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Structure of [*OC*-6-33]-{1,1-Bis(diphenylphosphinomethyl)-1-[(diphenylphosphine oxide)methyl]ethane}tricarbonylchlororhenium(I) Monohydrate

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Abstract. [$ReCl(CO)_3(C_{41}H_{39}OP_3)$].$H_2O$, M_r = 964·05, monoclinic, $P2_1/c$, $a = 21·309$ (5), $b = 8·771$ (2), $c = 21·530$ (6) Å, $\beta = 96·54$ (2)°, $V = 3997·9$ (18) Å^3, $Z = 4$, $D_x = 1·602$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70930 Å, $\mu = 0·344$ cm^{-1}, $F(000) = 2019·64$, $T = 298$ K, $R = 0·036$ for 3160 reflections with $I > 2·5\sigma(I)$. The Re atom is octahedrally coordinated by one Cl atom, two phosphine moieties, and three carbonyl ligands with the three carbonyl ligands occupying a face. The six-membered ring formed by Re, P1, P2, C4, C5 and C7 adopts a boat form. The phosphoranyl O and the water molecule are strongly hydrogen bonded such that inversion-related molecules are paired in the crystalline state.

Introduction. The reaction between an organometallic cluster compound and a multidentate phosphine ligand has been studied with interest because it is believed that the multidentate phosphine ligand is able to maintain the integrity of the metal cluster under severe reaction conditions and may serve as a template in the synthesis of new cluster compounds. Hence, we have investigated the reaction of a tripod ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane (tdppme) with $Re_2(CO)_{10}$ under photolytic conditions.

Experimental. A slight excess of tdppme tripod ligand (560 mg, 0·90 mmol) was stirred with $Re_2(CO)_{10}$ (528 mg, 0·81 mmol) in dichloromethane (30 ml) under photolyzing conditions for 8 h using a 450 W Hg lamp. After evaporating the solvent, the residue was separated by thin-layer chromatography using dichloromethane/*n*-hexane mixed solvent (2:1). The major product was found to be [*OC*-6-33]-[$ReCl(CO)_3$(tdppme)] (Lin, Cheng, Lee, Lee & Peng, 1986). The minor product was investigated with single-crystal X-ray diffraction studies and the results are reported here.

Nonius CAD-4 diffractometer with graphite monochromator, $2 < 2\theta < 50°$, Mo $K\alpha$, ω–2θ scan method with speed 0·9–6·7° min^{-1}, 2(0·7° + 0·35° tanθ) around maximum, h 0 to 25, k 0 to 10, l –25 to 25. 25 reflections (9·63–11·83°) used for lattice parameters. Data-crystal dimensions *ca* 0·25 × 0·25 × 0·40 mm. Three standard reflections ($1,\bar{2},\overline{10}$, $\bar{1},2,10$ and $44\bar{6}$) recollected after every 7200 s, no decay or decomposition found. Intensity variations within 2%. Absorption correction applied, min. and max. transmission factors 0·738 and 0·999. 7062 unique reflections measured, 3160 observed with $I > 2·5\sigma(I)$. Structure solved with Patterson and Fourier methods. Structure refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, w from counting statistics only. Calculations with anisotropic non-H and isotropic H. H only calculated

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and included. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final R 0·036 and wR 0·030. Max. Δ/σ for the last cycle 0·082. Max. and min. peak height in final difference map 0·83 and $-0·68$ e Å^{-3}. Computations carried out on a VAX 8800 with the NRCC package (Larson, Lee, Le Page & Gabe, 1986). A *SCHAKAL* (Keller, 1986) drawing of the molecule is shown in Fig. 1, final atomic fractional coordinates for non-H atoms are given in Table 1, and relevant bond lengths and angles in Table 2.*

Table 1. *Final atomic fractional coordinates for non-*H *atoms*

	x	y	z	B_{eq}*(Å^2)
Re	0·15590 (2)	0·99751 (8)	0·11981 (2)	3·08 (2)
Cl	0·2619 (2)	1·1239 (4)	0·1353 (1)	5·3 (2)
P1	0·1957 (1)	0·7645 (3)	0·1735 (1)	2·6 (1)
P2	0·1935 (1)	0·8852 (3)	0·0255 (1)	2·5 (1)
P3	0·4209 (1)	0·7186 (3)	0·1110 (1)	2·7 (1)
O1	0·1070 (7)	1·2767 (12)	0·0451 (4)	10·4 (8)
O2	0·0224 (4)	0·8750 (13)	0·1075 (4)	6·8 (6)
O3	0·1277 (5)	1·1355 (10)	0·2444 (4)	6·0 (5)
O4	0·4407 (3)	0·5825 (8)	0·0769 (3)	3·4 (3)
O*w*	0·5650 (4)	0·4892 (13)	0·0562 (3)	6·8 (5)
C1	0·1271 (8)	1·1729 (15)	0·0761 (7)	6·9 (9)
C2	0·0727 (6)	0·9159 (15)	0·1106 (5)	4·3 (6)
C3	0·1390 (6)	1·0882 (14)	0·1964 (6)	4·9 (7)
C4	0·2285 (5)	0·6244 (11)	0·1230 (4)	2·6 (5)
C5	0·2735 (5)	0·8073 (12)	0·0449 (4)	2·6 (5)
C6	0·3429 (5)	0·6986 (11)	0·1357 (4)	2·4 (4)
C7	0·2856 (5)	0·6663 (11)	0·0878 (4)	2·5 (5)
C8	0·2956 (5)	0·5242 (13)	0·0491 (4)	3·4 (5)
C11	0·2518 (5)	0·7725 (12)	0·2450 (4)	2·6 (5)
C12	0·2760 (5)	0·9106 (12)	0·2677 (5)	3·5 (5)
C13	0·3170 (5)	0·9101 (13)	0·3231 (5)	3·8 (6)
C14	0·3328 (6)	0·7766 (16)	0·3536 (5)	4·4 (6)
C15	0·3085 (6)	0·6415 (15)	0·3321 (5)	4·4 (6)
C16	0·2683 (5)	0·6383 (13)	0·2777 (5)	3·4 (5)
C21	0·1315 (5)	0·6559 (12)	0·2014 (5)	2·7 (5)
C22	0·1081 (6)	0·7038 (14)	0·2563 (5)	4·1 (6)
C23	0·0591 (6)	0·6277 (16)	0·2777 (6)	4·6 (7)
C24	0·0338 (5)	0·5027 (20)	0·2492 (5)	4·9 (7)
C25	0·0553 (6)	0·4526 (14)	0·1936 (6)	4·8 (6)
C26	0·1043 (5)	0·5282 (14)	0·1707 (5)	4·2 (6)
C31	0·1487 (5)	0·7361 (11)	−0·0205 (4)	2·6 (5)
C32	0·0886 (6)	0·6984 (17)	−0·0126 (5)	5·3 (7)
C33	0·0549 (7)	0·5930 (20)	−0·0483 (7)	7·8 (10)
C34	0·0845 (7)	0·5165 (19)	−0·0916 (6)	6·3 (8)
C35	0·1454 (7)	0·5531 (15)	−0·1026 (5)	5·6 (7)
C36	0·1773 (5)	0·6633 (14)	−0·0667 (5)	4·2 (6)
C41	0·2058 (5)	1·0262 (12)	−0·0350 (4)	2·8 (5)
C42	0·2589 (5)	1·1178 (13)	−0·0293 (5)	3·7 (5)
C43	0·2678 (6)	1·2180 (14)	−0·0774 (6)	4·4 (6)
C44	0·2274 (6)	1·2262 (13)	−0·1298 (5)	4·3 (6)
C45	0·1740 (6)	1·1370 (14)	−0·1352 (5)	5·0 (7)
C46	0·1631 (5)	1·0353 (13)	−0·0885 (5)	4·1 (6)
C51	0·4726 (5)	0·7587 (13)	0·1819 (5)	3·3 (5)
C52	0·5369 (6)	0·7414 (16)	0·1783 (5)	4·7 (7)
C53	0·5800 (6)	0·7707 (18)	0·2280 (6)	5·9 (8)
C54	0·5598 (7)	0·8213 (16)	0·2824 (6)	5·2 (7)
C55	0·4986 (7)	0·8334 (18)	0·2883 (5)	5·8 (8)
C56	0·4530 (6)	0·8040 (17)	0·2373 (6)	5·5 (8)
C61	0·4220 (5)	0·8935 (13)	0·0672 (5)	2·8 (6)
C62	0·4196 (6)	1·0343 (12)	0·0919 (5)	3·1 (6)
C63	0·4200 (7)	1·1638 (14)	0·0562 (6)	4·0 (6)
C64	0·4230 (6)	1·1502 (18)	−0·0073 (7)	4·0 (7)
C65	0·4241 (4)	1·0069 (23)	−0·0343 (4)	4·0 (5)
C66	0·4238 (6)	0·8798 (16)	0·0019 (6)	3·2 (6)

* B_{eq} is the mean of the principal axes of the thermal ellipsoids.

Discussion. As illustrated in Fig. 1, the molecule does not contain the original tdppme tripod ligand but, instead, a tripod oxide ligand. The minor product is hence an [*OC*-6-33]-[ReCl(CO)$_3$(tripod oxide)], with just one more O in its molecular formula than the major product, [*OC*-6-33]-[ReCl(CO)$_3$(tdppme)] (Lin *et al.*, 1986). The Re atom is octahedrally coordinated by one Cl atom, two phosphine moieties, and three carbonyl ligands with the three carbonyl ligands occupying a face. The third phosphine moiety has become a phosphine oxide moiety, owing to the chemistry during the work-up stage. It is known that a phosphine reacting with a halo-compound readily produces a phosphonium salt, which requires a base to produce a phosphine oxide.

The six-membered ring formed by Re, P1, P2, C4, C5 and C7 adopts a boat form: Re, P1, C5 and C7 are coplanar to within 0·03 Å, whereas P2 and C4 serve as the bow and stern, with distances from the boat base of 0·92 and 0·68 Å, respectively. The plane defined by Re, P1, P2 and C4 deviates up to 0·06 Å, and the plane defined by P2, C4, C5 and C7 up to 0·07 Å. Their geometry can be better described by their torsional angles P2—Re—P1—C4 of −2·4° and P2—C5—C7—C4 of −13·0°, which also indicate their flatness. These planes make a dihedral angle of 54·3 (4)°. In [ReCl(CO)$_3$(tdppme)], however, the same six-membered ring exhibits a chair form.

P3 of the tripod oxide ligand is almost equidistant from P1 and P2. The approximate isosceles triangle has edges P1—P3 of 5·194 (4) Å, P2—P3 of 5·146 (4) Å, and P1—P2 of 3·352 (4) Å. In [ReCl(CO)$_3$(tdppme)], the three P atoms also form an isosceles triangle but with the corresponding P1—P3 and P2—P3 distances shorter by 0·15–0·20 Å. In changing from tdppme to tripod oxide, the ligand dimensions increase slightly to accommodate the extra O atom. The tripod oxide ligand also changes its conformation: the three P atoms are not on the same side of the plane defined by C4, C5 and C6. In [ReCl(CO)$_3$(tdppme)], however, the three P atoms remain on the same side of the plane.

For chelating phosphine–rhenium complexes, a comparison of X-ray structures as shown in Table 3 can give detailed structural information concerning the ring strains. In a four-membered ring of Re(dppm), the small bite angle P—Re—P of 68·9 (1)° and the small angle P—C—P of 96·4 (4)° characterize the so-called small ring strain. The P—C—P angle is noticeably smaller than the regular tetrahedral 109·5°. On the other hand, for Re(tripod oxide) and Re(tdppme), both with a six-membered ring structure, the large P—C—C angles ranging from 118·9 (6) to 121·7 (7)° are apparently *ca* 10° larger than expected, a characteristic of large ring strain. In between, the five-

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* Lists of structure factors, anisotropic thermal parameters, calculated fractional coordinates for H atoms, bond distances and angles, least-squares planes, and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44967 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Bond distances and bond angles around the Re coordination sphere

Re—Cl	2·503 (3)	Re—C(1)	1·870 (14)
Re—P(1)	2·451 (3)	Re—C(2)	1·902 (13)
Re—P(2)	2·471 (3)	Re—C(3)	1·902 (12)
Cl—Re—P(1)	92·77 (11)	Cl—Re—P(2)	85·05 (10)
Cl—Re—C(1)	86·7 (5)	Cl—Re—C(2)	175·4 (4)
Cl—Re—C(3)	87·5 (4)	P(1)—Re—P(2)	85·86 (9)
P(1)—Re—C(1)	177·7 (4)	P(1)—Re—C(2)	90·2 (4)
P(1)—Re—C(3)	91·7 (4)	P(2)—Re—C(1)	91·9 (4)
P(2)—Re—C(2)	98·7 (3)	P(2)—Re—C(3)	172·0 (4)
C(1)—Re—C(2)	90·5 (7)	C(1)—Re—C(3)	90·5 (5)
C(2)—Re—C(3)	88·9 (5)		

Other relevant bond distances and bond angles

P(1)—C(4)	1·830 (10)	P(1)—C(11)	1·840 (10)
P(1)—C(21)	1·824 (10)	P(2)—C(5)	1·840 (10)
P(2)—C(31)	1·840 (11)	P(2)—C(41)	1·836 (10)
P(3)—O(4)	1·486 (7)	P(3)—C(6)	1·812 (10)
P(3)—C(51)	1·813 (11)	P(3)—C(61)	1·801 (11)
O(1)—C(1)	1·181 (17)	O(2)—C(2)	1·125 (16)
O(3)—C(3)	1·162 (14)		
Re—P(1)—C(4)	114·5 (3)	Re—P(1)—C(11)	121·3 (4)
Re—P(1)—C(21)	111·0 (3)	C(4)—P(1)—C(11)	105·4 (5)
C(4)—P(1)—C(21)	101·3 (5)	C(11)—P(1)—C(21)	100·6 (5)
Re—P(2)—C(5)	109·9 (3)	Re—P(2)—C(31)	121·9 (3)
Re—P(2)—C(41)	113·6 (3)	C(5)—P(2)—C(31)	105·6 (5)
C(5)—P(2)—C(41)	102·0 (4)	C(31)—P(2)—C(41)	101·8 (5)
O(4)—P(3)—C(6)	112·8 (4)	O(4)—P(3)—C(51)	113·1 (5)
O(4)—P(3)—C(61)	113·9 (5)	C(6)—P(3)—C(51)	105·1 (5)
C(6)—P(3)—C(61)	107·6 (5)	C(51)—P(3)—C(61)	103·5 (5)
Re—C(1)—O(1)	175·2 (14)	Re—C(2)—O(2)	175·6 (11)
Re—C(3)—O(3)	176·1 (11)		

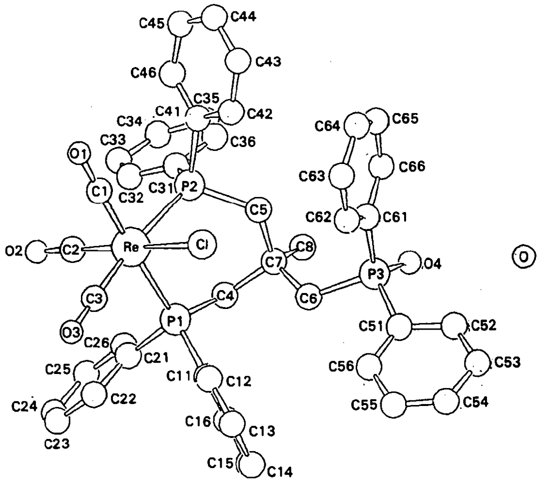

Fig. 1. *SCHAKAL* plot of the molecule with the atomic numbering sequence. The H atoms have been omitted for clarity.

Table 3. *Structural parameters for the four, five- and six-membered rings of chelating phosphine–rhenium complexes*

Compound	Ring size	Structure	Re—P (Å)	P—Re—P (°)	P···P (Å)	P—C—C P—C—P (°)
(1)	Four	Re(dppm)	2·441 (3) 2·422 (4)	68·9 (1)	2·76	96·4 (4)
(2)	Five	Re(dppe)	2·446 (2) 2·449 (2)	82·20 (8)	3·218	111·5 (6) 110·0 (6)
(3)	Six (chair)	Re(tdppme)	2·480 (2) 2·454 (3)	88·07 (8)	3·430 (3)	118·9 (6) 121·1 (6)
(4)	Six (boat)	Re(tripod oxide)	2·451 (2) 2·471 (3)	85·86 (9)	3·352 (3)	120·3 (7) 121·2 (7)

Compound (1) is [Re(CO)$_2$(dppm)(μ,η^1,η^2-CH=CH$_2$)(μ,η^1,η^2-C≡CPh)-Re(CO)$_3$] where dppm = bis(diphenylphosphino)methane (Lee, Pennington, Cordes & Brown, 1985). Compound (2) is [*OC*-6-33]-[Rc(CO)$_3$(dppe)-{C(O)SiPh$_3$}] where dppe = bis(diphenylphosphino)ethane (Anglin, Calhoun & Graham, 1977). Compound (3) is [*OC*-6-33]-[ReCl(CO)$_3$(tdppme)], where tdppme = 1,1,1-tris(diphenylphosphinomethyl)ethane (Lin *et al.*, 1986). Compound (4) is [*OC*-6-33]-[ReCl(CO)$_3$(tripod oxide)] (this report).

membered ring of Re(dppe) shows normal bond distances and angles for Re—P, P—Re—P, P···P and P—C—C. For an 18 e Re, the Re—P bond lengths are usually in the range 2·44–2·48 Å (Barder, Cotton, Lewis, Schwotzer, Tetrick & Walton, 1984; Mays, Prest & Raithby, 1980; Lee, Pennington, Cordes & Brown, 1984) although for a 16 e Re, the Re—P bond lengths are shortened by 0·1–0·2 Å (Hughes, Pombeiro, Pickett & Richards, 1983). The octahedral P—Re—P angle is ideally 90°, and the tetrahedral P—C—C angle is ideally 109·5°. A P···P distance longer than 3·2 Å is long enough to be regarded as a van der Waals contact. It has been well known for a long time that a five-membered ring system is much preferred for organometallic chelating compounds; Table 3 gives the structural evidence.

The phosphoranyl O and the water molecule participate in hydrogen-bonding interactions such that inversion-related molecules are paired in the crystalline state. The hydrogen-bonding parameters are: distances O4···O*w* 2·857 (10), O4···O*w*′ 2·923 (10), O4···H*wA* 1·981, O4···H*wB* 2·043, O*w*—H*wA* 0·876, and O*w*—H*wB* 0·880 Å, and angles O4···H*wA*—O*w* 177·5 and O4···H*wB*—O*w* 177·2°.

The Re—Cl bond length, 2·503 (3) Å, and the Re—C(carbonyl) bond lengths ranging between 1·875 (14) and 1·907 (12) Å are slightly shorter than those found in pentacarbonylchlororhenium(I) (Cotton & Daniels, 1983). The C≡O bond lengths are consistent with the normal values.

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Structure of μ-1,4,7,10,13,16-Hexathiacyclooctadecane(picrato)disilver Picrate

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Abstract. $[Ag_2(C_6H_2N_3O_7)(C_{12}H_{24}S_6)]^+.C_6H_2N_3O_7^-$, $M_r = 1032{\cdot}62$, monoclinic, $P2_1/c$, $a = 14{\cdot}579\,(7)$, $b = 16{\cdot}030\,(5)$, $c = 15{\cdot}985\,(8)$ Å, $\beta = 110{\cdot}67\,(3)°$, $V = 3495\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}95$, $D_x = 1{\cdot}962$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 15{\cdot}26$ cm^{-1}, $F(000) = 2064$, $T = 293$ K, final $R = 0{\cdot}036$ for 5669 observed reflections. There are two crystallographically different Ag atoms, Ag(1) and Ag(2), on opposite sides of the weighted mean plane through the non-H atoms of the asymmetric macrocyclic ligand (18S6) at distances of 1·395 (2) and −1·909 (2) Å, respectively, from it. The coordination polyhedron of Ag(1) is a distorted trigonal bipyramid with four S atoms at distances of 2·540 (1), 2·557 (1), 2·775 (2) and 3·005 (2) Å and the phenolic O atom from one picrate anion (pic) at a distance of 2·481 (3) Å from Ag(1). Ag(2) has a tetrahedrally distorted coordination with Ag(2)—S distances of 2·439 (2), 2·563 (2), 2·624 (1) and 2·671 (1) Å. All six ligand S atoms are engaged in the metal coordination but two of them are shared between adjacent Ag polyhedra causing polymeric chains of $[Ag_2(18S6)(pic)]^+$ cations running along **c**.

Introduction. Previous studies of complex formation of silver with potentially tetradentate and hexadentate macrocyclic polythiaethers 1,4,8,11-tetrathiacyclotetradecane (14S4) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) have shown that silver(I) picrate with these ligands forms various complexes (Sevdić, Fekete & Meider, 1980) whose composition depends on the ratio of silver(I) picrate to ligand in the solution. Complexes corresponding to the formula [Ag(14S4)(pic)], $[Ag_2(14S4)(pic)_2]$, [Ag(18S6)(pic)], $[Ag_2(18S6)(pic)_2]$ and $[Ag_3(18S6)(pic)_3]$ have been isolated.

As a continuation of our investigation on the coordination mode of macrocyclic polythiaethers (Herceg, Matković, Sevdić, Matković-Čalogović & Nagl, 1984; Galešić, Herceg & Sevdić, 1986) the crystal structure of the $[Ag_2(18S6)(pic)_2]$ complex has been investigated.

Experimental. The compound was prepared as described previously (Sevdić, Fekete & Meider, 1980). Crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. D_m by flotation in a mixture of CCl_4 and $CHBr_3$. Intensity data collected from a crystal of dimensions 0·25 × 0·25 × 0·34 mm on a Philips PW1100 four-circle diffractometer, θ–2θ scanning technique, scan width 1·60°, scan rate 0·04° s^{-1}. Unit-cell parameters obtained from least-squares analysis of 20 reflections with 2θ values ranging from 10 to 15°. From absent reflections $k0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ the space group $P2_1/c$ was determined. Out of 6931 reflections scanned within a quadrant $\pm h,k,l$ (h 19,−20; k 22; l 21) up to $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1}, 6704 unique reflections were classified as observed. Three standard reflections ($\bar{4}02$, 006, 060) measured every 2 h showed an average variation of 1%. Corrections applied for Lorentz and polarization effects. No corrections for absorption or extinction. Two crystallographically different Ag atoms located by heavy-atom method, all other non-H atoms from Fourier maps. H atoms located from a difference map. In final calculations four reflections (020, $\bar{4}04$, $\bar{7}24$, $\bar{7}44$) strongly affected by extinction were rejected. Block-diagonal least-squares refinement on F for the 5669 remaining reflections with $I > 3\sigma(I)$. Parameters of non-H atoms refined anisotropically, those of H atoms isotropically and separately in the subsequent cycles (470 and 113 parameters refined, respectively); R and wR 0·036 and 0·041, respectively; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1{\cdot}00/\sigma^2(F_o)$ giving $S = 1{\cdot}23$; $(\Delta/\sigma)_{\max} = 0{\cdot}14$. Final difference map revealed residuals between −0·55 and 0·49 e Å^{-3} except for two irregular maxima of 3·91 and 1·54 e Å^{-3} near the Ag atoms. Scattering factors of Cromer & Mann (1968) for non-H

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