Crystal and Molecular Structure of Tricarbonyldichlorobis(triethylphosphine)molybdenum(II)

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Crystals of the title compound are orthorhombic, space group *Iba*2, with *a* = 27.989(21), *b* = 12.356(13), *c* = 12.956(15) Å, *Z* = 8. The intensities of 1 175 independent reflections above backgrounds were collected by counter methods and refined to *R* 0.085. The molecule is a seven-co-ordinate monomer with the metal atom in a capped octahedral environment. One carbonyl group occupies the capping position [Mo–C 2.00(3)Å], two carbonyl groups [Mo–C 1.92(3) and 2.01(3) Å] and one phosphorus atom [Mo–P 2.556(9) Å] are in the capped face, and two chlorine atoms [Mo–Cl 2.478(7) and 2.537(9) Å] and one phosphorus atom [Mo–P 2.580(9) Å] are in the uncapped face. The two phosphorus atoms are mutually *trans*.

DURING our studies in the structures of seven-co-ordinate complexes,[1] we became interested in geometries intermediate between the capped octahedron (CO) and the capped trigonal prism (CTP). Many molecules with such geometries contain bidentate ligands,* *e.g.* $[MoBr_2(CO)_3(dppe)]$,[2] $[WI(CO)_2(dmpe)_2]^+$,[3] and $[MoBr_2(CO)_2(dpam)_2]$,[4] and it was thought that distortions are due to the formation of the five (or four) membered ring. However there are two examples of molecules with seven unidentate ligands which also exhibit such distortion *viz.* $[WI(CO)_3(PMe_2Ph)_3]^+$ [5] and $[MoCl_2(CO)_2(PMe_2Ph)_3]$.[6] It does not appear that ligand ··· ligand repulsions cause these distortions from ideal symmetry and therefore we concluded that the structures (both of which have C_s geometry) show the existence of a low-energy potential trough between the two geometries. As a further part of our investigation of this problem, we have determined, and report here, the structure of a related compound $[MoCl_2(CO)_3(PEt_3)_2]$.

EXPERIMENTAL

The complex was prepared as previously described[7] but with a few differences. $[MoCl_2(CO)_4]$ was prepared[8] from $[Mo(CO)_6]$ (0.75 g), dissolved in CH_2Cl_2 (30 cm^3) and filtered. Triethylphosphine (1.0 cm^3) was added by syringe to the solution (*ca.* 3 min). The mixture was left for 1 h at room temperature, the solvent was removed *in vacuo* and replaced by pentane (30 cm^3). The mixture was stored at 273 K overnight and the yellow solid filtered off. The filtrate was left at 273 K for 3 days to give well-formed yellow crystals; these were isolated from the mother liquor by decantation and pumped dry [i.r. spectrum; ν(CO) ($CHCl_3$) 2 004s, 1 946s, and 1 886s cm^{-1}].

Crystal Data.—$C_{15}H_{30}Cl_2MoO_3P_2$, $M = 487.19$, Orthorhombic, $a = 27.989(21)$, $b = 12.356(13)$, $c = 12.956(15)$ Å, $U = 4\,481.9$ Å^3, $D_m = 1.44$ g cm^{-3}, $Z = 8$, $D_c = 1.44$ g cm^{-3}, $F(000) = 2\,000$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 9.57 cm^{-1}. Space group *Iba*2 from systematic absences *hkl*, $h + k + l = 2n + 1$, $h0l$, $h = 2n + 1$ and the successful structure determination. A crystal with dimensions *ca.* 0.3 × 0.1 × 0.2 mm was mounted with the *c* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions, the latter *via* least-squares refinement of high-angle reflections. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections whose intensities were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured during the course of the experiment but no crystal decay was observed. 2 200 independent reflections with $2\theta < 50°$ were measured by the stationary-crystal–stationary-counter method. 1 175 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. No absorption or extinction corrections were applied.

Structure Determination.—The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. The molecule showed no crystallographic symmetry and was refined successfully in space group *Iba*2. The weighting scheme, chosen to give average values of F_o and of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 120$ and $w = (F_o/120)^2$ for $F_o > 120$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre with the programs described in ref. 9 and on an ICL 1904S computer at Reading University using our unpublished programs. Atomic scattering factors for Mo, Cl, P, C, and O were taken from ref. 10 as were corrections for the real and imaginary part of the anomalous dispersion of Mo, Cl, and P. The structure was refined with Mo, Cl, and P atoms refined anisotropically and C and O isotropically to *R* 0.0850. (The opposite rejected enantiomorph has *R* 0.0852.) Refinement was completed when all shifts were $< 0.05\sigma$. The anisotropic thermal parameters

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* Abbreviations: dppe = bis(diphenylphosphino)ethane, dmpe = bis(dimethylphosphino)ethane, and dpam = bis-(diphenylarsino)methane.

[1] M. G. B. Drew, *Progr. Inorg. Chem.*, in the press.

[2] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.

[3] M. G. B. Drew and A. P. Wolters, *Acta Cryst.*, accepted for publication.

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[7] A. D. Westland and N. Muriithi, *Inorg. Chem.*, 1973, **12**, 2356.

[8] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1966, **19**, 1143.

[9] '*X*-Ray system of programs,' July 1970 version, ed. J. M. Stewart, University of Maryland Technical Report TR 192.

[10] 'International Tables for *X*-Ray Crystallography,' vol. IV, 1975, The Kynoch Press, Birmingham.

used were defined as $\exp[-2\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_i]$ (i, j = 1,2, or 3), b_i being the i'th reciprocal cell dimension. The isotropic thermal parameters were defined as $\exp[-8\pi^2\sin^2\theta/\lambda^2]$. The 1 025 zero-weighted reflections showed no large discrepancies. The final difference-Fourier map showed no significant peaks. Final positional co-ordinates and thermal parameters are given in Tables 1 and 2. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21855 (6 pp., 1 microfiche).* Bond lengths and angles together with estimated standard deviations are given in Table 3.

TABLE 1

Positional parameters ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for (1) with estimated standard deviations in parentheses

Atom	x	y	z	U
Mo	1 230(1)	2 370(1)	0 000 [a]	[b]
Cl(1)	1 331(3)	0 590(6)	0 853(8)	[b]
Cl(2)	1 882(3)	3 155(7)	1 137(8)	[b]
P(1)	0 770(3)	2 680(7)	1 678(9)	[b]
P(2)	1 870(3)	1 719(6)	−1 292(8)	[b]
C(1)	0 647(11)	3 196(25)	−0 419(24)	62(8)
O(1)	0 310(8)	3 632(19)	−0 700(21)	83(7)
C(2)	0 880(10)	1 371(21)	−0 966(24)	50(7)
O(2)	0 627(8)	0 877(17)	−1 461(19)	74(6)
C(3)	1 405(10)	3 687(25)	−0 696(27)	60(8)
O(3)	1 555(8)	4 464(17)	−1 122(20)	80(7)
C(11)	1 131(21)	2 317(45)	2 852(56)	146(22)
C(12)	0 898(19)	2 272(39)	3 902(48)	131(17)
C(13)	0 550(20)	4 085(43)	2 067(48)	142(19)
C(14)	0 828(16)	4 992(49)	1 439(44)	132(16)
C(15)	0 219(18)	1 786(45)	1 878(49)	142(19)
C(16)	−0 094(16)	1 545(31)	1 080(37)	102(13)
C(21)	1 871(11)	2 431(23)	−2 585(27)	67(27)
C(22)	1 428(14)	2 318(30)	−3 172(33)	84(10)
C(23)	1 842(10)	0 230(21)	−1 626(24)	55(7)
C(24)	2 272(12)	−0 126(32)	−2 247(29)	82(10)
C(25)	2 497(11)	1 949(25)	−0 865(26)	63(8)
C(26)	2 642(11)	1 179(24)	−0 019(36)	80(9)

[a] Parameter fixed. [b] Anisotropic thermal parameters in Table 2.

DISCUSSION

The molecule $[MoCl_2(CO)_3(PEt_3)_2]$, (1), is shown in Figure 1 together with the atomic numering scheme.

TABLE 2

Anisotropic thermal parameters ($\times 10^3$) for (1)

Atom	U_{11}	U_{22}	U_{33}
Mo	34.0(8)	42.6(11)	46.4(9)
Cl(1)	70(5)	63(4)	71(5)
Cl(2)	43(4)	80(5)	76(6)
P(1)	59(5)	67(5)	73(5)
P(2)	50(5)	54(4)	54(5)
Atom	U_{12}	U_{13}	U_{23}
Mo	−00.5(10)	−9.3(15)	−0.4(20)
Cl(1)	13(4)	3(5)	13(4)
Cl(2)	−01(4)	−6(4)	−16(5)
P(1)	5(4)	8(4)	−9(5)
P(2)	−6(3)	2(4)	−11(4)

The environment of the metal atom is an almost ideal capped octahedron with C(1) the capping atom [Mo–C 2.00(3) Å], C(2) and C(3) [Mo–C 2.01(3) and 1.92(3) Å] together with P(1) [Mo–P 2.556(9) Å] in the capped face and P(2) [Mo–P 2.580(9)] and Cl(1), Cl(2) [Mo–Cl 2.478(7) and 2.537(9) Å] in the uncapped face. The geometry as shown by the L–M–L angles is far more ideal than in $[MoCl_2(CO)_2(PMe_2Ph)_3]$, (2).

TABLE 3

Molecular dimensions (distances Å, angles °)

Mo–Cl(1)	2.478(7)	C(1)–Mo–C(2)	75.4(12)
Mo–Cl(2)	2.537(9)	C(1)–Mo–C(3)	69.5(13)
Mo–P(1)	2.556(9)	C(1)–Mo–P(1)	75.1(9)
Mo–P(2)	2.580(9)	C(1)–Mo–Cl(1)	131.8(9)
Mo–C(1)	1.998(31)	C(1)–Mo–Cl(2)	123.3(9)
Mo–C(2)	2.012(29)	C(1)–Mo–P(2)	123.3(9)
Mo–C(3)	1.923(32)	C(2)–Mo–C(3)	110.5(13)
C(1)–O(1)	1.15(4)	C(2)–Mo–P(1)	112.1(8)
C(2)–O(2)	1.14(4)	C(2)–Mo–Cl(1)	77.8(8)
C(3)–O(3)	1.18(4)	C(2)–Mo–Cl(2)	161.0(8)
Mo–C(1)–O(1)	176(3)	C(2)–Mo–P(2)	75.1(9)
Mo–C(2)–O(2)	170(2)	C(3)–Mo–P(1)	113.6(10)
Mo–C(3)–O(3)	174(3)	C(3)–Mo–Cl(1)	158.6(9)
P(1)–C(11)	1.88(6)	C(3)–Mo–Cl(2)	76.5(10)
P(1)–C(13)	1.91(5)	C(3)–Mo–P(2)	77.5(10)
P(1)–C(15)	1.91(4)	P(1)–Mo–Cl(1)	79.1(3)
P(2)–C(21)	1.89(3)	P(1)–Mo–Cl(2)	79.1(3)
P(2)–C(23)	1.89(3)	P(1)–Mo–P(2)	161.5(3)
P(2)–C(25)	1.86(3)	Cl(1)–Mo–Cl(2)	89.9(3)
		Cl(1)–Mo–P(2)	86.2(3)
		Cl(2)–Mo–P(2)	89.8(3)
C(11)–C(12)	1.51(9)	C(21)–C(22)	1.46(5)
C(13)–C(14)	1.59(8)	C(23)–C(24)	1.51(4)
C(15)–C(16)	1.39(7)	C(25)–C(26)	1.51(5)
Mo–P(1)–C(11)	112.4(20)	Mo–P(2)–C(21)	115.5(10)
Mo–P(1)–C(13)	121.5(19)	Mo–P(2)–C(23)	115.1(10)
Mo–P(1)–C(15)	115.7(19)	Mo–P(2)–C(25)	114.4(11)
C(11)–P(1)–C(13)	100.2(26)	C(21)–P(2)–C(23)	104.4(14)
C(11)–P(1)–C(15)	100.7(26)	C(21)–P(2)–C(25)	100.9(14)
C(13)–P(1)–C(15)	103.2(24)	C(23)–P(2)–C(25)	104.8(13)
P(1)–C(11)–C(12)	120.3(41)	P(2)–C(21)–C(22)	114.5(24)
P(1)–C(13)–C(14)	110.4(38)	P(2)–C(23)–C(24)	111.9(21)
P(1)–C(15)–C(16)	122.2(43)	P(2)–C(25)–C(26)	111.9(22)

In both (1) and (2) [which has Mo–Cl 2.486(16), 2.561(14) Å] the two Mo–Cl bonds differ in length by a significant amount (*ca.* 0.075 Å). Explanations for this in (2) are easy to find. First, the shorter bond is *trans* to phosphorus, the longer to carbonyl; secondly, the shorter bond is in a slightly less crowded site because of the distortion towards the CTP. Neither explanation suffices for (1) as the environment of the two chlorine atoms in the co-ordination sphere is identical. However

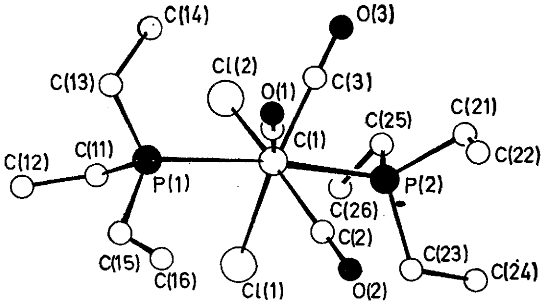

FIGURE 1 $[MoCl_2(CO)_3(PEt_3)_2]$

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* For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

there is a difference in the orientation of the adjacent PEt_3 groups with respect to the chlorine atoms which could well account for this difference (see below).

Another feature in common with (2) is that the Mo–P(1) bond is shorter than Mo–P(2). The difference in (1) is 0.024 Å and a similar value was found in $[WBr_2(CO)_3(dpam)_2]$ [11] for W–As bonds. This is not unreasonable as the phosphorus P(2) in the uncapped face is more *trans* to the carbonyl in the capping position than P(1). However the difference is much greater in (2) [Mo–P 2.528(15) and 2.623(16) Å]; this could be due to the fact that in this structure there are only two carbonyl groups and thus π overlap is more important, or alternatively that as in $[WI_2(CO)_3(dmpe)]$, (3),[12] two phosphorus atoms are mutually *cis* [P–Mo–P 83.8(5)°], a situation that may lead to bond weakening because of steric effects. The variations in the Mo–C distances are not significant; as usual the Mo · · · O distances are more equivalent. Not surprisingly these two bulky phosphine ligands are kept well apart, being mutually *trans*; a similar arrangement was found in $[WBr_2(CO)_3(dpam)_2]$.[11]

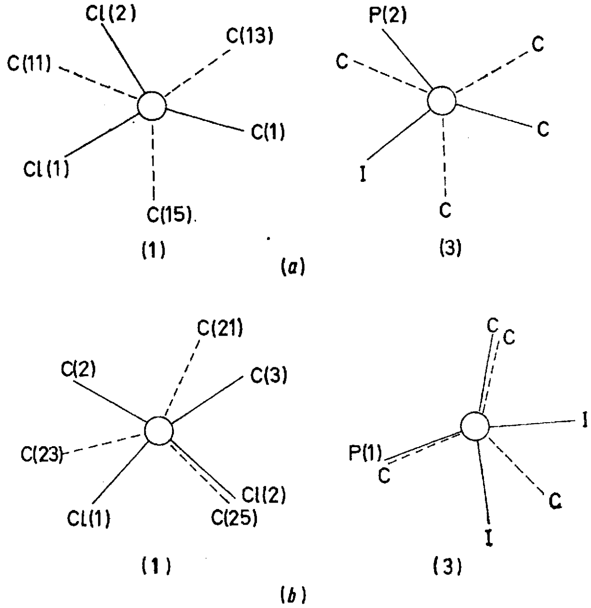

FIGURE 2 (*a*) Projection down the M–P(1) bond. (*b*) Projection down the M–P(2) bond. Dotted lines represent bonds to phosphorus, unbroken lines to the metal atom [Mo in (1), W in (3)]

Of particular interest in the present molecule is the orientation of the PEt_3 groups. We have analysed the orientation of the carbon atoms around the W–P bonds in (3) and similar orientations are found in a number of other capped octahedra which contain just one bidentate and five monodentate ligands.[1] In these molecules the chelating ligands occupy an edge between a site in the capped face and one in the uncapped face.

Torsion angles in (1) are given in Table 4 and compared to those found in (3) in Figure 2. P(1) in the capped face has just three close neighbours in the co-ordination sphere, C(1), Cl(1), and Cl(2) and its three carbon atoms [C(11), C(13), and C(15)] are staggered with respect to them. There are eclipsed orientations with respect to C(2) and C(3) which share the capped face with P(1) [C(2)–Mo–P(1)–C(15) is 8.6 and C(3)–Mo–P(1)–C(13) is 8.5°] but with C–Mo–P angles of *ca.* 113° this does not lead to short C · · · C contacts. This orientation is more staggered than in (3) and similar structures where the formation of the ring causes an internal ring torsion angle [say P(2)–W–P(1)–C] of *ca.* 25°.

Compounds (1) and (3) also exhibit a different set of torsion angles for the atom P(2) in the uncapped face. This atom has four nearest neighbours in the co-ordination sphere C(2), C(3) of the capped face and Cl(1), Cl(2) of the uncapped face, the former two being the closest. The arrangement (Figure 2) is such that Cl(2) is eclipsed with respect to C(25) (4.7°) and the other eleven torsion angles are >36°. This contrasts with the arrangement in (3) in which there is a staggered arrangement with respect to the two iodine atoms in the uncapped face and an eclipsed one with respect to the two atoms in the capped face. Not surprisingly, therefore, in (1) Mo–Cl(2) is longer than Mo–Cl(1) due to the potentially short Cl(2) · · · C(25) contact [3.45 Å]. However, there is one other contact [Cl(2) · · · C(11) 3.23 Å] which may also be a determining factor; a consequence of the Cl(2)–Mo–P(1) angle of 79.1° and a torsion angle Cl(2)–Mo–P(1)–C(11) of −40.3°. Other intramolecular contacts <3.5 Å are given in Table 4. The torsion angles are very similar in (1) and (2) and can therefore be con-

TABLE 4

Torsion angles (°)

(*a*) For angles atom–Mo–P–C where the atom–Mo–P angle is <100°

C(1)–Mo–P(1)–C(11)	−169.3
C(1)–Mo–P(1)–C(13)	−50.7
C(1)–Mo–P(1)–C(15)	75.7
Cl(1)–Mo–P(1)–C(11)	51.8
Cl(1)–Mo–P(1)–C(13)	170.4
Cl(1)–Mo–P(1)–C(15)	−63.2
Cl(2)–Mo–P(1)–C(11)	−40.3
Cl(2)–Mo–P(1)–C(13)	78.3
Cl(2)–Mo–P(1)–C(15)	−155.2
C(2)–Mo–P(2)–C(21)	79.9
C(2)–Mo–P(2)–C(23)	−42.1
C(2)–Mo–P(2)–C(25)	−163.5
C(3)–Mo–P(2)–C(21)	−35.7
C(3)–Mo–P(2)–C(23)	−157.7
C(3)–Mo–P(2)–C(25)	80.9
Cl(1)–Mo–P(2)–C(21)	158.2
Cl(1)–Mo–P(2)–C(23)	36.3
Cl(1)–Mo–P(2)–C(25)	−85.2
Cl(2)–Mo–P(2)–C(21)	−111.8
Cl(2)–Mo–P(2)–C(23)	126.2
Cl(2)–Mo–P(2)–C(25)	4.7

(*b*) Others

Mo–P(1)–C(11)–C(12)	−170.2	Mo–P(2)–C(21)–C(22)	−60.8
Mo–P(1)–C(13)–C(14)	−18.2	Mo–P(2)–C(23)–C(24)	−170.9
Mo–P(1)–C(15)–C(16)	−40.7	Mo–P(2)–C(25)–C(26)	73.3

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[11] M. G. B. Drew, A. W. Johans, A. P. Wolters, and I. B. Tomkins, *Chem. Comm.*, 1971, 819.

[12] M. G. B. Drew and C. J. Rix, *J. Organometallic Chem.*, 1975, **102**, 467.

sidered as the most likely for atoms occupying these two sites in the capped octahedron.

The geometry of (1) is an almost ideal capped octahedron as indeed is [$WBr_2(CO)_3(dpam)_2$]. We have described[1] a method for calculating root-mean-square deviations from C_{3v} and C_{2v} symmetry for a particular co-ordination sphere. This calculation, after normalisation, gave values of 0.04 and 0.14 Å for (1), and 0.06 and 0.11 Å for (2), for these two geometries respectively. The main reason for the difference is probably that in (1) the two bulky PEt_3 ligands are kept well apart but for the PMe_2Ph ligands in (2) this is not possible and two are mutually *cis*.

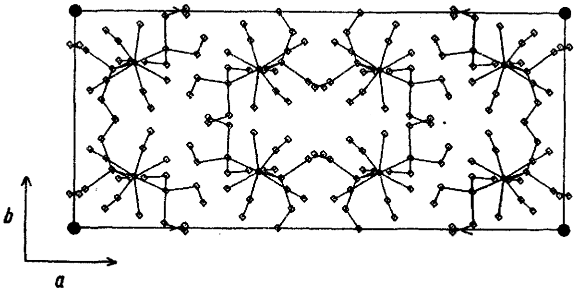

FIGURE 3 (1) in the *c* projection of the unit cell

It is noteworthy that all the four structures[1] containing two halogen atoms that have a geometry distorted from the CO to the CTP contain two chlorine atoms. Presumably when the halogen is the larger bromine or iodine then ligand · · · ligand repulsions are more important and the X–M–X angle is *ca.* 90°, an angle best suited to the CO geometry.

In (1) the thermal parameters of the P(1) ethyl groups are very much higher than those of the P(2) ethyl groups and this is reflected in the high standard deviations for this ligand. The dimensions of these ethyl groups are as expected. The torsion angles Mo–P–C–C are all *ca.* 180 or ±60°; the one exception being Mo–P(1)–C(13)–C(14) which is an unexpectedly low −18.2°. The packing of the molecules in the unit cell is not particularly efficient, there being only seven intermolecular contacts <3.75 Å (Table 5). The packing of the molecules is shown in Figure 3, a view in the *c* projection.

TABLE 5

(*a*) Intermolecular contacts <3.75 Å *			
C(15) · · · O(2$^{\text{I}}$)	3.39	O(3) · · · C(26$^{\text{II}}$)	3.40
C(16) · · · O(2$^{\text{I}}$)	3.61	Cl(1) · · · C(23$^{\text{III}}$)	3.71
C(12) · · · C(16$^{\text{I}}$)	3.72	Cl(1) · · · C(24$^{\text{III}}$)	3.65
O(3) · · · C(24$^{\text{II}}$)	3.63		
(*b*) Intramolecular contacts <3.50 Å			
Cl(1) · · · C(11)	3.40	C(2) · · · C(22)	3.45
Cl(2) · · · O(3)	3.47	C(2) · · · C(23)	3.16
Cl(2) · · · C(11)	3.23	C(3) · · · C(21)	3.18
Cl(2) · · · C(25)	3.45	O(3) · · · C(21)	3.27
C(1) · · · O(2)	3.17	C(21) · · · C(24)	3.38
C(1) · · · O(3)	3.12	C(23) · · · C(26)	3.27
C(1) · · · C(13)	3.41	C(24) · · · C(26)	3.46
C(1) · · · C(16)	3.50	C(24) · · · C(25)	3.19
O(1) · · · C(2)	3.24	C(12) · · · C(13)	3.41
O(1) · · · C(3)	3.07	C(12) · · · C(15)	3.29
C(1) · · · C(14)	3.31		

* Roman numerals as superscripts refer to the following equivalent positions relative to the set at *x*, *y*, *z* in Table 1: I $-x, y, \frac{1}{2} + z$; II $\frac{1}{2} - x, \frac{1}{2} + y, z$; III $x, -y, \frac{1}{2} + z$.

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