Acta Cryst. (1978). B**34**, 2629–2632

Tris(imidotetraphenyldithiodiphosphino-*S*,*S*)tetracopper(I) Dichlorocuprate(I) Carbon Tetrachloride Solvate*

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(*Received* 7 *February* 1978; *accepted* 29 *March* 1978)

Abstract. $[(C_{24}H_{20}NP_2S_2)_3Cu_4]^+.[CuCl_2]^-.CCl_4$, M_r = 1887·9, monoclinic, $P2_1/c$, a = 11·417 (9), b = 37·904 (3), c = 20·622 (14) Å, β = 116·18 (5)°, U = 8008·7 Å^3, D_m = 1·562, Z = 4, D_c = 1·565 g cm^{-3}, μ(Cu $K\alpha$) = 61·7 cm^{-1}. The cations contain a tetrahedral cluster of Cu^I atoms coordinated by three bidentate imidotetraphenyldithiodiphosphinate ligands, each of which chelates one Cu atom and bridges two others.

Introduction. The title compound represents the reduced form of a mixed-valence Cu complex which shows the intense electronic absorption band near 600 nm which is characteristic of blue Cu proteins. A summary account has been given of the synthesis of both compounds, the resonance Raman spectrum of the mixed-valence compound, and the X-ray work on the reduced form (Siiman, Huber & Post, 1977). Crystals of the title compound are pale-pink prisms, elongated along *c*. The space group and approximate cell dimensions were determined from precession photographs. The density was measured by flotation in chloroform–carbon tetrachloride. Data were collected on a Picker four-circle diffractometer with a crystal 0·25 × 0·25 × 0·45 mm. Cell parameters were determined from high-angle axial reflections [λ(Cu $K\alpha_1$) = 1·54051 Å, λ(Cu $K\alpha_2$) = 1·54433 Å]. Intensities were measured in the $\theta/2\theta$ scan mode with Ni-filtered Cu radiation using a scintillation counter. Collection was restricted to about 6000 reflections with $2\theta \leq 87°$ in order to limit subsequent computing expenses. Scan ranges were 1·6° for $2\theta \leq 40°$, and 2·0° for $40 < 2\theta \leq 87°$. 4568 independent reflections (76%) were considered observed on the basis that their net intensities were greater than 10% of the corresponding background count and greater than a threshold of 10 (deca) counts. Lorentz and polarization corrections were applied, and absorption corrections were also made, using a Gaussian integration formula with 6 × 6 × 5 subdivisions. Maximum and minimum transmission factors were 0·421 and 0·114 respectively. Direct methods gave the Cu, S, and P positions, and the rest of the structure appeared on subsequent difference maps.

The CCl_4 molecule is probably disordered; peaks corresponding to the Cl atoms were mostly very extended, and these atoms had extremely high temperature factors. The H atoms appeared quite clearly on a difference map, and therefore their contributions to the structure factors were included, with isotropic temperature factors fixed at 6·5 Å^2, in the last three cycles. Refinement by block-diagonal least squares, with anisotropic temperature factors for non-hydrogen atoms, led to a final *R* value of 0·081 for the observed reflections. Scattering factors were all taken from *International Tables for X-ray Crystallography* (1974), as were f' values; the curves for Cu$^+$, Cl$^-$, Cl, S and P were each corrected for the real component of anomalous dispersion. The function minimized was $\sum w(F_o - F_c)^2$ and the weighting scheme used in the later cycles was of the form $w = w_1 w_2$ with $w_1 = 1/\{1 + [(F_o - b)/a]^2\}$, $a = 35·0$, $b = 50·0$, $11·3 < |F_o| < 588·1$; $w_2 = 5 \sin^2\theta$ if $\sin^2\theta < 0·2$, otherwise $w_2 = 1$.

Near the end of the refinement an analysis was made of the thermal motion of the CCl_4 group using the *MGTLS* program (Schomaker & Trueblood, 1968) and this indicated a principal libration axis with an r.m.s. value of 30° which was nearly parallel to one of the C–Cl bonds [C(120)–Cl(124)]. A disordered model was then tried, in which the CCl_4 molecule was represented by two half-occupancy orientations separated by a rotation of ~24° about this bond. This made no significant difference to the structure-factor agreement, but essentially stopped the tendency of the Cl thermal parameters to become non-ellipsoidal, and was therefore accepted. Some of the Cl positions [Cl(121), Cl(131), Cl(123), Cl(133)] still gave poor geometry for the CCl_4 group, and ultimately the positions for these atoms were calculated from the

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* Issued as NRCC No. 16697.

Table 1. *Final coordinates and their estimated standard deviations* ($\times 10^4$) *for the non-hydrogen atoms*

	x	*y*	*z*		*x*	*y*	*z*
Cu(1)	4668 (2)	6151 (1)	8062 (1)	C(53)	4188 (34)	4220 (5)	7605 (17)
Cu(2)	3118 (2)	5854 (1)	6708 (1)	C(54)	2983 (28)	4194 (7)	7614 (15)
Cu(3)	3158 (2)	6590 (1)	6896 (1)	C(55)	2376 (21)	4465 (5)	7732 (12)
Cu(4)	5318 (2)	6249 (1)	6923 (1)	C(56)	2959 (19)	4802 (5)	7843 (11)
S(1)	3624 (3)	6656 (1)	8077 (2)	C(61)	5232 (12)	4995 (3)	6243 (7)
S(2)	6683 (3)	6142 (1)	8100 (2)	C(62)	6058 (15)	4704 (4)	6451 (9)
S(3)	3505 (3)	5639 (1)	7809 (2)	C(63)	5762 (19)	4406 (4)	6061 (10)
S(4)	4474 (3)	5777 (1)	6188 (2)	C(64)	4619 (19)	4389 (4)	5437 (9)
S(5)	1434 (3)	6243 (1)	6223 (2)	C(65)	3781 (18)	4667 (4)	5201 (10)
S(6)	4592 (3)	6799 (1)	6506 (2)	C(66)	4110 (15)	4986 (4)	5614 (9)
P(1)	5104 (3)	7024 (1)	8414 (2)	C(71)	7339 (12)	5494 (4)	6954 (7)
P(2)	7342 (3)	6643 (1)	8424 (2)	C(72)	7587 (14)	5729 (4)	6514 (8)
P(3)	4944 (3)	5273 (1)	8001 (2)	C(73)	8819 (16)	5785 (5)	6608 (10)
P(4)	5694 (3)	5387 (1)	6807 (2)	C(74)	9846 (16)	5610 (5)	7111 (11)
P(5)	1302 (3)	6299 (1)	5199 (2)	C(75)	9606 (15)	5377 (5)	7564 (11)
P(6)	3621 (3)	6711 (1)	5416 (2)	C(76)	8375 (14)	5322 (5)	7485 (9)
N(1)	6291 (10)	6949 (3)	8233 (6)	C(81)	757 (13)	5890 (4)	4740 (7)
N(3)	5788 (10)	5311 (3)	7576 (6)	C(82)	−353 (17)	5723 (4)	4734 (10)
N(5)	2599 (9)	6406 (3)	5131 (5)	C(83)	−823 (21)	5414 (6)	4352 (11)
C(1)	4401 (13)	7432 (4)	7964 (7)	C(84)	−99 (20)	5251 (5)	4050 (10)
C(2)	3323 (17)	7569 (4)	8018 (10)	C(85)	975 (20)	5404 (5)	4067 (10)
C(3)	2775 (17)	7885 (5)	7659 (11)	C(86)	1417 (15)	5726 (4)	4405 (8)
C(4)	3242 (19)	8053 (5)	7255 (10)	C(91)	32 (13)	6617 (4)	4755 (8)
C(5)	4360 (17)	7921 (4)	7196 (10)	C(92)	−105 (14)	6897 (4)	5142 (9)
C(6)	4907 (15)	7609 (4)	7566 (9)	C(93)	−1056 (18)	7163 (5)	4751 (11)
C(11)	5620 (13)	7083 (4)	9366 (7)	C(94)	−1740 (16)	7145 (5)	4035 (10)
C(12)	5984 (16)	7410 (4)	9702 (8)	C(95)	−1583 (16)	6864 (5)	3641 (10)
C(13)	6502 (19)	7427 (5)	10443 (10)	C(96)	−716 (13)	6601 (5)	4000 (8)
C(14)	6564 (19)	7152 (5)	10848 (9)	C(101)	2891 (12)	7123 (4)	5002 (7)
C(15)	6216 (22)	6833 (5)	10554 (10)	C(102)	3296 (17)	7435 (4)	5368 (9)
C(16)	5708 (20)	6785 (5)	9784 (9)	C(103)	2721 (21)	7767 (5)	5026 (12)
C(21)	8383 (13)	6620 (4)	9377 (8)	C(104)	1784 (19)	7756 (5)	4333 (11)
C(22)	9223 (15)	6903 (4)	9711 (8)	C(105)	1332 (17)	7435 (5)	3943 (10)
C(23)	9940 (17)	6913 (5)	10432 (9)	C(106)	1923 (14)	7124 (4)	4300 (8)
C(24)	9856 (18)	6637 (5)	10869 (9)	C(111)	4820 (13)	6615 (3)	5095 (8)
C(25)	9063 (20)	6359 (6)	10529 (10)	C(112)	4405 (15)	6570 (4)	4354 (8)
C(26)	8342 (18)	6347 (5)	9801 (9)	C(113)	5316 (19)	6502 (5)	4100 (11)
C(31)	8331 (12)	6758 (3)	7978 (7)	C(114)	6633 (16)	6502 (5)	4574 (10)
C(32)	8195 (15)	7071 (4)	7636 (8)	C(115)	7053 (15)	6538 (4)	5284 (11)
C(33)	8974 (16)	7154 (5)	7273 (9)	C(116)	6158 (14)	6603 (4)	5557 (8)
C(34)	9879 (17)	6898 (6)	7294 (9)	Cl(1)	1186 (11)	5532 (2)	1724 (6)
C(35)	10034 (16)	6594 (4)	7635 (10)	Cu(5)	993 (4)	5957 (1)	2295 (2)
C(36)	9270 (15)	6520 (4)	7983 (10)	Cl(2)	719 (12)	6369 (3)	2788 (5)
C(41)	6045 (14)	5303 (4)	8944 (8)	C(120)	2533 (18)	5949 (5)	−97 (10)
C(42)	5589 (18)	5348 (6)	9443 (9)	Cl(121)	3867 (48)	5924 (16)	648 (25)
C(43)	6429 (21)	5375 (7)	10181 (10)	Cl(131)	3856 (41)	5765 (10)	493 (23)
C(44)	7732 (20)	5367 (5)	10389 (9)	Cl(122)	1461 (36)	6175 (9)	40 (22)
C(45)	8169 (18)	5320 (6)	9901 (10)	Cl(132)	2020 (39)	6238 (9)	308 (24)
C(46)	7369 (16)	5295 (5)	9172 (8)	Cl(123)	1975 (63)	5555 (12)	−364 (33)
C(51)	4141 (15)	4851 (4)	7850 (8)	Cl(133)	1420 (52)	5650 (12)	−472 (29)
C(52)	4750 (26)	4569 (5)	7723 (13)	Cl(124)	2830 (9)	6139 (2)	−707 (5)

others. Unless otherwise indicated, all computations were done with the NRC set of crystallographic programs (Ahmed, Hall, Pippy & Huber, 1973). Final positional parameters for the non-hydrogen atoms are given in Table 1.*

Discussion. Fig. 1 shows a stereoscopic view of the contents of one asymmetric unit, indicating the numbering scheme. As can be seen, an approximate (non-crystallographic) threefold symmetry axis passes through Cu(4), which is coordinated by the S atoms of three different ligands, and through the mid-point of the other three Cu atoms. The phenyl group including C(51) is, however, twisted by about 55° out of the symmetric orientation in order to accommodate the CCl_4 molecule. Each of the Cu atoms is approximately trigonally coordinated and Cu(1), Cu(2), Cu(3), Cu(4)

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* Tables of structure factors, anisotropic thermal parameters for the non-hydrogen atoms, coordinates for the H atoms, bond lengths involving only C atoms, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33494 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

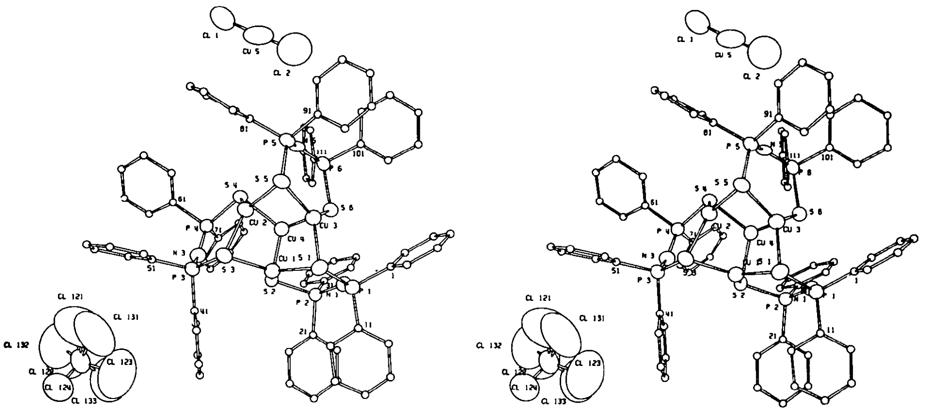

Fig. 1. Stereoscopic view (Johnson, 1970) of the contents of one asymmetric unit. The thermal ellipsoids enclose 50% probability; C atoms are shown as spheres of arbitrarily small radius.

Table 2. *Interatomic distances other than* C—C *and* C—H (Å)

Cu(1)···Cu(2)	2·799 (3)	P(3)—N(3)	1·57 (1)
Cu(1)···Cu(3)	2·805 (3)	P(4)—N(3)	1·57 (1)
Cu(2)···Cu(3)	2·815 (3)	P(5)—N(5)	1·60 (1)
Cu(1)···Cu(4)	2·781 (3)	P(6)—N(5)	1·56 (1)
Cu(2)···Cu(4)	2·786 (3)	P(1)—C(1)	1·80 (1)
Cu(3)···Cu(4)	2·763 (3)	P(1)—C(11)	1·80 (1)
Cu(1)—S(1)	2·262 (4)	P(2)—C(21)	1·80 (1)
Cu(1)—S(2)	2·267 (5)	P(2)—C(31)	1·80 (2)
Cu(1)—S(3)	2·278 (4)	P(3)—C(41)	1·79 (1)
Cu(2)—S(3)	2·265 (4)	P(3)—C(51)	1·80 (2)
Cu(2)—S(4)	2·257 (4)	P(4)—C(61)	1·82 (1)
Cu(2)—S(5)	2·275 (4)	P(4)—C(71)	1·81 (2)
Cu(3)—S(1)	2·266 (4)	P(5)—C(81)	1·78 (1)
Cu(3)—S(5)	2·262 (4)	P(5)—C(91)	1·80 (2)
Cu(3)—S(6)	2·262 (5)	P(6)—C(101)	1·80 (1)
Cu(4)—S(2)	2·268 (4)	P(6)—C(111)	1·80 (2)
Cu(4)—S(4)	2·266 (4)	Cu(5)—Cl(1)	2·06 (1)
Cu(4)—S(6)	2·268 (4)	Cu(5)—Cl(2)	1·96 (1)
S(1)—P(1)	2·063 (5)	C(120)—Cl(121)	1·62 (5)
S(2)—P(2)	2·044 (5)	C(120)—Cl(122)	1·62 (5)
S(3)—P(3)	2·051 (5)	C(120)—Cl(123)	1·62 (5)
S(4)—P(4)	2·047 (5)	C(120)—Cl(131)	1·62 (5)
S(5)—P(5)	2·061 (5)	C(120)—Cl(132)	1·64 (5)
S(6)—P(6)	2·050 (5)	C(120)—Cl(133)	1·62 (6)
P(1)—N(1)	1·58 (1)	C(120)—Cl(124)	1·61 (2)
P(2)—N(1)	1·59 (1)		

are respectively 0·118 (2), 0·122 (2), 0·108 (2) and 0·088 (2) Å out of the corresponding planes defined by their three coordinating S atoms. These displacements are all to the outside of the octahedron formed by the six S atoms.

Table 2 lists interatomic distances other than C—C or C—H. The C—C aromatic bond lengths vary from 1·32 to 1·45 Å with an average of 1·38 Å; the shorter bonds are at the free ends of the aromatic rings, and their apparent lengths are probably affected by thermal motion. The average C—H distance is 0·96 Å. The accuracy of at least the light-atom parameters may be adversely affected because of the restricted data set.

The Cu···Cu distances fall into two groups, with the distances between the unique atom Cu(4) and each of the other three Cu atoms [average = 2·777 (3) Å] being significantly shorter than the Cu···Cu distances involving only Cu(1), Cu(2), Cu(3) [average = 2·806 (3) Å]. All of the Cu···Cu distances are significantly shorter than analogous Cu···Cu distances [2·833 to 3·093 (2) Å] in $Cu_4[SC(NH_2)_2]_6.(NO_3)_4.4H_2O$ (Griffith, Hunt & Amma, 1976), but longer than the Cu···Cu distances in $[(C_2H_5)_2NCS_2Cu]_4$ [2·658 and 2·757 (5) Å] (Hesse, 1963). Cu—S distances involving Cu(4) are not significantly different from the other Cu—S distances in the present compound, and the whole range of values (2·257–2·278 Å) is narrower than in these other structures [Hesse (1963): 2·246–2·290 Å; Griffith, Hunt & Amma (1976): 2·19–2·31 Å].

Most of the bond lengths and angles in the ligands are in good general agreement with corresponding values in other structures. However, the S—P bonds in this structure [average 2·053 (5) Å], perhaps because of the bridging S atoms, are significantly longer than those in the structures of $Ni[SP(CH_3)_2NP(CH_3)_2S]_2$ [2·023 (6) Å] (Churchill, Cooke, Fennessey & Wormald, 1971), $Fe[SP(CH_3)_2NP(CH_3)_2S]_2$ [2·020 (8) Å] (Churchill & Wormald, 1971), and $Mn[SP(C_6H_5)_2NP(C_6H_5)_2S]_2$ [2·013 (5) Å] (Siiman & Gray, 1974). Also, the average P—N—P angle here, 138·0°, is somewhat larger than those in these other three structures (128·4, 132·3 and 133·5° respectively), perhaps because of the long S—P bonds, although the spread of values here (134·7 to 142·8°) and in the Mn and Fe complexes (131·9–134·7 and 128·6–136·1° respectively) probably indicates that this angle is most sensitive to small deformation forces. The largest value (142·8°) is associated with the ligand containing the twisted phenyl group.

In this structure, because of the flattened chair conformation of the chelate rings, there is some unfavourable axial phenyl–phenyl interaction, which is reflected in enlarged N—P—C angles (average 111·5°) for axial phenyl groups, compared with an average N—P—C angle of 106·1° for equatorial phenyl groups. A similar effect occurs in one of the chelate rings of the Fe complex.

The S—Cu—S angles within the three chelate rings [average 123·6 (2)°] are significantly larger than interligand S—Cu—S angles (average 118·5°). This feature is also evident, although to a lesser extent, in the Mn complex, where the average intrachelate S—Mn—S angle is 111·9° and the average interligand S—Mn—S angle is 108·3°; this is in contrast to the situation in the Ni and Fe complexes where distortions from tetrahedral coordination are mostly small and random.

Packing of the crystal structure is determined largely by van der Waals forces; there are no particularly short contacts. The cation charge is effectively buried inside the shell of phenyl groups, and the closest contacts of the $CuCl_2^-$ group are all to phenyl-group H atoms.

OS acknowledges support by the National Institutes of Health through USPHS Grant GM-23072.

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Acta Cryst. (1978). B**34**, 2632–2634

Bis(hydroxylamido)(1,2-ethanediol-*O*,*O*)dioxouranium(VI)

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(*Received* 10 *March* 1978; *accepted* 13 *April* 1978)

Abstract. $UO_2(NH_2O)_2.HOCH_2CH_2OH$, monoclinic, $C2/c$, $a = 9{\cdot}3891$ (9), $b = 8{\cdot}7671$ (8), $c = 9{\cdot}8766$ (8) Å, $\beta = 104{\cdot}400$ (8)°, $V = 787{\cdot}8$ (1) Å^3, $Z = 4$, $D_c = 3{\cdot}42$ Mg m^{-3}. The structure was solved by the heavy-atom method and refined to $R_w = 0{\cdot}052$ for 500 unique diffractometer data. All three ligands are coordinated to the U atom through bidentate bonds.

Introduction. Remarkably stable compounds with structural formulae $UO_2(NH_2O)_2.xL$ or $UO_2(NH_2O)_2.xL_1.yL_2$ can be formed, where L_1 and L_2 are neutral ligands (*e.g.* H_2O or NH_2OH). It has been found that in all such structures six coordinating O or N bonds are formed to the U atom, including two from the neutral ligands (Van Tets & Adrian, 1977; Adrian & Van Tets, 1977, 1978*a*,*b*). The new compound described here is no exception. It was prepared from a solution containing 3·5 g $NH_2OH.HCl$, 50 cm^3 HOC_2H_4OH and 3 cm^3 0·5 *M* aqueous UO_2Cl_2 by slow absorption of neutralizing ammonia vapour from a dilute aqueous solution of ammonium carbonate.

Accurate *d* values were obtained from a powder diffractogram taken on a Huber Guinier camera (114·6 mm diameter) with an internal Si standard and quartz-monochromated Cu $K\alpha_1$ radiation. By the use of an analytical method (Azaroff & Buerger, 1958), together with an automatic powder-indexing routine (Visser, 1969), a monoclinic cell was found from the first forty lines. The whole powder pattern was indexed using this cell. A least-squares refinement on 53 non-overlapping reflections gave the final cell constants. The extinctions indicate space group Cc or $C2/c$. Z must be 4 by analogy with the volumes occupied by similar molecules (Adrian & Van Tets, 1977, 1978*a*,*b*). $C2/c$ with its eight general positions is the more likely space group. No extinctions due to special positions were observed. The U atom was therefore assumed to occupy the special position $0,y,\frac{1}{4}$. The y coordinate was determined by calculating a Patterson map from 45 Lp-corrected powder intensities (Hellner, 1954) and from a strong peak in the Harker section (line $0,v,\frac{1}{2}$) y was found to be 0·17. Refinement of the U atom using these reflections resulted in $R = 0{\cdot}128$ with $y = 0{\cdot}166$ (2).