Crystal and Molecular Structure of μ-[1,2-Bis(phenylthio)ethane]-bis-[chlorogold(I)]

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Crystals of the title compound are triclinic, spacegroup $P\bar{1}$, with a = 6·382(9), b = 14·878(12) c = 8·975(9) Å, α = 85·91(11), β = 100·94(12), γ = 87·46(13)°, Z = 2. The intensities of 1040 independent reflections were collected by counter methods; the structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods to R 0·074. The asymmetric unit contains two independent C_7H_7SClAu ' half-dimer ' units. Thus both dimers are centrosymmetric, with planar S–C–C–S linkages. While this linkage has the *trans*-conformation in both dimers, the remaining atoms have conformations which differ by a rotation of *ca.* 113° of the S–Au–Cl grouping about the S–C bonds. Each gold atom is bonded to a sulphur atom [2·258(11) and 2·260(12) Å] and to a chlorine atom [2·329(8) and 2·293(10) Å] with almost linear Cl–Au–S groups [177·8(4) and 173·5(4)°]. In the crystal, there are infinite chains of almost linear ·Au · · · Au · · · Au· contacts [3·187(2) and 3·209(2) Å].

A SERIES of complexes of gold(I) with the heterocyclic ligands 1,4-thioxan and 1,4-dithian and with bidentate thioethane ligands of the type $RS\cdot[CH_2]_2\cdot SR$ (R = Me or Ph) have been prepared.[1] I.r. studies on these compounds have been interpreted in terms of ligand conformation.[2] To corroborate these assignments, we have determined the crystal structure of one of these compounds, namely μ-[1,2-bis(phenylthio)ethane]-bis-[chlorogold(I)].

EXPERIMENTAL

Preparation of the Complex.—Hydrogen tetrachloroaurate(III) (0·1 g, 0·24 mmol) in absolute ethanol was added to a solution of 1,2-diphenylthioethane (0·3 g, 1·15 mmol) in absolute ethanol. After *ca.* 12 h, the yellow solution became colourless and fine white needle-shaped crystals were

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[1] M. J. Riedl, unpublished work.

[2] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, to be submitted to *Inorg. Nuclear Chem. Letters.*

formed (Found: C, 23·3; H, 1·9; Cl, 10·2. $C_{14}H_{14}S_2Cl_2Au_2$ requires C, 23·6; H, 2·0; Cl, 10·0%).

Crystal Data.—$C_{14}H_{14}Au_2Cl_2S_2$, $M = 709{\cdot}2$, Triclinic, $a = 6{\cdot}382(9)$, $b = 14{\cdot}878(12)$, $c = 8{\cdot}975(9)$ Å, $\alpha = 85{\cdot}91(11)$, $\beta = 100{\cdot}94(12)$, $\gamma = 87{\cdot}46(13)^\circ$, $U = 833{\cdot}2$ Å^3, $D_c = 2{\cdot}82$, $Z = 2$, $D_m = 2{\cdot}85(3)$, $F(000) = 644$. Space-group confirmed as $P\bar{1}$ by the structure determination. Mo-K_α radiation $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 189{\cdot}3$ cm^{-1}. A crystal with dimensions $0{\cdot}30 \times 0{\cdot}10 \times 0{\cdot}10$ mm was mounted with the a^* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. A molybdenum tube was used with a zirconium filter at the receiving slit. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. 1565 independent reflections were measured with $2\theta < 40^\circ$. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I)^2]^{\frac{1}{2}}$, where I is the intensity and E the background. 1044 reflections with $I > 3\sigma(I)$ were used in the subsequent calculations. No extinction correction was applied. An absorption correction was applied by use of the program ABSCOR;[3] transmission factors (on F) varying between 0·38 and 0·46.

Structure Determination.—The structure was determined from Patterson and Fourier syntheses and refined by full-matrix least-squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 50$ and $\sqrt{w} = 50/F_o$ for $F_o > 50$. Calculations were made on an ATLAS computer at S.R.C. Chilton, Berkshire with the programs described in ref. 3. Atomic scattering factors for gold, sulphur, chlorine, and carbon were taken from ref. 4, as were the corrections for the real and imaginary part of the anomalous dispersion for gold, chlorine, and sulphur. The anisotropic thermal parameter is defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_j)$, $i,j = 1$—3. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. Gold atoms were refined anisotropically and the chlorine, sulphur, and carbon atoms isotropically, to R 0·074 for the 1044 observed reflections. No significant drop in R was obtained by refining the chlorine and sulphur atoms anisotropically. The 521 zero reflections showed no large discrepancies. Difference Fourier syntheses showed no significant peaks and in the final cycle of refinement, all shifts were $< 0{\cdot}040\sigma$. The final list of co-ordinates and thermal parameters is in Table 1. Table 2 lists the bond distances and angles. The final observed and calculated structure factors are listed in Supplementary Publication SUP 20539 (6 pp., 1 microfiche).*

TABLE 1

Final positional co-ordinates, and thermal parameters, with estimated standard deviations in parentheses

	x	y	z	U(× 10²)
Au(1)	0·0269(3)	0·2250(1)	0·0013(2)	*a*
Au(2)	0·5223(3)	0·2384(1)	−0·0044(2)	*a*
S(1)	0·1081(20)	0·0990(7)	0·1614(12)	4·3(3)
S(2)	0·5969(19)	0·3650(7)	0·1158(12)	4·4(3)
Cl(1)	−0·0459(14)	0·3577(6)	−0·1581(8)	2·2(2)
Cl(2)	0·4738(16)	0·1150(6)	−0·1435(10)	3·1(2)
C(1)	−0·052(7)	0·009(3)	0·067(4)	4·0(10)
C(2)	0·490(7)	0·454(3)	−0·020(5)	4·5(11)
C(11)	−0·019(6)	0·117(2)	0·318(4)	2·1(8)
C(12)	−0·200(7)	0·078(3)	0·337(5)	4·9(11)
C(13)	−0·288(8)	0·097(3)	0·467(5)	5·5(13)
C(14)	−0·173(9)	0·150(3)	0·578(5)	7·1(15)
C(15)	0·022(8)	0·190(3)	0·554(5)	5·3(12)
C(16)	0·100(7)	0·174(3)	0·420(4)	4·9(12)
C(21)	0·445(6)	0·374(3)	0·263(5)	2·4(8)
C(22)	0·230(7)	0·412(3)	0·237(5)	4·6(10)
C(23)	0·138(7)	0·421(3)	0·360(5)	4·8(12)
C(24)	0·258(7)	0·398(3)	0·509(5)	4·5(11)
C(25)	0·455(11)	0·361(4)	0·534(7)	9·8(20)
C(26)	0·570(9)	0·356(3)	0·407(5)	6·6(14)

[a] Anisotropic thermal parameters (× 10²; U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}) are for Au(1): 4·28(14), 2·78(12), 5·02(12), −0·40(9), 2·15(9), and −0·92(9); and for Au(2): 4·26(14), 3·05(12), 6·09(14), −0·19(10), 2·48(10), and −0·52(8).

TABLE 2

Molecular geometry *

(*a*) Bond distances (Å)

Au(1)–S(1)	2·258(11)	Au(2)–S(2)	2·260(12)
Au(1)–Cl(1)	2·329(8)	Au(2)–Cl(2)	2·293(10)
S(1)–C(1)	1·87(4)	S(2)–C(2)	1·75(4)
S(1)–C(11)	1·78(4)	S(2)–C(21)	1·78(4)
C(1)–C(1$^{\text{I}}$)	1·51(6)	C(2)–C(2$^{\text{II}}$)	1·45(6)
C(11)–C(12)	1·34(6)	C(21)–C(22)	1·44(6)
C(12)–C(13)	1·43(7)	C(22)–C(23)	1·36(7)
C(13)–C(14)	1·43(7)	C(23)–C(24)	1·42(5)
C(14)–C(15)	1·45(8)	C(24)–C(25)	1·32(8)
C(15)–C(16)	1·43(5)	C(25)–C(26)	1·47(9)
C(11)–C(16)	1·42(5)	C(21)–C(26)	1·39(5)

(*b*) Angles (deg.)

Cl(1)–Au(1)–S(1)	177·8(4)	Cl(2)–Au(2)–S(2)	173·5(4)
Au(1)–S(1)–C(1)	106·0(12)	Au(2)–S(2)–C(2)	104·7(15)
Au(1)–S(1)–C(11)	105·9(11)	Au(2)–S(2)–C(21)	110·2(12)
C(1)–S(1)–C(11)	101·8(19)	C(2)–S(2)–C(21)	104·4(20)
S(1)–C(1)–C(1$^{\text{I}}$)	103·6(20)	S(2)–C(2)–C(2$^{\text{II}}$)	119·3(20)
S(1)–C(11)–C(12)	123(3)	S(2)–C(21)–C(22)	124(3)
S(1)–C(11)–C(16)	111(3)	S(2)–C(21)–C(26)	113(3)
C(12)–C(11)–C(16)	126(4)	C(22)–C(21)–C(26)	123(4)
C(11)–C(12)–C(13)	118(4)	C(21)–C(22)–C(23)	118(3)
C(12)–C(13)–C(14)	119(5)	C(22)–C(23)–C(24)	119(5)
C(13)–C(14)–C(15)	121(5)	C(23)–C(24)–C(25)	120(4)
C(14)–C(15)–C(16)	119(4)	C(24)–C(25)–C(26)	122(5)
C(15)–C(16)–C(11)	117(4)	C(25)–C(26)–C(21)	120(5)

* Roman numerals as superscripts in the Table and elsewhere refer to atoms in the following equivalent positions relative to the reference co-ordinates at x, y, z:

I $-x, -y, -z$
II $1 - x, 1 - y, -z$
III $1 + x, y, z$
IV $-1 + x, y, z$
V $1 + x, y, z - 1$
VI $x, y, 1 + z$
VII $-x, 1 - y, -z$

DISCUSSION

The c projection of the unit cell is shown in Figure 1. The unit cell contains two molecules of μ-[1,2-bis(phenylthio)ethane]-bis[chlorogold(I)]. Both dimers are centrosymmetric: dimer (1) around (0,0,0) and dimer (2) around $(\frac{1}{2},\frac{1}{2},0)$. Thus the asymmetric unit contains two independent (C_7H_7SClAu) units. In both dimers, the S–C–C–S linkage is perforce planar and also has the *trans*-configuration. However, the remaining atoms in the two dimers have entirely different conformations. This is shown in Figure 2 which shows projections of the two

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[3] '*X*-Ray '67' system of programs, J. M. Stewart, University of Maryland Technical Report, 67 58, 1967, revised July, 1970.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

dimers on the plane containing the S–C–C–S linkage, together with distances (Å) of atoms from the plane. In the atomic numbering scheme, the first digit in each atom name is 1 or 2, pertaining to the particular dimer.

In dimer (1), the benzene rings are almost coplanar with the S–C–C–S atoms, while the C(1^{I})–C(1)–S(1)–Au(1) dihedral angle is 69·4°. In dimer (2), it is the Au,Cl grouping which is almost coplanar with the S–C–C–S atoms, while the C(2^{II})–C(2)–S(2)–C(21) dihedral angle is 64·0°. These two conformations differ by a rotation (allowing for variations in dimensions) of *ca.* **113°** about the S–C bond. Both conformations would appear equally stable on steric grounds, both giving one dihedral angle of *ca.* 60° and one of *ca.* 180°, thus minimising intramolecular contacts.[2] Least-squares planes calculations and dihedral angles are given in Tables 3 and 4.

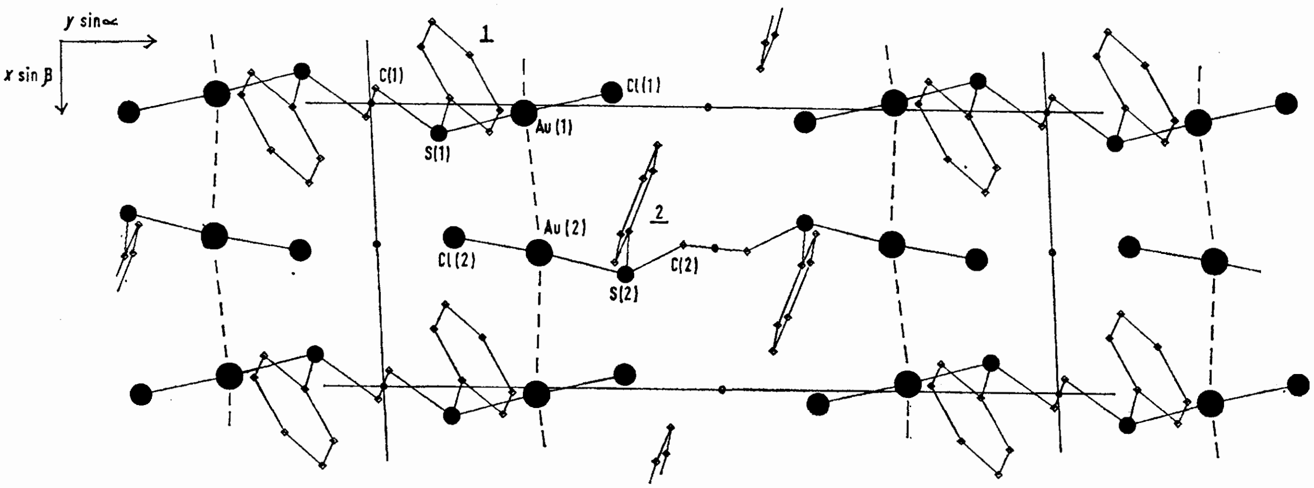

FIGURE 1 The unit cell projected along the *c* axis. Closed circles: large, gold; medium, chlorine; small, sulphur. Small open squares, carbon: small open circles, centres of symmetry

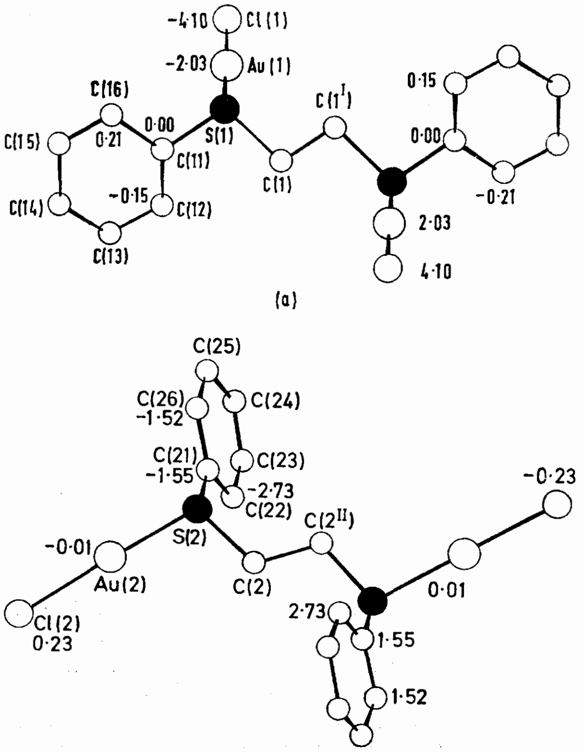

FIGURE 2 Projections of (a) dimer (1) and (b) dimer (2) on the S–C–C–S plane, showing distances (Å) of atoms from the plane

Each gold atom forms two strong bonds, one to chlorine [2·329(8) and 2·293(10) Å] and one to sulphur [2·258(11) and 2·260(12) Å]. The Au^{I} covalent radius has been estimated as 1·32 Å, from a study of structures containing metal–metal bonds.[5] Thus, while the Au–Cl bond lengths are roughly equivalent to the sum of covalent radii, the Au–S bonds show a contraction of *ca.*

TABLE 3

Least-squares planes in the form $Lx + My + Nz = P$, where x, y, z are the crystallographic fractional coordinates of the atoms. Distances (Å) of the relevant atoms from the planes are given in square brackets

	L	M	N	P
Plane (1): S(1), C(1), C(1^{I}), S(1^{I})	−3·21	9·50	−3·68	0·00
[C(11) 0·00, Cl(1) −4·09, Au(1) −2·03]				
Plane (2): S(2), C(2), C(2^{II}), S(2^{II})	6·01	0·58	−4·35	3·30
[C(21) −1·55, Au(2) −0·01, Cl(2) 0·23]				

TABLE 4

Dihedral angles (deg.)

C(2^{II})–C(2)–S(2)–C(21)	64·0
C(2^{II})–C(2)–S(2)–Au(2)	179·8
C(1^{I})–C(1)–S(1)–Au(1)	69·4
C(1^{I})–C(1)–S(1)–C(11)	−180·0
S(1)–Au(1) · · · Au(2)–Cl(2)	71·1
R(2)–C(21)–S(2)–C(2) *	31·6
R(1)–C(11)–S(1)–C(1) *	−9·4

* Symbols R(1), R(2) represent the phenyl rings, which are planar within experimental error. The calculated dihedral angle is between these rings and the plane of the other three atoms listed.

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[5] T. L. Blundell and H. M. Powell, *J. Chem. Soc.* (*A*), 1971, 1685.

0·10 Å ($r_{\rm Cl}$ 0·99, $r_{\rm S}$ 1·04 Å [6]). This is presumably due to a small amount of $d_\pi \rightarrow d_\pi$ overlap, similar to that found for the Au–P bond in the $[(\mathrm{PPh_3})(\mathrm{AuCCF_3})]_2$ dimer, where the contraction from the sum of Au,P covalent radii is 0·14 Å.[7] It is not clear whether the two Au–Cl bond lengths are significantly different, but they are similar to those found in other linear $\mathrm{Au^I}$ complexes, *viz.* $[\mathrm{AuCl_2}]^-$ 2·31 Å,[8] and $(\mathrm{Cl_3P})\mathrm{AuCl}$ 2·33 Å.[9] The two Cl–Au–S angles [177·8(4) and 173·5(4)°] are significantly different, presumably because of intermolecular forces: complexes of low co-ordination number being particularly sensitive to such effects.

The remaining dimensions in the dimers have high standard deviations. One reason for this is that the gold atoms have related co-ordinates (roughly x,y,z and $\frac{1}{2}+x,y,z$) and consequently reflections with $h = 2n + 1$ are weak. The gold atoms are thus responsible for a high proportion of the scattering of the reflections with $h = 2n$. The dimensions in the phenyl rings are well within 2σ of the expected values for C–C bond lengths and C–C–C angles. The dimensions involving the C–S–C–C–S–C linkages show greater variation than those of the phenyl rings which suggests that differences, particularly in the C–C–S and C–S–C angles, may, if significant, be due to intermolecular forces.

Each gold atom has close contacts with two other gold atoms at distances of 3·187(2) and 3·209(2) Å. These two nearest neighbours are in the square planar positions, the full list of angles being given in Table 5. Similar Au $\cdots$ Au contacts are in ref. 7 (3·34 Å), but distances comparable to the $\mathrm{Au^I}$ covalent diameter are found in the dimeric $[\mathrm{Bu^n{}_2(NCS)_2Au}]_2$ molecule.[10] In the present molecules the Au $\cdots$ Au contacts are well above the $\mathrm{Au^I}$ covalent diameter, but the striking mode of packing found in the unit cell (Figure 1) indicates that the formation of the ·Au $\cdots$ Au $\cdots$ Au· approximately linear polymeric chains play an indispensable part in the stabilising of the molecules in the crystal. The S(1)–Au(1) $\cdots$ Au(2)–Cl(2) dihedral angle is 71·1°. This would indicate that the Au $\cdots$ Au interaction is a weak σ bond, without any π overlap. The positions of the Au, S, and Cl atoms in the unit cell are closely related to the equivalent positions found in spacegroup $P2_1/a$, namely $x,y,z : \bar{x},\bar{y},\bar{z}$ for dimer (1) and $\frac{1}{2}+x,\frac{1}{2}-y,z : \frac{1}{2}-x,\frac{1}{2}+y,\bar{z}$ for dimer (2). Thus there are approximate screw axes running through the gold chains, parallel to the x axis at $y \approx 1/4$, 3/4 and $z \approx 0$. That the space group of the crystal is $P\bar{1}$ and not $P2_1/a$ is presumably because the different configurations of the two dimers present more efficient packing than a symmetric arrangement.

TABLE 5

Geometry of the Au $\cdots$ Au contacts *

Au(1) $\cdots$ Au(2)	3·187(2) Å
Au(1) $\cdots$ Au($2^{\rm III}$)	3·209(2) Å
Au(2) $\cdots$ Au(1) $\cdots$ Au($2^{\rm III}$)	172·8(1)°
Au($2^{\rm III}$) $\cdots$ Au(1)–S(1)	89·2(3)
Au($2^{\rm III}$) $\cdots$ Au(1)–Cl(1)	89·3(2)
Au(2) $\cdots$ Au(1)–Cl(1)	84·1(2)
Au(2) $\cdots$ Au(1)–S(1)	97·4(3)
Au($1^{\rm IV}$) $\cdots$ Au(2) $\cdots$ Au(1)	172·8(1)°
Au($1^{\rm IV}$) $\cdots$ Au(2)–S(2)	83·6(3)
Au($1^{\rm IV}$) $\cdots$ Au(2)–Cl(2)	91·4(3)
Au(1) $\cdots$ Au(2)–S(2)	101·7(3)
Au(1) $\cdots$ Au(2)–Cl(2)	83·7(3)

* See footnote to Table 2.

Both dimers, as we have shown, have sensible dihedral angles around the S–C bonds which minimise intramolecular contacts. However, presumably the rotations of the benzene rings about the C–C axes are affected by intermolecular forces as are some of the molecular dimensions. Inter and intra-molecular contacts <3·80 Å are in Table 6. In general, there are a considerable number of short van der Waals contacts which are indicative of the efficient packing of the dimers, in particular between Cl(2) and C($12^{\rm I}$), C($1^{\rm III}$), and C($14^{\rm V}$). In all three cases, the hydrogen atom (assuming tetrahedral or trigonal position) on the carbon atom is directed towards Cl(2) resulting in Cl $\cdots$ H contacts of 2·8, 2·5, and 2·7 Å, values below the sum of van der Waals radii (3·0 Å).[6] Cl(1) is less affected than Cl(2) by these intermolecular forces and this may account for the Cl(1)–Au(1)–S(1) angle being closer to 180° than the Cl(2)–Au(2)–S(2) angle.

TABLE 6

Intramolecular and intermolecular contacts (<3·8 Å) *

Au(1) $\cdots$ C(22)	3·75	C(21) $\cdots$ C($2^{\rm II}$)	3·34
Cl(1) $\cdots$ C(2)	3·79	C(26) $\cdots$ C($14^{\rm III}$)	3·52
C(24) $\cdots$ C(15)	3·53	Cl(2) $\cdots$ C($1^{\rm III}$)	3·50
C(16) $\cdots$ C(24)	3·63	C(26) $\cdots$ C($15^{\rm III}$)	3·69
C(16) $\cdots$ C(25)	3·75	C(2) $\cdots$ Cl($1^{\rm III}$)	3·69
C(16) $\cdots$ C(23)	3·71	Cl(2) $\cdots$ C($14^{\rm V}$)	3·70
C(1) $\cdots$ Cl($2^{\rm I}$)	3·47	C(15) $\cdots$ Cl($1^{\rm VI}$)	3·79
Cl(2) $\cdots$ C($12^{\rm I}$)	3·79	Cl(1) $\cdots$ C($22^{\rm VII}$)	3·54
		C(23) $\cdots$ Cl($1^{\rm VII}$)	3·61

* See footnote to Table 2.

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[2/1006 *Received, 5th May*, 1972]

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[10] R. Hess, in 'Advance in the Chemistry of the Co-ordination Compounds,' MacMillan, New York, 1961, p. 314.