—C(14)	1.41 (1)
C(3)—C(4)	1.43 (1)	C(14)—C(13)	1.40 (1)
C(4)—C(5)	1.38 (1)	C(13)—C(12)	1.40 (1)
C(5)—N(1)	1.35 (1)	C(12)—N(2)	1.37 (1)
C(5)—C(6)	1.46 (1)	C(12)—C(11)	1.46 (1)
C(6)—N(4)	1.30 (2)	C(11)—N(3)	1.27 (1)
N(4)—C(7)	1.48 (1)	N(3)—C(10)	1.46 (1)
C(7)—C(8)	1.53 (1)	C(10)—C(9)	1.51 (2)
C(8)—C(9)	1.46 (2)		
N(1)—C(1)—C(2)	123.0 (1.6)°	N(2)—C(16)—C(15)	123.4 (1.8)°
C(1)—C(2)—C(3)	119.5 (1.7)	C(16)—C(15)—C(14)	116.3 (1.5)
C(2)—C(3)—C(4)	117.7 (1.7)	C(15)—C(14)—C(13)	121.4 (1.8)
C(3)—C(4)—C(5)	118.0 (1.5)	C(14)—C(13)—C(12)	117.9 (1.7)
C(4)—C(5)—N(1)	123.5 (1.5)	C(13)—C(12)—N(2)	120.6 (1.4)
C(5)—N(1)—C(1)	118.1 (1.5)	C(12)—N(2)—C(16)	120.3 (1.5)
C(5)—N(1)—Cu	113.9 (0.8)	C(12)—N(2)—Cu	108.3 (0.7)
N(1)—C(5)—C(6)	115.5 (1.3)	N(2)—C(12)—C(11)	117.0 (1.3)
C(5)—C(6)—N(4)	116.5 (1.7)	C(12)—C(11)—N(3)	117.5 (1.4)
C(6)—N(4)—Cu	112.8 (1.4)	C(11)—N(3)—Cu	116.9 (1.0)
C(6)—N(4)—C(7)	119.8 (1.8)	C(11)—N(3)—C(10)	118.3 (1.6)
Cu—N(4)—C(7)	127.3 (1.5)	Cu—N(3)—C(10)	124.7 (1.1)
N(4)—C(7)—C(8)	111.9 (1.2)	N(3)—C(10)—C(9)	112.5 (1.5)
C(7)—C(8)—C(9)	119.5 (1.9)	C(10)—C(9)—C(8)	124.7 (2.2)
Thiourea molecule			
S—C(17)	1.72 (1) Å	S—C(17)—N(5)	121.1 (1.2)°
C(17)—N(5)	1.31 (1)	S—C(17)—N(6)	119.9 (1.4)
C(17)—N(6)	1.29 (1)	N(5)—C(17)—N(6)	118.8 (2.0)
Perchlorate anions			
Cl(1)—O(1)	1.31 (1) Å	O(1)—Cl(1)—O(2)	117.8 (2.0)°
Cl(1)—O(2)	1.30 (1)	O(1)—Cl(1)—O(3)	104.6 (1.4)
Cl(1)—O(3)	1.38 (1)	O(1)—Cl(1)—O(4)	110.4 (1.6)
Cl(1)—O(4)	1.35 (1)	O(2)—Cl(1)—O(3)	105.8 (1.4)
		O(2)—Cl(1)—O(4)	111.1 (1.5)
		O(3)—Cl(1)—O(4)	106.2 (1.3)
Cl(2)—O(5)	1.31 (1)	Cl(2)—O(5)	1.31 (1) Å
Cl(2)—O(6)	1.22 (2)	Cl(2)—O(9)	1.43 (2)
Cl(2)—O(7)	1.40 (2)	Cl(2)—O(10)	1.40 (1)
Cl(2)—O(8)	1.43 (2)	Cl(2)—O(11)	1.35 (2)
O(5)—Cl(2)—O(6)	115.4 (2.3)°	O(5)—Cl(2)—O(9)	113.7 (2.4)°
O(5)—Cl(2)—O(7)	109.8 (1.9)	O(5)—Cl(2)—O(10)	110.8 (1.7)
O(5)—Cl(2)—O(8)	103.2 (1.8)	O(5)—Cl(2)—O(11)	117.0 (2.1)
O(6)—Cl(2)—O(7)	118.5 (3.2)	O(9)—Cl(2)—O(10)	111.1 (2.3)
O(6)—Cl(2)—O(8)	109.2 (2.7)	O(9)—Cl(2)—O(11)	94.3 (2.1)
O(7)—Cl(2)—O(8)	98.0 (1.9)	O(10)—Cl(2)—O(11)	108.8 (2.1)

In both complexes there are two perchlorate ions having different structural behaviour, one being in a well defined position, the other being disordered over two sites, as shown in Fig. 1. Bond distances and angles in them agree with those usually found in these ions.

In both complexes packing is determined by the N—H···O hydrogen bonds which the NH<sub>2</sub> thiourea groups form with the perchlorate oxygen atoms and by van der Waals contacts as shown in Tables 5 and 6 and in Figs. 4 and 5.

Table 4. Bond distances and angles with *e.s.d.*'s for Cu(bipy)<sub>2</sub>tu(ClO<sub>4</sub>)<sub>2</sub>

Coordination polyhedron			
Cu—N(1)	1.974 (7) Å	N(1)—Cu—N(2)	79.6 (0.3)°
Cu—N(2)	2.097 (7)	N(1)—Cu—N(4)	94.9 (0.3)
Cu—N(3)	1.985 (7)	N(1)—Cu—S	92.3 (0.2)
Cu—N(4)	2.098 (7)	N(1)—Cu—N(3)	173.9 (0.3)
Cu—S	2.369 (4)	N(2)—Cu—N(3)	98.9 (0.3)
		N(2)—Cu—N(4)	110.5 (0.3)
		N(2)—Cu—S	124.4 (0.2)
		N(3)—Cu—N(4)	80.0 (0.3)
		N(3)—Cu—S	93.4 (0.2)
Bipyridyl molecules			
N(1)—C(1)	1.39 (1) Å	N(3)—C(11)	1.32 (1) Å
N(1)—C(5)	1.37 (1)	N(3)—C(15)	1.36 (1)
C(1)—C(2)	1.39 (1)	C(11)—C(12)	1.36 (1)
C(2)—C(3)	1.38 (2)	C(12)—C(13)	1.33 (2)
C(3)—C(4)	1.44 (2)	C(13)—C(14)	1.44 (2)
C(4)—C(5)	1.40 (1)	C(14)—C(15)	1.39 (1)
C(5)—C(6)	1.42 (1)	C(15)—C(16)	1.45 (1)
N(2)—C(6)	1.33 (1)	N(4)—C(16)	1.35 (1)
N(2)—C(10)	1.38 (1)	N(4)—C(20)	1.36 (1)
C(6)—C(7)	1.43 (1)	C(16)—C(17)	1.39 (1)
C(7)—C(8)	1.37 (2)	C(17)—C(18)	1.40 (2)
C(8)—C(9)	1.36 (2)	C(18)—C(19)	1.39 (2)
C(9)—C(10)	1.39 (2)	C(19)—C(20)	1.38 (1)
C(1)—N(1)—C(5)	121.7 (0.7)°	C(11)—N(3)—C(15)	118.7 (0.8)°
N(1)—C(1)—C(2)	119.3 (1.0)	N(3)—C(11)—C(12)	126.2 (1.0)
C(1)—C(2)—C(3)	120.7 (1.0)	C(11)—C(12)—C(13)	115.9 (0.9)
C(2)—C(3)—C(4)	119.8 (0.9)	C(12)—C(13)—C(14)	121.8 (1.0)
C(3)—C(4)—C(5)	118.0 (0.9)	C(13)—C(14)—C(15)	117.1 (1.0)
C(4)—C(5)—N(1)	120.5 (0.8)	C(14)—C(15)—N(3)	120.1 (0.8)
N(1)—C(5)—C(6)	113.6 (0.7)	N(3)—C(15)—C(16)	116.0 (0.7)
C(6)—C(5)—C(4)	125.8 (0.9)	C(14)—C(15)—C(16)	123.9 (0.8)
C(5)—C(6)—N(2)	118.7 (0.8)	N(4)—C(16)—C(15)	115.3 (0.7)
C(5)—C(6)—C(7)	121.7 (0.8)	C(15)—C(16)—C(17)	123.4 (0.8)
N(2)—C(6)—C(7)	119.6 (0.8)	N(4)—C(16)—C(17)	121.3 (0.7)
C(6)—C(7)—C(8)	117.3 (0.9)	C(16)—C(17)—C(18)	118.5 (0.9)
C(7)—C(8)—C(9)	122.9 (1.0)	C(17)—C(18)—C(19)	120.3 (1.0)
C(8)—C(9)—C(10)	119.0 (1.1)	C(18)—C(19)—C(20)	117.8 (1.0)
C(9)—C(10)—N(2)	118.8 (1.0)	C(19)—C(20)—N(4)	122.4 (0.9)
C(10)—N(2)—C(6)	122.4 (0.8)	C(20)—N(4)—C(16)	119.6 (0.7)
Thiourea molecule			
S—C(21)	1.72 (1) Å	S—C(21)—N(5)	123.1 (0.8)°
N(5)—C(21)	1.29 (1)	S—C(21)—N(6)	117.9 (0.8)
N(6)—C(21)	1.38 (1)	N(5)—C(21)—N(6)	118.9 (1.0)
Perchlorate anions			
Cl(1)—O(1)	1.31 (1) Å	O(1)—Cl(1)—O(2)	95.7 (0.9)°
Cl(1)—O(2)	1.38 (2)	O(2)—Cl(1)—O(3)	110.2 (1.0)
Cl(1)—O(3)	1.31 (1)	O(3)—Cl(1)—O(4)	104.1 (0.7)
Cl(1)—O(4)	1.40 (1)	O(1)—Cl(1)—O(4)	108.3 (0.6)
		O(2)—Cl(1)—O(4)	111.3 (0.9)
		O(1)—Cl(1)—O(3)	127.0 (0.8)
Cl(2)—O(5)	1.44 (1)	Cl(2)—O(5)	1.44 (1) Å
Cl(2)—O(6)	1.44 (1)	Cl(2)—O(9)	1.46 (2)
Cl(2)—O(7)	1.39 (2)	Cl(2)—O(10)	1.45 (2)
Cl(2)—O(8)	1.47 (2)	Cl(2)—O(11)	1.42 (2)
O(5)—Cl(2)—O(6)	113.8 (0.6)°	O(5)—Cl(2)—O(9)	116.2 (0.8)°
O(6)—Cl(2)—O(7)	118.2 (1.0)	O(9)—Cl(2)—O(10)	121.5 (1.1)
O(7)—Cl(2)—O(8)	96.5 (1.0)	O(10)—Cl(2)—O(11)	99.1 (1.1)
O(8)—Cl(2)—O(5)	102.9 (0.8)	O(11)—Cl(2)—O(5)	119.4 (0.8)
O(7)—Cl(2)—O(5)	113.0 (0.8)	O(10)—Cl(2)—O(5)	94.8 (0.9)
O(6)—Cl(2)—O(8)	109.7 (0.8)	O(9)—Cl(2)—O(11)	105.3 (1.0)

Fig. 5.  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ . Projection of the structure on (001).Table 5. Contacts less than 3.5 Å for  $\text{Cu}(\text{pib})\text{tu}(\text{ClO}_4)_2$ 

O(2)—O(2 <sup>i</sup> )	2.95 (2) Å
N(6)—O(10 <sup>ii</sup> )	3.06 (2)
O(7)—N(5 <sup>iii</sup> )	3.08 (2)
N(5)—O(2 <sup>iv</sup> )	3.09 (1)
O(11)—N(5 <sup>iii</sup> )	3.13 (2)
N(5)—O(4 <sup>iv</sup> )	3.27 (1)
N(6)—O(3 <sup>ii</sup> )	3.29 (1)
N(6)—O(5 <sup>ii</sup> )	3.37 (3)
O(2)—N(5 <sup>iii</sup> )	3.43 (2)
O(10)—N(6 <sup>iii</sup> )	3.45 (2)

i	$\bar{x}$	$1-y$	$\bar{z}$
ii	$1-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$
iii	$x$	$\frac{1}{2}-y$	$z-\frac{1}{2}$
iv	$\bar{x}$	$y-\frac{1}{2}$	$\frac{1}{2}-z$

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Table 6. Contacts less than 3.5 Å for  $\text{Cu}(\text{bipy})_2\text{tu}(\text{ClO}_4)_2$ 

O(8)—N(4 <sup>i</sup> )	3.21 (2) Å
O(8)—N(5 <sup>i</sup> )	2.89 (2)
O(11)—N(5 <sup>i</sup> )	2.72 (2)
O(3)—N(6 <sup>ii</sup> )	3.26 (1)
O(4)—N(6 <sup>ii</sup> )	3.00 (1)
N(5)—O(1 <sup>iii</sup> )	2.96 (1)
N(6)—O(2 <sup>iii</sup> )	3.02 (2)

i	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$x$	$y$	$1+z$
iii	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$1-z$

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