X-Ray Crystal Structures of Tetrakis(imidazolidine-2-thionato)copper(I) Nitrate and Dichloro-μ-imidazolidine-2-thionato-tris(imidazolidine-2-thionato)dicopper(I)

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The *X*-ray structures of the title compounds have been determined from diffractometer data by the heavy-atom method and refined by least-squares. Crystal data: $[Cu(C_3H_6N_2S)_4]NO_3$, (I), $a = 13.22(1)$, $b = 11.21(1)$, $c = 7.55(1)$ Å, $\alpha = 82.0(1)$, $\beta = 78.3(1)$, $\gamma = 87.2(1)°$, $Z = 2$, space group $P\bar{1}$, final R 8.5%; $[Cu(C_3H_6N_2S)_2Cl]_2$, (II) $a = 7.43(1)$, $b = 18.71(1)$, $c = 16.37(1)$ Å, $\beta = 94.4(1)°$, $Z = 4$, space group $P2_1/c$, final R 9.4%. In (I) copper co-ordination is tetrahedral and involves the sulphur atoms of four 2-thioimidazolidine (etu) molecules (Cu–S 2.34, 2.36, 2.34, and 2.33 Å). Complex (II) is binuclear containing two kinds of Cu^I atoms: one tetrahedrally co-ordinated by three etu molecules (Cu–S 2.26, 2.28, and 2.63 Å) and by one chlorine ion (Cu–Cl 2.32 Å), the other trigonally co-ordinated by two etu molecules (Cu–S 2.20 Å) and one chlorine ion (Cu–Cl 2.28 Å). In both compounds conformation and packing are mainly determined by hydrogen bonds of the type N–H ··· O (I) or N–H ··· Cl (II), and N–H ··· S.

THE investigation of the crystal structures of the title compounds was carried out as part of our programme of research on metal complexes of ligands containing sulphur as donor atom.

EXPERIMENTAL

Crystals of (I) $[Cu(etu)_4]NO_3$ and (II) $[Cu_2(etu)_4Cl_2]$ (etu = imidazolidine-2-thionato) were prepared according to the method of ref. 1.

Physical Measurements.—I.r. spectra were measured on a Perkin-Elmer 457 spectrophotometer by the KBr technique. *X*-Ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer, by the ω—2θ scan technique.

Crystal Data.—(*a*) (I). $C_{12}H_{24}CuN_9O_3S_4$, $M = 534.2$, Triclinic, $a = 13.22(1)$, $b = 11.21(1)$, $c = 7.55(1)$ Å, $\alpha = 82.0(1)$, $\beta = 78.3(1)$, $\gamma = 87.2(1)°$, $U = 1\,085$ Å^3, $D_m = 1.68$ g cm^{-3}, $Z = 2$, $D_c = 1.67$ g cm^{-3}, $F(000) = 552$. Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 51.9$ cm^{-1}. Space group $P\bar{1}$ from structural analysis.

(*b*) (II). $[C_6H_{12}ClCuN_4S_2]_2$, $M = 303.2$, Monoclinic, $a = 7.43(1)$, $b = 18.71(1)$, $c = 16.37(1)$ Å, $\beta = 94.4(1)°$, $U = 2\,268$ Å^3, $D_m = 1.78$ g cm^{-3}, $Z = 4$, $D_c = 1.77$ g cm^{-3}, $F(000) = 1\,232$. Cu-K_α radiation; $\mu(\text{Cu-}K_\alpha) = 79.5$ cm^{-1}. Space group $P2_1/c$.

For both compounds, cell dimensions were determined from rotation and Weissenberg photographs and refined by the least-squares fit to the $(\theta, \chi, \phi)_{hkl}$ values for 15 reflections measured on the diffractometer.

Data Collection.—For both compounds all the reflections with $2\theta \leqslant 140°$ [4 115 (I) and 4 342 (II)] were collected, of which 3 911 for (I) and 3 735 for (II), having $I > 2\sigma(I)$ were considered observed and used in the structure analysis. No absorption corrections were used (cross-section of crystals both 0.33 × 0.19 mm). After the usual data reduction, structure amplitudes were brought to an absolute scale first by Wilson's [2] method and later by correlation of observed with the calculated values.

Structure Analysis.—For both structures, copper atoms were located from three-dimensional Patterson maps and the positions of the other atoms determined by the heavy-atom technique in successive Fourier syntheses. Refinements were carried out by block-diagonal anisotropic least-squares, the function minimized being $\Sigma w|\Delta F|^2$ at first with unit weights, then with the weighting scheme $w = 1/(A + BF_o)^2$ with $A = 0.50$ and $B = 0.11$ for (I) and $A = 0.95$ and $B = 0.46$ for (II). At the end of the refinement the final R indices were 8.5 (I) and 9.4% (II). For (I) the three strongest reflections [($\bar{3}$01) (102) (202)] were excluded from the refinement, and, in addition, it was found necessary to correct for extinction. This correction was applied empirically to the F_o values by use of the formula $|F_o|_{\text{corr.}} = F_o(1 + gI_c)$ (ref. 3) with $g = 1.3 \times 10^{-5}$.

Final atomic and thermal parameters are listed in Tables 1 and 2 for the two structures. Observed and calculated structure factors are given in Supplementary Publication No. SUP 21485 (38 pp., 1 microfiche).† Atomic scattering factors used throughout the calculations were taken from ref. 4.

All calculations were performed on a CDC 6 600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale with programs of Immirzi.[5]

RESULTS AND DISCUSSION

Spectroscopic data (4 000—250 cm^{-1}) for both compounds are similar and characterized by the vibrational bands of the N–H and C=S groups: in particular the frequency values indicate co-ordination through the sulphur atom. In (I) bonds at 1 380s and 820m cm^{-1} indicate ionic nitrate.

The clinographic projections of the two structures are shown in Figures 1 and 2. In (I) co-ordination around copper is tetrahedral and involves the sulphur atoms of four independent etu molecules. The Cu–S distances in the co-ordination polyhedron are in good agreement with those found in Cu^I thiourea tetrahedral complexes.[6] Bond distances and angles for both compounds are listed in Tables 3 and 4.

The structure of (II) is binuclear, with two independent copper atoms exhibiting two different kinds of co-ordination: trigonal planar [Cu only 0.03 Å out of the S(1), S(2), Cl(1) plane] and tetrahedral [Cu 0.57 Å out

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† See notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[1] T. Morgan and H. Burstall, *J. Chem. Soc.*, 1928, 143.

[2] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

[3] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, London, 1968, 411.

[4] D. T. Cromer and G. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] A. Immirzi, *Ricerca Sci.*, 1967, **34**, 743.

[6] L. Capacchi Calzolari, L. Cavalca, G. Fava Gasparri, and M. Ferrari, *Ricerca Sci.*, 1969, **39**, 662.

Table 1

Final atomic fractional co-ordinates (× 10^4) and thermal parameters * (× 10 Å^2) for (I), with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2 135(1)	2 902(1)	3 680(1)	38(0)	33(0)	53(0)	−5(0)	−12(0)	6(0)
S(1)	530(1)	2 830(1)	5 678(1)	34(0)	20(0)	35(0)	−7(0)	−4(0)	2(0)
S(2)	1 832(1)	3 015(1)	686(1)	42(0)	15(0)	35(0)	1(0)	−7(0)	1(0)
S(3)	2 866(1)	4 631(1)	4 250(1)	25(0)	32(0)	40(0)	−5(0)	−2(0)	−8(0)
S(4)	3 184(1)	1 167(1)	3 714(1)	36(0)	24(0)	38(0)	3(0)	−11(0)	2(0)
O(1)	3 925(3)	7 871(3)	3 897(7)	45(2)	43(2)	84(2)	4(1)	−13(2)	−11(2)
O(2)	2 299(3)	8 251(4)	4 836(6)	55(2)	51(2)	72(2)	−5(1)	4(2)	0(2)
O(3)	2 821(4)	7 809(5)	2 134(6)	75(2)	71(2)	52(2)	6(2)	−19(2)	−8(2)
N(1)	−686(3)	1 115(3)	7 728(5)	34(1)	26(1)	42(1)	−9(1)	−1(1)	3(1)
N(2)	827(3)	436(3)	6 509(5)	36(1)	23(1)	52(2)	−4(1)	−2(1)	3(1)
N(3)	1 131(3)	4 751(3)	−1 572(4)	45(2)	23(1)	32(1)	1(1)	−10(1)	0(1)
N(4)	1 781(3)	5 446(3)	518(5)	53(2)	18(1)	49(2)	3(1)	−22(1)	−2(1)
N(5)	4 733(3)	5 574(3)	2 803(6)	29(1)	33(1)	57(2)	−7(1)	2(1)	−3(1)
N(6)	4 679(3)	3 651(3)	2 700(6)	30(1)	34(1)	62(2)	−2(1)	1(1)	−4(1)
N(7)	3 378(4)	1 520(4)	7 063(6)	66(2)	47(2)	50(2)	22(2)	−26(2)	−12(2)
N(8)	3 848(4)	−257(3)	6 409(6)	63(2)	35(1)	42(2)	13(1)	−22(2)	−2(1)
N(9)	3 025(3)	7 984(3)	3 611(6)	46(2)	28(1)	58(2)	0(1)	−3(1)	3(1)
C(1)	230(3)	1 397(3)	6 667(5)	31(1)	24(1)	31(1)	−7(1)	−9(1)	−1(1)
C(2)	−791(3)	−207(3)	8 145(6)	42(2)	25(1)	40(2)	−13(1)	−5(1)	0(1)
C(3)	309(4)	−660(3)	7 510(6)	49(2)	22(1)	37(2)	−1(1)	−13(1)	0(1)
C(4)	1 565(3)	4 450(3)	−115(4)	25(1)	19(1)	29(1)	0(1)	0(1)	0(1)
C(5)	1 103(3)	6 063(3)	−2 093(6)	45(2)	26(1)	37(2)	3(1)	−9(1)	5(1)
C(6)	1 374(3)	6 522(3)	−450(6)	44(2)	16(1)	46(2)	1(1)	−10(1)	0(1)
C(7)	4 130(3)	4 617(3)	3 211(5)	29(1)	30(1)	31(1)	−5(1)	−6(1)	−1(1)
C(8)	5 785(3)	5 290(4)	1 908(6)	29(2)	47(2)	45(2)	−10(1)	−3(1)	−1(2)
C(9)	5 775(3)	3 920(5)	1 982(8)	26(1)	47(2)	60(2)	0(1)	1(1)	0(2)
C(10)	3 483(3)	793(3)	5 817(5)	23(1)	25(1)	37(1)	0(1)	−4(1)	0(1)
C(11)	3 727(5)	939(6)	8 723(7)	67(3)	67(3)	39(2)	19(1)	−21(2)	−10(2)
C(12)	4 010(6)	−346(6)	8 243(7)	78(3)	75(3)	36(2)	41(3)	−13(2)	2(2)

* The anisotropic temperature factors are in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^*\cos\gamma^* + 2B_{13}hla^*c^*\cos\beta^* + 2B_{23}klb^*c^*\cos\alpha^*)]$.

Table 2

Final atomic fractional co-ordinates (× 10^4) and thermal parameters * (× 10 Å^2) for (II), with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	2 107(1)	1 734(1)	759(1)	43(0)	40(0)	44(0)	5(0)	5(0)	−6(0)
Cu(2)	2 099(1)	65(1)	2 743(1)	45(0)	76(1)	42(0)	−13(0)	12(0)	−16(0)
Cl(1)	254(2)	2 535(1)	67(1)	47(1)	53(1)	31(1)	21(1)	4(1)	1(1)
Cl(2)	272(2)	147(1)	3 826(1)	28(1)	38(1)	27(1)	1(0)	8(0)	−2(0)
S(1)	4 590(2)	1 669(1)	116(1)	38(1)	40(1)	32(1)	10(1)	6(1)	10(1)
S(2)	1 275(2)	1 224(1)	1 884(1)	38(1)	31(1)	46(1)	12(1)	13(1)	7(1)
S(3)	5 040(2)	176(1)	3 180(1)	28(1)	40(1)	25(1)	1(1)	8(0)	−3(0)
S(4)	1 559(2)	−854(1)	1 841(1)	41(1)	32(1)	26(1)	−1(0)	11(0)	−3(0)
N(1)	7 209(7)	713(3)	122(3)	37(2)	54(3)	33(2)	15(2)	14(2)	9(2)
N(2)	5 607(8)	583(3)	1 150(3)	47(3)	46(3)	37(2)	20(2)	17(2)	13(2)
N(3)	−1 358(9)	1 536(3)	2 838(4)	52(3)	43(2)	52(3)	21(2)	21(2)	12(2)
N(4)	−1 412(7)	2 181(3)	1 723(3)	37(2)	43(2)	43(2)	15(2)	11(2)	3(2)
N(5)	6 622(7)	714(3)	4 575(3)	31(2)	51(3)	36(2)	3(2)	4(2)	−7(2)
N(6)	3 844(7)	1 041(3)	4 340(3)	35(2)	37(2)	41(2)	5(2)	4(2)	−6(2)
N(7)	−1 114(8)	−1 809(3)	1 626(3)	46(2)	42(2)	39(2)	−8(2)	8(2)	−8(2)
N(8)	−1 161(8)	−1 191(3)	2 752(3)	52(3)	35(2)	32(2)	−14(2)	11(2)	−4(2)
C(1)	5 819(7)	967(3)	487(3)	27(2)	35(2)	23(2)	2(2)	3(2)	−3(2)
C(2)	8 070(10)	95(4)	559(4)	43(3)	44(3)	33(2)	12(2)	7(2)	2(2)
C(3)	6 925(10)	12(4)	1 281(4)	44(3)	42(3)	40(3)	17(2)	7(2)	8(2)
C(4)	−617(8)	1 663(3)	2 157(4)	30(2)	27(2)	39(2)	2(2)	6(2)	−2(2)
C(5)	−2 884(9)	2 007(4)	2 931(5)	40(3)	43(3)	54(3)	11(2)	19(2)	4(2)
C(6)	−3 063(8)	2 408(3)	2 117(4)	34(2)	35(2)	46(3)	7(2)	8(2)	−3(2)
C(7)	5 158(7)	659(3)	4 070(3)	28(2)	33(2)	29(2)	−2(2)	6(2)	7(2)
C(8)	6 345(9)	1 213(4)	5 249(4)	41(3)	43(3)	39(3)	−9(2)	3(2)	−10(2)
C(9)	4 328(9)	1 289(3)	5 179(4)	44(3)	33(2)	40(3)	4(2)	8(2)	−7(2)
C(10)	−298(8)	−1 296(3)	2 088(3)	38(2)	25(2)	22(2)	4(2)	2(2)	1(1)
C(11)	−2 739(9)	−2 073(4)	1 975(4)	49(3)	41(3)	30(2)	−9(2)	3(2)	2(2)
C(12)	−2 739(10)	−1 658(4)	2 778(4)	47(3)	40(3)	38(3)	−15(2)	13(2)	−1(2)

* See footnote to Table 1.

of the plane through S(3), S(4), Cl(2)]. Both copper atoms are co-ordinated by chlorine and sulphur with distances involving chlorine being longer than those involving sulphur. The distances in the tetrahedral environment are significantly longer than those involving trigonal copper and the bridging sulphur is more loosely bound to the tetrahedral copper. This unusual existence of two different kinds of co-ordination polyhedra for the same Cu^{I} species in the same compound has already been observed with thiourea in $Cu_2SO_4[SC(NH_2)_2]_5{\cdot}2H_2O$,[6] where polymeric chains of alternating trigonal and tetrahedral copper(I) are present.

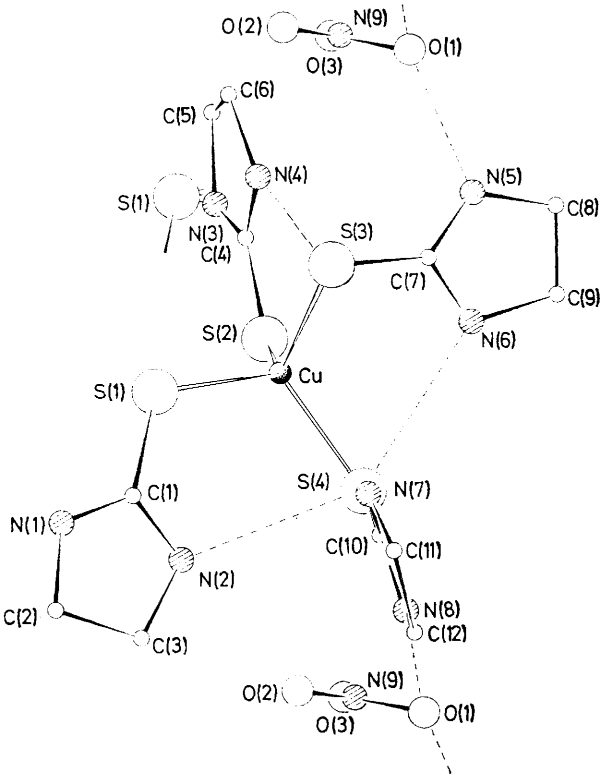

FIGURE 1 Clinographic projection of the structure of (I)

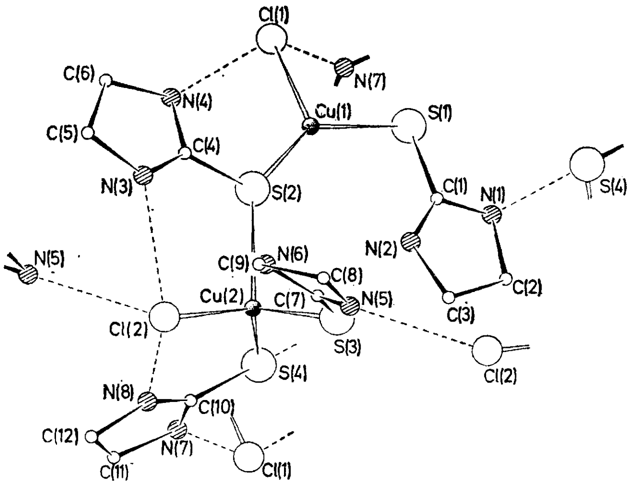

FIGURE 2 Clinographic projection of the structure of (II)

TABLE 3

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for (I)

(*a*) In the co-ordination sphere			
Cu–S(1)	2.339(3)	Cu–S(3)	2.337(3)
Cu–S(2)	2.360(3)	Cu–S(4)	2.333(3)
S(1)–Cu–S(2)	107.7(3)	S(3)–Cu–S(4)	115.7(2)
S(1)–Cu–S(3)	103.2(2)	Cu–S(1)–C(1)	111.8(4)
S(1)–Cu–S(4)	117.8(3)	Cu–S(2)–C(4)	110.2(4)
S(2)–Cu–S(3)	113.8(3)	Cu–S(3)–C(7)	107.4(3)
S(2)–Cu–S(4)	98.8(2)	Cu–S(4)–C(10)	109.9(4)
(*b*) in the etu molecules			
S(1)–C(1)	1.704(4)	C(2)–C(3)	1.522(6)
S(2)–C(4)	1.685(4)	C(5)–C(6)	1.519(7)
S(3)–C(7)	1.696(4)	C(8)–C(9)	1.530(7)
S(4)–C(10)	1.705(5)	C(11)–C(12)	1.544(10)
Mean	1.70	Mean	1.53
C(1)–N(1)	1.335(5)	N(1)–C(2)	1.479(5)
C(1)–N(2)	1.309(5)	N(2)–C(3)	1.471(5)
C(4)–N(3)	1.337(5)	N(3)–C(5)	1.469(5)
C(4)–N(4)	1.339(5)	N(4)–C(6)	1.459(5)
C(7)–N(5)	1.332(5)	N(5)–C(8)	1.459(6)
C(7)–N(6)	1.332(5)	N(6)–C(9)	1.471(6)
C(10)–N(7)	1.311(6)	N(7)–C(11)	1.478(8)
C(10)–N(8)	1.305(5)	N(8)–C(12)	1.433(8)
Mean	1.33	Mean	1.46
S(1)–C(1)–N(1)	122.7(6)	S(3)–C(7)–N(5)	125.0(6)
S(1)–C(1)–N(2)	126.7(6)	S(3)–C(7)–N(6)	125.6(7)
C(1)–N(1)–C(2)	110.8(6)	C(7)–N(5)–C(8)	112.8(7)
C(1)–N(2)–C(3)	112.2(6)	C(7)–N(6)–C(9)	112.2(7)
N(1)–C(1)–N(2)	110.7(6)	N(5)–C(7)–N(6)	109.3(6)
N(1)–C(2)–C(3)	102.3(5)	N(5)–C(8)–C(9)	102.6(6)
N(2)–C(3)–C(2)	102.6(5)	N(6)–C(9)–C(8)	102.5(6)
S(2)–C(4)–N(3)	123.2(6)	S(4)–C(10)–N(7)	124.7(8)
S(2)–C(4)–N(4)	126.9(6)	S(4)–C(10)–N(8)	124.7(7)
C(4)–N(3)–C(5)	111.5(6)	C(10)–N(7)–C(11)	111.7(8)
C(4)–N(4)–C(6)	111.1(6)	C(10)–N(8)–C(12)	113.5(9)
N(3)–C(4)–N(4)	109.8(7)	N(7)–C(10)–N(8)	110.6(7)
N(3)–C(5)–C(6)	102.1(5)	N(7)–C(11)–C(12)	101.5(8)
N(4)–C(6)–C(5)	103.1(6)	N(8)–C(12)–C(11)	102.5(8)
(*c*) In the nitrate ion			
N(9)–O(1)	1.249(6)	O(1)–N(9)–O(2)	120.2(9)
N(9)–O(2)	1.247(7)	O(1)–N(9)–O(3)	121.6(1.1)
N(9)–O(3)	1.242(7)	O(2)–N(9)–O(3)	118.2(1.0)

There are no significant differences between corresponding distances and angles in the etu molecules in (I) and (II) which are also similar to those in unco-ordinated etu and in other etu—metal complexes.[7] The Cu–S–C angles are not far from the tetrahedral values [excepting of course Cu(2)–S(2)–C(4), which involves a long Cu–S interaction], and differences can probably be accounted for by packing interactions. The etu molecules are not strictly planar; in both compounds the most important distortion concerns the ethylenic moiety, as observed for bis(2-thioimidazolidine)nickel(II) thiocyanate.[8] The nitrate ion in (I) is planar and bond distances and angles in it are as expected. The structural function of this ion is mainly that of joining the complex cations through hydrogen bonds of the type

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[7] M. S. Weininger, G. W. Hunt, and E. L. Amma, *J.C.S. Chem. Comm.*, 1972, 1140; M. Nardelli, G. Fava Gasparri, A. Musatti, and A. Manfredotti, *Acta Cryst.*, 1966, **21**, 910; L. Cavalca, M. Nardelli, and G. Fava, *ibid.*, 1960, **13**, 125; P. J. Wheatley, *ibid.*, 1953, **6**, 369.

[8] M. Nardelli, G. Fava Gasparri, A. Musatti, and A. Manfredotti, *Acta Cryst.*, 1966, **21**, 910.

N–H ··· O as shown [Figure 1 and Table 5(*a*)]. The conformation of the complex cations, and in particular the orientation of the etu molecules, is conditioned by intramolecular N–H ··· S hydrogen bonds. An intermolecular N–H ··· S hydrogen bond plays a rôle in determining packing. In (II) hydrogen bonding is also important both for packing and for determining conformation in the complex; the hydrogen bonds here are of the type N–H ··· Cl and N–H ··· S [Figure 2 and Table 5(*b*)]. Contacts <3.5 Å are quoted in Table 6.

TABLE 4

Bond distances (Å) and angles (°), with estimated standard deviation in parentheses, for (II)

(*a*) In the co-ordination sphere			
Cu(1)–Cl(1)	2.277(3)	Cl(2)–Cu(2)–S(2)	103.2(2)
Cu(1)–S(1)	2.196(3)	Cl(2)–Cu(2)–S(3)	111.2(3)
Cu(1)–S(2)	2.204(3)	Cl(2)–Cu(2)–S(4)	117.4(2)
		S(2)–Cu(2)–S(3)	105.9(2)
Cl(1)–Cu(1)–S(1)	107.2(3)	S(2)–Cu(2)–S(4)	104.7(2)
Cl(1)–Cu(1)–S(2)	120.2(2)	S(3)–Cu(2)–S(4)	113.1(3)
S(1)–Cu(1)–S(2)	132.5(4)	Cu(1)–S(1)–C(1)	108.8(4)
		Cu(1)–S(2)–C(4)	107.3(5)
Cu(2)–Cl(2)	2.319(3)	Cu(2)–S(2)–C(4)	114.6(3)
Cu(2)–S(2)	2.631(3)	Cu(2)–S(4)–C(10)	108.7(4)
Cu(2)–S(3)	2.256(4)	Cu(2)–S(3)–C(7)	107.7(4)
Cu(2)–S(4)	2.282(3)	Cu(2)–S(2)–Cu(1)	137.3(3)
(*b*) In the etu molecules			
S(1)–C(1)	1.686(6)	C(2)–C(3)	1.516(10)
S(2)–C(4)	1.717(7)	C(5)–C(6)	1.526(10)
S(3)–C(7)	1.711(6)	C(8)–C(9)	1.501(10)
S(4)–C(10)	1.684(6)	C(11)–C(12)	1.527(10)
Mean	1.70	Mean	1.52
C(1)–N(1)	1.321(8)	N(1)–C(2)	1.479(9)
C(1)–N(2)	1.321(7)	N(2)–C(3)	1.454(10)
C(4)–N(3)	1.303(10)	N(3)–C(5)	1.453(10)
C(4)–N(4)	1.315(8)	N(4)–C(6)	1.491(8)
C(7)–N(5)	1.319(7)	N(5)–C(8)	1.472(9)
C(7)–N(6)	1.314(8)	N(6)–C(9)	1.468(8)
C(10)–N(7)	1.338(8)	N(7)–C(11)	1.461(9)
C(10)–N(8)	1.318(8)	N(8)–C(12)	1.466(10)
Mean	1.32	Mean	1.47
S(1)–C(1)–N(1)	122.6(8)	S(3)–C(7)–N(5)	124.1(8)
S(1)–C(1)–N(2)	128.6(9)	S(3)–C(7)–N(6)	125.7(9)
N(2)–C(1)–N(1)	108.8(9)	N(5)–C(7)–N(6)	110.2(9)
C(1)–N(1)–C(2)	112.8(1.0)	C(7)–N(5)–C(8)	111.3(9)
C(1)–N(2)–C(3)	113.5(1.0)	C(7)–N(6)–C(9)	110.6(9)
N(1)–C(2)–C(3)	102.1(8)	N(5)–C(8)–C(9)	101.5(8)
N(2)–C(3)–C(2)	102.8(9)	N(6)–C(9)–C(8)	102.3(8)
S(2)–C(4)–N(3)	123.0(1.0)	S(4)–C(10)–N(7)	124.1(9)
S(2)–C(4)–N(4)	123.7(9)	S(4)–C(10)–N(8)	125.7(1.0)
N(3)–C(4)–N(4)	113.3(1.1)	N(7)–C(10)–N(8)	110.2(9)
C(4)–N(3)–C(5)	111.3(1.1)	C(10)–N(7)–C(11)	112.0(1.0)
C(4)–N(4)–C(6)	109.1(9)	C(10)–N(8)–C(12)	112.1(1.1)
N(3)–C(5)–C(6)	102.9(9)	N(7)–C(11)–C(12)	102.7(9)
N(4)–C(6)–C(5)	102.6(9)	N(8)–C(12)–C(11)	103.0(9)

TABLE 5

Contacts (Å) which can be interpreted as hydrogen bonds

(*a*) In (I)			
S(3) ··· N(4)	3.410(6)	O(1) ··· N(5)	2.902(6)
S(4) ··· N(2)	3.455(6)	N(3) ··· S(1$^{\text{I}}$)	3.415(5)
S(4) ··· N(6)	3.402(5)		
(*b*) In (II)			
Cl(1) ··· N(4)	3.136(6)	Cl(2) ··· N(8)	3.194(6)
Cl(1) ··· N(7$^{\text{II}}$)	3.195(6)	Cl(2) ··· N(5$^{\text{III}}$)	3.239(7)
Cl(2) ··· N(3)	3.246(6)	N(1) ··· S(4$^{\text{IV}}$)	3.418(6)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, y, z - 1$ II $\bar{x}, \bar{y}, \bar{z}$
III $x - 1, y, z$ IV $1 - x, \bar{y}, \bar{z}$

TABLE 6

Contacts (Å) <3.5 Å

(*a*) In (I)			
N(5) ··· N(9)	3.475(6)	N(8) ··· N(9$^{\text{V}}$)	3.440(8)
N(8) ··· O(1$^{\text{V}}$)	3.003(7)	N(1) ··· O(2$^{\text{VI}}$)	3.153(7)
S(4) ··· O(2$^{\text{V}}$)	3.460(6)	N(1) ··· O(3$^{\text{VI}}$)	3.003(7)
N(2) ··· O(2$^{\text{V}}$)	3.283(7)	N(8) ··· N(8$^{\text{VII}}$)	3.367(8)
N(8) ··· O(2$^{\text{V}}$)	3.206(8)		
(*b*) In (II)			
Cl(2) ··· N(6)	3.195(6)	S(3) ··· N(2)	3.466(6)

Roman numeral superscripts refer to the following equivalent positions:

V $x, y - 1, z$ VI $\bar{x}, 1 - y, 1 - z$
VII $1 - x, \bar{y}, 1 - z$

[4/2340 *Received, 8th November,* 1974]