A Novel 'Tent-like' Structure of a Copper(I) Aggregate. The Crystal and Molecular Structure of Nona[*N*-(diethoxythiophosphoryl)-*N'*-phenylisothioureato]decacopper(I) Perchlorate†

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The pale yellow complex formed by the reaction of copper(II) and *N*-(diethoxythiophosphoryl)-*N'*-phenylthiourea is shown to be a cationic Cu^I aggregate, $[Cu_{10}\{(EtO)_2P(S){-}N{=}C(S^-)NHPh\}_9]^+$ Crystals were obtained with ClO_4^- as a counter ion and the structure of the aggregate was determined by *X*-ray diffraction. The unit cell is triclinic, space group $P\bar{1}$, with a = 16.06(1), b = 22.19(1), c = 22.455(6) Å, α = 90.16(3), β = 108.63(4), γ = 91.37(5)°, and Z = 2. The intensities of 8 903 reflections were collected ($\theta_{max.}$ = 18°). The final weighted residual for 7 249 reflections with $I > 2\sigma(I)$ was 0.100. Each aggregate comprises: ten Cu^I atoms arranged in an approximate tetrahedron whose sides are each delineated by three Cu atoms; nine ligand molecules, each chelating one copper atom *via* two sulphur atoms; and one perchlorate anion neutralising the positive charge carried by a single, non-chelated copper. This $Cu^I_{10}S_{18}$ core represents the novel member of a family of copper–sulphur aggregates. Observed Cu–Cu distances (3.11—4.06 Å) indicate the absence of any significant metal–metal bonding. Sulphur co-ordination varies from one and two for P=S centres to two and three for $C{-}S^-$ groups.

Copper(I) forms numerous types of complexes which include mono-, bi-, and poly-nuclear structures with copper being two-, three-, or four-co-ordinate, or forming infinite chains of atoms.[1] A large family of copper(I)–sulphur complexes is represented by a variety of structures, determined by the nature of the sulphur ligand. For example, $[Cu(SPMe_3)_3]ClO_4$ exists as a mononuclear species,[2] while the similar tris(thiourea)copper(I) chloride forms infinite chains in which one of the three thiourea molecules bridges two Cu atoms.[3] A Cu^I complex of thiophenol consists of a Cu_4 tetrahedron, with the Cu atoms bridged by sulphur to give a Cu_4S_6 skeleton having an adamantane-type structure.[4] A growing family of structures attracting increasing attention is the type characterised by a $Cu^I_8S_{12}$ core, comprising a cube of Cu^I atoms, inside an icosahedron of sulphur atoms and found in Cu^I complexes with 1,1- and 1,2-dithiolate ligands, such as 1,1-dicyanoethylene-2,2-dithiolate[5] or 3,4-dimercaptocyclobutene-1,2-dionate[6] anions. The same $Cu^I_8S_{12}$ core has been recognised[7] in the structure of the Cu^I/Cu^{II} mixed-valence cluster complex formed by the reaction of Cu^{II} and D-penicillamine (H_2pen). In the same reaction, Cu^I formed by reduction of Cu^{II} by H_2pen can form a polymeric 1 : 1 Cu^I–Hpen complex, characterised spectroscopically by Sugiura and Tanaka.[8]

In view of the great diversity of copper(I)–sulphur complexes, the stoicheiometry of which gives little clue to their structure, we decided to investigate the reaction between copper(I) salts and the bifunctional, neutral sulphur substrate *N*-(diethoxythiophosphoryl)-*N'*-phenylthiourea (HL^1). Our reasons for choosing this compound as a ligand for our structural study were as follows. It contains two different sulphur centres: the thiophosphoryl group, P=S, capable of the formation with Cu^I mononuclear species,[2] and the thiocarbonyl function which can act as a neutral donor centre, or, due to the tautomeric equilibrium, equation (1), can produce the thiol type ligand (HL^2).

$$\underset{HL^1}{(EtO)_2P(S){-}NH{-}C(S){-}NHPh} \rightleftharpoons \underset{HL^2}{(EtO)_2P(S){-}N{=}C(SH){-}NHPh} \quad (1)$$

The SH group of HL^2 would be expected to reduce Cu^{II} ions in a manner similar to other thiols and thus to give rise to a Cu^I–L^2 complex. The ligand HL^1 also represents the 1,5-dithio system, and such a geometry could result in a structure for the copper complex quite different from those obtained for monothio or 1,1- and 1,2-dithio ligands. In addition, it was recently reported[9] that HL^1 forms the S-mercury derivative which then easily undergoes fragmentation to the carbodi-imide $(EtO)_2P(S){-}N{=}C{=}NPh$, a useful intermediate for the synthesis of phosphorylated guanidines, isoureas, and isothioureas.

Results and Discussion

When an ethanolic solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (or $CuCl_2{\cdot}2H_2O$) is added at −60 °C to an ethanolic solution of HL^1 (ligand:copper ratio ⩾ 2:1), an intensely purple solution is obtained immediately. The colour disappears after the addition is complete and a pale yellow precipitate is formed. The same precipitate is directly obtained when mixing is carried out at room or elevated (60 °C) temperature. Elemental analysis (C, H, N) of the precipitate indicated an approximate 1:1 Cu–L^1 composition, and ^1H n.m.r. showed that the structure of the ligand remained intact. The observed behaviour corresponds closely to that reported[7] for the reaction between Cu^{II} and penicillamine, *i.e.* fast reduction of Cu^{II} to Cu^I by the SH group of the ligand, initial formation of a Cu^I/Cu^{II} mixed-valence complex (purple), and finally precipitation of an almost colourless, polymeric Cu^I complex.

We have varied the conditions of complex formation (reagent concentration, temperature, rate of mixing, *etc.*) and although the same product was always obtained, it was in all cases unsuitable for *X*-ray diffraction experiments. We have found that crystals suitable for *X*-ray analysis can be conveniently

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

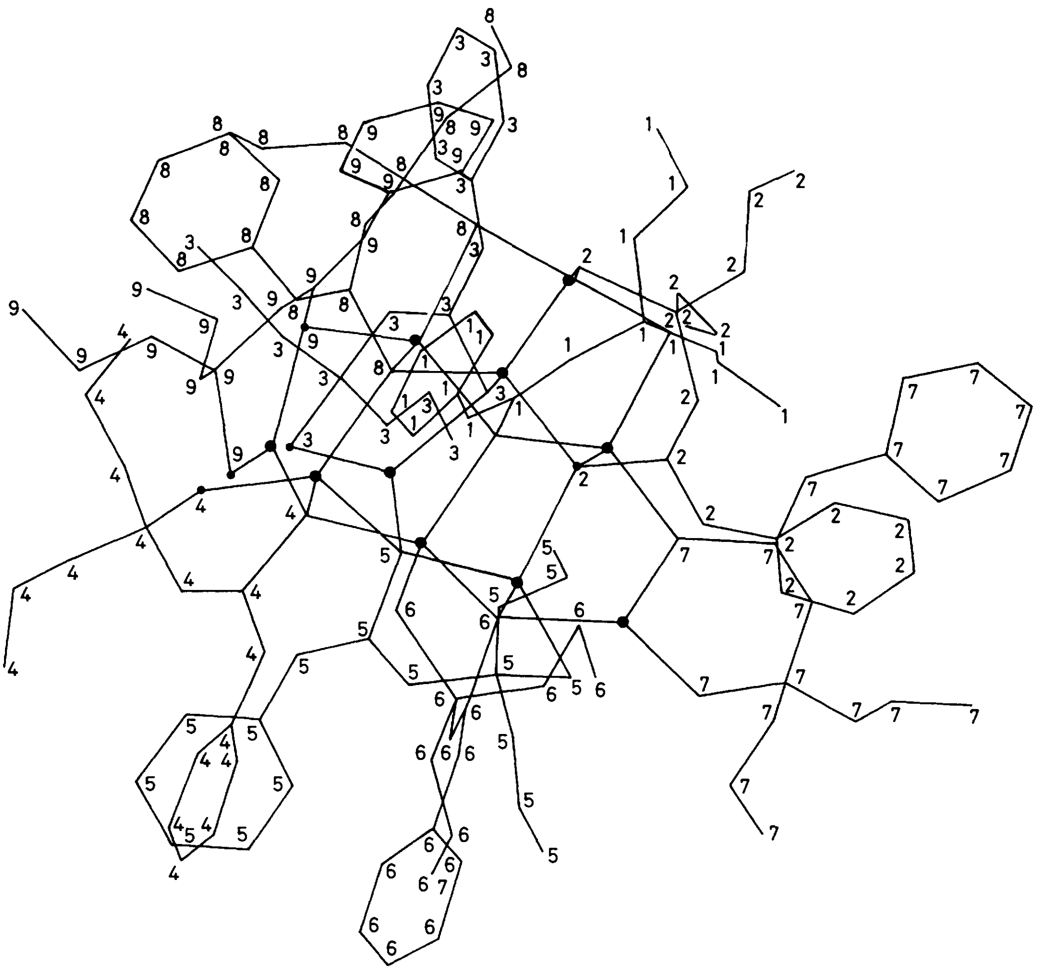


Figure 1. The $[Cu_{10}(L^2)_9]^+$ aggregate (ClO_4^- anion has been omitted for clarity). Copper atoms are represented by black dots and numbers 1—9 refer to the nine ligands

obtained when the reaction between Cu^{II} and HL^1 is carried out in the presence of copper powder which assists the formation of Cu^I ions,[10] equation (2). Crystallographic experimental details

$$Cu^{2+} + Cu^0 \rightleftharpoons 2Cu^+ \qquad (2)$$

and results are given in Table 1. Fractional atomic co-ordinates are given in Table 2.

X-Ray Crystal Structure.—Within the unit cell there are two discrete aggregates which are crystallographically equivalent. Each aggregate (Figure 1) has ten Cu atoms which are co-ordinated to nine ligands, each one bidentate and chelating through its two sulphur atoms. The ligand molecules have all lost one proton at N(X1); hence the charge on each aggregate is + 1. Electrical neutrality is then achieved by the cocrystallisation of one perchlorate anion per aggregate.

Arrangement of the Cu *and* S *atoms.* Within an aggregate Cu–Cu distances are all in the range 3.11(6)—4.06(7) Å. Previously reported Cu–Cu distances in various Cu^I complexes are not much greater than those in metallic copper (2.56 Å);[11] *e.g.*, 2.78 Å in $[Cu_4I_4(AsEt_3)_4]$;[12a] 2.45 and 2.69 Å in $[\{Cu(CCPh)(PMe_3)\}_4]$;[12b] 2.95 Å in $K[Cu_2(CN)_3]\cdot H_2O$;[12c] 2.74 and 2.94 Å in $[Cu_4\{S_2P(OPr^i)_2\}_4]$;[12d] 2.70—3.06 Å in $[\{Cu[SC(O)NPr_2]\}_6]$;[12e] and 2.83 Å in $[AsPh_4]_4[Cu_8L_6]$ $[L = S_2C_2(CN)_2]$.[5] These distances have been interpreted in terms of the Cu–Cu bonding; it is argued however[10] that the Cu–Cu distance is dictated by ligand geometry (there are ligand bridges in every case) and that the d^{10} configuration does not promote intermetallic bonding. Molecular orbital calculations[13] indicate weak or negligible Cu–Cu bonding in most polynuclear complexes. Hence we do not believe that in our case, where the 1,5-dithio geometry of the ligand allows greater intermetallic distances, there are any significant metal–metal bonds, and consequently[10] we refer to our complex as an aggregate, not a cluster. The Cu^I atoms are therefore four- and three-co-ordinate to the sulphur atoms of the ligands.

As shown in Figure 2, the ten Cu atoms are arranged in an approximate tetrahedron whose sides are delineated by the atoms Cu(9) ••• Cu(5) ••• Cu(8), Cu(9) ••• Cu(6) ••• Cu(10), Cu(9) ••• Cu(4) ••• Cu(7), Cu(8) ••• Cu(3) ••• Cu(7), Cu(7) ••• Cu(1) ••• Cu(10), and Cu(10) ••• Cu(2) ••• Cu(8). In each case the three Cu atoms forming a side are not linear (the angle subtended at the centre Cu atom by the other two is in the range 162—167°); hence the description of the shape as a tetrahedron is a simplification. The framework of the copper atoms (Figure 2) more closely resembles a tent-like structure, and we therefore propose this as distinctive for the novel structural arrangement of Cu atoms in the $Cu_{10}S_{18}$ aggregate, different from the more common tetrahedral structure of the Cu_4S_6 system[4] or the cube structure of the Cu_8S_{12} system.[5,6]

As far as the copper co-ordination is concerned, Cu(1), Cu(2), Cu(3), Cu(4), Cu(5), and Cu(6) are four-co-ordinate to the sulphurs (with the S–Cu–S angles in the range 98.5—131.0°),

Table 1. Crystal data, details of the data collection, and final refinements for $[Cu_{10}(L^2)_9]ClO_4$

Molecular formula	$C_{99}H_{144}ClCu_{10}N_{18}O_{22}P_9S_{18}$
M	3 465.04
Space group	$P\bar{1}$
a/Å	16.06(1)
b/Å	22.19(1)
c/Å	22.455(6)
α/°	90.16(3)
β/°	108.63(4)
γ/°	91.37(5)
U/Å^3	7 580
D_m/g cm^{-3} (bromobenzene–CCl_4)	1.52
D_c/g cm^{-3} (for $Z = 2$)	1.51
$F(000)$	3 506
μ(Mo-K_α)/cm^{-1}	17.14
Crystal dimensions (mm)	0.25 × 0.37 × 0.43
Scan mode	ω—2θ
Scan width (°)	$(0.85 + 0.35 \tan \theta)$
Aperture width (mm)	$(2.40 + 1.05 \tan \theta)$
θ Range scanned (°)	1—18
Range of h, k, l	$\pm 13, \pm 19, 0 + 19$
Number of unique reflections collected	8 903
R_{merge}	0.044
Number of observed reflections, N, with $I_{rel} > 2\sigma(I_{rel})$	7 249
Number of parameters, N_P	799
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\| = \Sigma\Delta/\Sigma\|F_o\|$	0.101
$R' = \Sigma w^{\frac{1}{2}}\|\Delta\|/\Sigma w^{\frac{1}{2}}\|F_o\|$	0.100
$S = (\Sigma w\|\Delta\|^2/N - N_P)$	12.6
Crystal stability (%)	9.7

while Cu(7), Cu(8), Cu(9), and Cu(10) are three-co-ordinate (with the S–Cu–S angles in the range 111.0—131.8°) (Figure 2). Nine out of ten Cu atoms in the aggregate [Cu(1)—Cu(8), Cu(10)] are each chelated by the thiophosphoryl (P=S) and thiolato sulphur atoms of one ligand molecule, forming nine six-membered CuSCNPS rings. One [Cu(7), Cu(8), Cu(10)] or two [Cu(1)—Cu(6)] additional co-ordinations take place with the thiolate centres of the adjacent ligand molecules. A single Cu atom [Cu(9)] is unique within the aggregate; it is not chelated but co-ordinates trigonally to three sulphur atoms of the neutral thiophosphoryl groups of the three adjacent molecules of L^2 (ligands 1, 2, and 8). Consequently, Cu(9) carries a full positive charge, counterbalanced by the perchlorate anion present in the structure.

The co-ordination numbers of the 18 sulphur atoms in the aggregate show a marked difference between the thiophosphoryl and the (ionised) isothioureate sulphurs. Six of the P=S sulphurs [S(31), S(41), S(51), S(61), S(71), and S(91)] are one-co-ordinate (Cu–S distance in the range 2.20—2.31 Å), involved only in the chelation of six copper atoms. Three remaining thiophosphoryl centres [S(11), S(21), and S(81)] are two-co-ordinate because of the additional co-ordination to the positively charged 'unique' Cu(9) atom. Three of the thiolato sulphurs [S(32), S(72), and S(92)] are also two-co-ordinate; the Cu–S distances of all two-co-ordinate sulphurs are in the range 2.20—2.38 Å. Six other thiolato sulphurs each form a bridge among three coppers (Cu–S distances in the range 2.23—2.38 Å).

The bonding network between the copper and sulphur atoms gives rise to a system of 14 six-membered CuSCuSCuS rings. As shown in Table 3, a conformational analysis[14] of these rings has been carried out. The three rings involving Cu(9) are each in the chair conformation; the two rings involving Cu(7), Cu(8), and Cu(10) respectively (six in all) have at least some boat character. The rings involving Cu(2, 3, 5), Cu(1 ,3, 4), and Cu(1, 2, 6) are boats or screw-boat/half-chair, while the remaining two rings Cu(1, 2, 3) and Cu(4, 5, 6) are chairs.

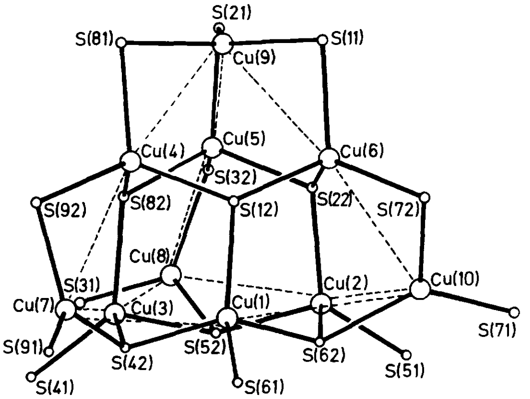


Figure 2. The Cu–S–Cu framework of the aggregate $[Cu_{10}(L^2)_9]^+$

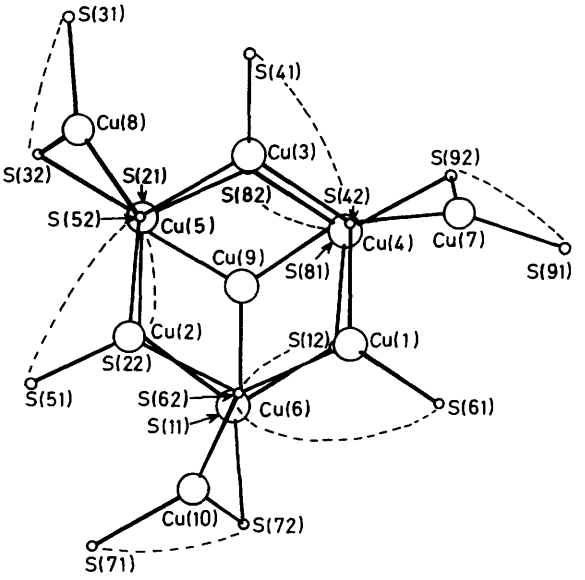


Figure 3. Projection of the aggregate $[Cu_{10}(L^2)_9]^+$ down the line joining Cu(9) and the centre point of the Cu(1, 2, 3) triangle

A view of the aggregate projected down the line joining Cu(9) and the centre point of the Cu(1, 2, 3) triangle (Figure 3) reveals clearly that the aggregate has approximate C_3 symmetry.

The ligands. The ranges of molecular parameters observed for the nine co-ordinated ligands ($C_{11}H_{16}N_2O_2PS_2$) are reported in Table 4. Owing to the large size of the whole structure and the instability of the aggregate (the reason that data were collected only out to $\theta = 18°$), the location of some of the atoms (particularly the lighter ones) is not very precise. This problem was greatest for the carbons of the ethoxy groups which all have extremely high thermal parameters. Hence little significance can be attached to the large ranges observed for these parameters.

Experimental

N-(*Diethoxythiophosphoryl*)-N′-*phenylthiourea* (HL^1).—The ligand HL^1 was prepared by heating aniline and $(EtO)_2P(S)NCS$[15] (1.2:1 ratio) in toluene for 3 h, then precipitating the product with cold light petroleum (b.p. 30—

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for $[Cu_{10}(L^2)_9]ClO_4$

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	1 659(2)	7 194(2)	3 759(2)
Cu(2)	2 754(2)	8 546(2)	2 987(2)
Cu(3)	3 126(2)	6 789(2)	2 672(2)
Cu(4)	559(2)	6 605(2)	2 142(2)
Cu(5)	1 583(2)	7 815(2)	1 402(2)
Cu(6)	253(2)	8 281(2)	2 507(2)
Cu(7)	1 647(3)	5 776(2)	3 480(2)
Cu(8)	3 777(3)	7 731(2)	1 795(2)
Cu(9)	−440(2)	7 577(2)	1 206(2)
Cu(10)	1 459(3)	8 990(2)	3 682(2)
S(11)	−1 080(5)	8 237(4)	1 652(4)
S(12)	447(5)	7 309(3)	2 870(4)
P(1)	−1 732(6)	7 722(4)	2 089(4)
S(21)	253(5)	7 901(3)	556(4)
S(22)	1 449(5)	8 479(3)	2 150(4)
P(2)	231(5)	8 809(4)	573(4)
S(31)	4 693(6)	7 154(4)	1 502(5)
S(32)	2 707(5)	8 135(4)	1 005(4)
P(3)	4 364(6)	7 449(4)	637(5)
S(41)	4 329(5)	6 220(4)	2 734(4)
S(42)	2 615(5)	6 520(3)	3 491(4)
P(4)	4 325(6)	5 750(4)	3 473(4)
S(51)	3 605(5)	9 421(4)	3 269(4)
S(52)	3 627(5)	7 810(3)	2 749(4)
P(5)	4 609(6)	9 135(4)	3 031(4)
S(61)	1 579(5)	6 960(4)	4 734(4)
S(62)	2 280(5)	8 175(3)	3 812(4)
P(6)	1 994(6)	7 739(4)	5 155(4)
S(71)	1 975(6)	9 940(4)	3 788(5)
S(72)	21(5)	8 867(4)	3 310(4)
P(7)	872(6)	10 261(4)	3 834(5)
S(81)	−657(5)	6 586(4)	1 221(4)
S(82)	1 787(5)	6 872(3)	1 874(4)
P(8)	−33(5)	6 159(4)	701(4)
S(91)	1 349(7)	5 289(5)	4 244(6)
S(92)	703(5)	5 631(4)	2 523(4)
P(9)	482(8)	4 741(5)	3 663(6)
O(11)	−2 227(15)	8 205(10)	2 325(11)
C(111)	−2 668(33)	8 043(22)	2 736(24)
C(112)	−2 980(53)	8 502(35)	3 093(34)
O(12)	−2 419(14)	7 308(9)	1 620(11)
C(121)	−3 018(26)	7 532(18)	1 069(19)
C(122)	−2 894(31)	7 276(20)	507(24)
N(11)	−1 319(16)	7 263(10)	2 642(11)
C(1)	−561(18)	7 061(12)	2 958(14)
N(12)	−504(16)	6 687(11)	3 407(12)
C(11)	−1 142(24)	6 306(16)	3 594(18)
C(12)	−1 961(21)	6 269(14)	3 203(16)
C(13)	−2 554(26)	5 856(17)	3 403(19)
C(14)	−2 160(29)	5 534(19)	3 938(21)
C(15)	−1 397(30)	5 614(20)	4 321(22)
C(16)	−866(25)	6 045(16)	4 158(19)
O(21)	667(13)	8 989(9)	77(10)
C(211)	1 091(27)	9 517(19)	68(20)
C(212)	1 773(26)	9 491(19)	−276(20)
O(22)	−740(13)	9 011(9)	334(10)
C(221)	−1 364(23)	8 730(16)	−205(18)
C(222)	−2 268(33)	8 803(21)	−178(23)
N(21)	622(14)	9 218(10)	1 209(11)
C(2)	1 130(17)	9 179(12)	1 757(13)
N(22)	1 432(15)	9 653(11)	2 122(11)
C(21)	1 280(21)	10 265(14)	1 964(14)
C(22)	1 984(21)	10 652(15)	2 127(15)
C(23)	1 897(23)	11 256(16)	2 035(16)
C(24)	1 053(25)	11 454(17)	1 730(17)
C(25)	381(25)	11 089(17)	1 574(17)
C(26)	512(22)	10 480(15)	1 690(15)
C(422)	2 721(31)	4 869(22)	2 371(23)
N(41)	4 243(14)	6 077(9)	4 061(10)
C(4)	3 590(18)	6 362(12)	4 116(13)
N(42)	3 614(16)	6 627(10)	4 675(12)
C(41)	4 290(25)	6 631(15)	5 270(18)
C(42)	5 116(28)	6 679(17)	5 279(22)
C(43)	5 793(29)	6 717(16)	5 878(20)
C(44)	5 518(28)	6 743(16)	6 348(21)
C(45)	4 693(26)	6 701(16)	6 384(20)
C(46)	4 079(25)	6 622(15)	5 790(18)
O(51)	4 462(13)	9 065(9)	2 334(10)
C(511)	4 019(30)	9 500(21)	1 872(22)
C(512)	4 375(46)	9 499(32)	1 425(33)
O(52)	5 351(17)	9 616(12)	3 183(14)
C(521)	5 684(31)	9 844(22)	3 726(24)
C(522)	6 323(31)	10 374(21)	3 737(24)
N(51)	5 056(14)	8 531(10)	3 354(10)
C(5)	4 721(18)	8 000(13)	3 258(13)
N(52)	5 112(14)	7 527(10)	3 583(11)
C(51)	5 948(22)	7 549(15)	4 035(16)
C(52)	6 432(24)	7 070(17)	4 083(19)
C(53)	7 336(28)	7 021(20)	4 556(20)
C(54)	7 585(28)	7 506(19)	4 950(20)
C(55)	7 066(28)	7 971(19)	4 940(21)
C(56)	6 212(23)	7 991(16)	4 459(16)
O(61)	2 181(15)	7 622(10)	5 855(11)
C(611)	2 641(33)	8 039(23)	6 352(24)
C(612)	2 611(47)	7 876(32)	6 933(30)
O(62)	1 262(15)	8 246(10)	4 959(11)
C(621)	176(32)	8 091(24)	4 745(25)
C(622)	148(45)	8 266(30)	5 283(28)
N(61)	2 892(15)	8 055(10)	5 098(11)
C(6)	3 037(18)	8 246(12)	4 574(14)
N(62)	3 815(15)	8 523(10)	4 635(12)
C(61)	4 587(18)	8 650(13)	5 159(14)
C(62)	4 803(21)	8 297(15)	5 710(15)
C(63)	5 530(22)	8 418(15)	6 159(17)
C(64)	6 010(24)	8 894(16)	6 092(17)
C(65)	5 825(22)	9 261(16)	5 600(16)
C(66)	5 084(20)	9 121(14)	5 082(16)
O(71)	932(13)	10 963(10)	3 856(11)
C(711)	1 062(27)	11 303(19)	3 363(20)
C(712)	575(39)	11 869(22)	3 225(29)
O(72)	669(15)	10 111(10)	4 444(11)
C(721)	1 273(40)	9 981(26)	5 080(29)
C(722)	1 413(40)	10 365(26)	5 372(29)
N(71)	27(16)	10 126(11)	3 282(12)
C(7)	−312(21)	9 615(15)	3 048(16)
N(72)	−1 096(17)	9 554(12)	2 549(13)
C(71)	−1 622(26)	10 030(19)	2 197(19)
C(72)	−2 379(30)	9 847(22)	1 711(21)
C(73)	−2 956(36)	10 291(24)	1 448(25)
C(74)	−2 743(31)	10 896(22)	1 516(22)
C(75)	−2 017(33)	11 041(25)	1 919(23)
C(76)	−1 438(31)	10 637(21)	2 322(22)
O(81)	−268(16)	5 482(11)	783(12)
C(811)	347(28)	4 994(19)	915(21)
C(812)	−10(25)	4 499(18)	1 163(21)
O(82)	−419(14)	6 339(9)	2(10)
C(821)	−1 364(24)	6 520(17)	−334(19)
C(822)	−1 948(33)	6 092(20)	−334(25)
N(81)	997(17)	6 240(11)	806(13)
C(8)	1 713(22)	6 410(13)	1 213(15)
N(82)	2 466(17)	6 261(11)	1 155(12)
C(81)	2 628(22)	5 877(15)	680(17)
C(82)	2 164(25)	5 905(17)	45(19)
C(83)	2 377(27)	5 496(18)	−339(21)

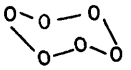
Table 2 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
O(31)	4 820(14)	8 077(10)	650(11)	C(84)	3 090(31)	5 160(21)	−100(24)
C(311)	4 690(28)	8 396(20)	104(21)	C(85)	3 535(37)	5 119(24)	476(27)
C(312)	5 280(33)	8 874(20)	161(24)	C(86)	3 326(25)	5 508(17)	942(20)
O(32)	4 787(14)	7 088(11)	223(11)	N(91)	−314(17)	4 981(12)	3 077(13)
C(321)	4 532(30)	6 573(22)	72(23)	C(9)	−248(19)	5 314(12)	2 589(14)
C(322)	4 803(45)	6 256(32)	−339(32)	N(92)	−961(17)	5 445(11)	2 163(12)
N(31)	3 346(16)	7 463(11)	212(11)	C(91)	−1 815(25)	5 298(17)	2 072(17)
C(3)	2 668(19)	7 730(12)	342(14)	C(92)	−2 479(25)	5 680(18)	1 771(17)
N(32)	1 870(15)	7 670(10)	−106(11)	C(93)	−3 458(34)	5 534(23)	1 663(23)
C(31)	1 630(21)	7 418(14)	−681(16)	C(94)	−3 599(33)	4 974(21)	1 846(21)
C(32)	712(21)	7 316(14)	−981(16)	C(95)	−3 029(29)	4 539(21)	2 152(20)
C(33)	405(31)	7 063(18)	−1 552(21)	C(96)	−2 058(28)	4 726(19)	2 238(19)
C(34)	870(28)	6 909(17)	−1 888(21)	O(91)	860(17)	4 296(12)	3 374(13)
C(35)	1 721(29)	7 012(18)	−1 608(21)	C(911)	1 641(40)	3 968(28)	3 698(29)
C(36)	2 171(28)	7 299(16)	−1 054(19)	C(912)	1 710(41)	3 447(28)	3 275(28)
O(41)	5 239(13)	5 442(9)	3 693(10)	O(92)	16(21)	4 415(14)	4 160(15)
C(411)	5 424(26)	5 020(18)	4 210(18)	C(921)	−1 017(33)	4 147(22)	3 979(25)
C(412)	6 033(27)	5 231(21)	4 796(21)	C(922)	−653(38)	3 614(25)	3 799(29)
O(42)	3 605(13)	5 232(9)	3 321(10)	PC(1)	6 830(9)	7 150(6)	8 189(6)
C(421)	3 478(29)	4 783(20)	2 802(21)				

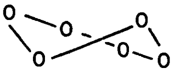
Table 3. Ring puckering co-ordinates for the $\overline{\text{Cu–S–Cu–S–Cu–S}}$ rings[a]

Ring	*Q*2/Å	*Q*3/Å	θ2/°	Total puckering amplitude/Å	θ2/°	Conformation[b]
Cu(1)S(62)Cu(2)S(52)Cu(3)S(42)	0.043(7)	−0.717(8)	−147(10)	0.718(8)	176.6(6)	Chair
Cu(1)S(62)Cu(2)S(22)Cu(6)S(12)	1.288(6)	−0.106(7)	57.1(3)	1.292(6)	94.7(3)	Boat
Cu(1)S(62)Cu(10)S(72)Cu(6)S(12)	1.298(8)	0.346(8)	−151.8(3)	1.344(8)	75.1(4)	Screw-boat
Cu(1)S(12)Cu(4)S(92)Cu(7)S(42)	1.450(8)	−0.282(8)	113.1(3)	1.477(8)	101.0(3)	Boat/envelope
Cu(1)S(42)Cu(3)S(82)Cu(4)S(92)	1.872(7)	−1.336(7)	149.1(2)	2.300(8)	125.5(2)	Screw-boat/ half-chair
Cu(2)S(52)Cu(8)S(32)Cu(5)S(22)	1.201(7)	0.277(7)	−146.3(3)	1.233(7)	77.0(3)	Screw-boat
Cu(2)S(52)Cu(3)S(82)Cu(5)S(22)	1.276(7)	−0.073(7)	59.4(3)	1.278(7)	93.3(3)	Boat
Cu(2)S(22)Cu(6)S(72)Cu(10)S(62)	1.360(6)	−0.368(6)	111.5(3)	1.409(6)	105.1(3)	Boat/envelope
Cu(3)S(82)Cu(4)S(92)Cu(7)S(42)	1.144(7)	−0.229(7)	−36.7(4)	1.167(7)	101.3(3)	Twist-boat/ screw-boat
Cu(3)S(52)Cu(8)S(32)Cu(5)S(82)	1.421(7)	0.303(7)	66.7(3)	1.453(7)	78.0(3)	Boat/envelope
Cu(4)S(12)Cu(6)S(11)Cu(9)S(81)	0.235(7)	1.031(7)	−154(2)	1.058(7)	12.9(4)	Chair
Cu(4)S(82)Cu(5)S(21)Cu(9)S(81)	0.332(7)	−1.084(7)	90(1)	1.134(7)	163.0(3)	Chair
Cu(4)S(12)Cu(6)S(22)Cu(5)S(82)	0.081(8)	−0.946(7)	117(5)	0.949(7)	175.1(5)	Chair
Cu(5)S(21)Cu(9)S(11)Cu(6)S(22)	0.274(6)	1.068(7)	92(1)	1.102(7)	14.4(3)	Chair

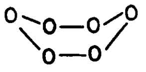
[a] See ref. 14(*a*). [b] Based on an analysis by Boeyens[14b] see below.



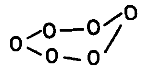
Chair



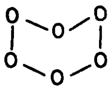
Half-chair



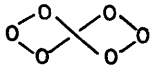
Boat



Envelope



Screw-boat



Twist-boat

40 °C). Yield 60%, m.p. 94—96 °C (lit.[16] 96 °C). ^1H N.m.r. ($CDCl_3$): δ 1.38 (6 H, t, *J* = 7, 2 CH_3), 4.20 (4 H, dq, *J* = 11 and 7 Hz, 2 CH_2), 7.0—8.0 (7 H, m, upon D_2O wash reduced to 5 H, m, 2 NH, C_6H_5).

Crystals of $[Cu_{10}(L^2)_9]ClO_4$. The ligand HL^1 (0.75 g, 2.47 mmol) and $Cu(ClO_4)_2·6H_2O$ (0.37 g, 1 mmol) were dissolved in ethanol (100 cm^3); an excess of copper powder was added and the mixture was stirred at room temperature for 10 min. The copper powder was then filtered off and the pale yellow solution was left in an open flask at room temperature overnight. The crystalline precipitate formed was filtered off, washed rapidly with cold ethanol and subject to spectroscopic (^1H n.m.r.) and elemental analysis. The ^1H n.m.r. spectrum [$(CD_3)_2SO$] was practically identical to that of HL^1 (except some down-field shift of signals) indicating that no change in the ligand structure has taken place (Found: C, 34.35; H, 4.10; N, 7.20. Calc. for $C_{99}H_{144}ClCu_{10}N_{18}O_{22}P_9S_{18}$: C, 34.3; H, 4.20; N, 7.30%).

X-*Ray data collection and solution of the structure*. The compound was found to be unstable to air. Hence on recrystallisation from an ethanol solution, a suitable single crystal was selected and placed rapidly in a Lindemann tube together with mother-liquor. After sealing of the tube at both

Table 4. Ranges of bond lengths (Å) and angles (°) for the co-ordinated ligands*

Cu–S(XY)	2.20(1)—2.38(1)	P(X)–N(X1)	1.54(2)—1.69(4)	N(X1)–C(X)	1.25(3)—1.36(4)
S(X1)–P(X)	1.96(1)—2.02(1)	O(X2)–C(X12)	1.34(4)—1.45(5)	C(X)–N(X2)	1.28(3)—1.40(3)
S(X2)–C(X)	1.72(3)—1.80(3)	C(X11)–C(X12)	1.37(9)—1.53(7)	N(X2)–C(X1)	1.34(4)—1.47(5)
P(X)–O(X1)	1.52(2)—1.61(2)	C(X21)–C(X22)	1.05(8)—1.54(7)	$C(XZ)_{ring}$–$C(XZ)_{ring}$	1.26(6)—1.55(6)
P(X)–O(X2)	1.43(3)—1.61(2)				
S(XY)–Cu–S(XY)	98.5(3)—131.8(5)	P(X)–O(X1)–C(X11)	119(2)—125(3)	N(X1)–C(X)–N(X2)	116(3)—123(3)
S(X1)–P(X)–N(X1)	117(1)—127(1)	O(X1)–C(X11)–C(X12)	108(5)—122(5)	S(X2)–C(X)–N(X2)	107(2)—117(2)
S(X1)–P(X)–O(X2)	101(1)—115(1)	P(X)–O(X2)–C(X21)	119(3)—130(3)	C(X)–N(X2)–C(X1)	124(3)—135(3)
S(X1)–P(X)–O(X1)	101(1)—116(1)	O(X2)–C(X21)–C(X22)	83(4)—122(5)	N(X2)–C(X1)–C(X6)	111(3)—128(3)
O(X2)–P(X)–N(X1)	101(1)—107(2)	P(X)–N(X1)–C(X)	127(2)—142(3)	N(X2)–C(X1)–C(X2)	116(4)—124(3)
O(X1)–P(X)–N(X1)	103(2)—111(1)	S(X2)–C(X)–N(X1)	124(2)—129(3)	$C(XZ)_{ring}$–$C(XZ)_{ring}$–$C(XZ)_{ring}$	112(4)—132(5)
O(X1)–P(X)–O(X2)	98(1)—110(2)				

* X = 1—9; Y = 1 or 2; Z = 1—6.

ends, the crystal was mounted on an Enraf-Nonius CAD4 diffractometer and irradiated with Mo-K_α radiation (λ = 0.7107 Å). Least-squares analysis on the setting angles of 24 reflections $10 \leqslant \theta \leqslant 11°$ yielded the triclinic cell reported. During the data collection reorientation and intensity checks were carried out periodically to monitor crystal and machine stability. The data were corrected for Lorentz polarisation effects and an empirical absorption correction[17] was applied.

The ten copper atoms were located by direct methods using SHELX 86[18] and remaining non-hydrogen atoms of the aggregate were revealed in subsequent difference Fourier syntheses using SHELX 76.[19]

Methylene hydrogens were placed in calculated positions at 1.00 Å from their parent carbons as were the single amino protons on N(X2) and the phenyl hydrogens. The methyl hydrogens were treated as rigid groups, again with a single thermal parameter. The Cl of the perchlorate anion was easily located at this stage. However, considerable disorder of the four oxygen atoms of ClO_4 led us to adopt an approach involving calculation of the spherically averaged molecular scattering factor for ClO_4 using dummy co-ordinate input to NORMAL of MULTAN.[20] An approximation of the scattering with $\sin\theta/\lambda$ was then obtained in the form suitable for SHELX 76 by the addition of normal distribution functions: $f(x) = 38.8[\exp(43.4x^2)] + 4.0[\exp(1.79x^2)] + 1.5[\exp(0.63x^2)] + 5.69$, where $x = \sin\theta/\lambda$.

The molecular scatterer was then placed at the location of the Cl atom with U_{iso} fixed at 0.35 Å^2 to model disorder. In the final refinements, the Cu atoms were treated anisotropically and all other atoms isotropically. A weighting scheme, $w = (\sigma^2 F)^{-1}$ was employed. In the final difference map, maximum and minimum residual electron densities were 1.3 and −1.6 e Å^{-3}. Complex neutral atom scattering factors were taken from Cromer and Mann[21] for non-hydrogen atoms (excluding ClO_4) and from Stewart *et al.*[22] for H, with dispersion corrections from Cromer and Liberman.[23] Molecular parameters were calculated using PARST[24] and drawings obtained using PLUTO.[25] All computations were performed at the Computer Centre of the University of Cape Town on a Sperry 1100/81 computer. Full details of the data collection, structure solution and refinement are given in Table 1.

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

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References

1 F. J. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 116.
2 P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 1971, 105.
3 A. F. Wells, 'Structural Inorganic Chemistry,' 5th edn., Clarendon Press, Oxford, 1984, p. 1108.
4 J. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, 1976, **19**, L41.
5 L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Am. Chem. Soc.*, 1968, **90**, 7357.
6 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, 1974, **96**, 5646.
7 P. J. M. W. L. Birker and H. C. Freeman, *J. Am. Chem. Soc.*, 1977, **99**, 6890.
8 Y. Sugiura and H. Tanaka, *Chem. Pharm. Bull.*, 1970, **18**, 368.
9 V. N. Zontova, A. F. Grapov, and N. N. Melnikov, *Dokl. Akad. Nauk SSSR*, 1980, **251**, 882; *Zh. Obshch. Khim.*, 1982, **52**, 64.
10 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, ch. 21-H-2.
11 Ref. 3, p. 1104.
12 (*a*) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1899; (*b*) P. W. R. Carfield and H. M. M. Shearer, *Acta Crystallogr.*, 1966, **21**, 957; (*c*) D. T. Cromer and A. C. Larson, *Acta Crystallogr.*, 1962, **15**, 397; (*d*) S. L. Lawton, W. J. Rohrbaugh, and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 612; (*e*) R. Hesse and U. Aava, *Acta Chem. Scand.*, 1970, **24**, 1355.
13 A. Avdeef and J. P. Fackler, *Inorg. Chem.*, 1978, **17**, 2182; P. K. Mehrota and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187.
14 (*a*) D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354; (*b*) J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, 1978, **8(6)**, 317.
15 J. Michalski and J. Wieczorkowski, *Rocz. Chem.*, 1957, **31**, 585.
16 G. Schrader, G. P. 952712/1955; *Chem. Zentralbl.*, 1957, 3651.
17 A. C. T. North, D. C. Phillips, and F. Scott Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
18 G. M. Sheldrick, SHELX 86, in 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, 1985, p. 175.
19 G. M. Sheldrick, SHELX 76, in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. von Koningsveld, and G. C. Bassi, Delft University Press, 1978, p. 34.
20 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, MULTAN 78, Universities of York (England) and Louvain (Belgium), 1978.
21 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
22 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
23 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
24 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
25 W. D. S. Motherwell, PLUTO, Structure plotting program, personal communication, 1974.

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