1987) as in the (EDTTTF)$_2X$ salts and the superconducting (ET)$_2X$ salts (Williams *et al.*, 1987). These crystals show metallic behavior down to 125 K at ambient pressure (Terzis *et al.*, 1988) and the metallic behavior is extended down to 30 K at 0·48 GPa pressure (Hilti *et al.*, 1989).

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Structures of Tetraaquabis(hydroxymethanesulfonato)magnesium(II) and Hexaaquaaluminium(III) Hydroxymethanesulfonate

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Abstract. (I) $C_2H_{14}MgO_{12}S_2$, $[Mg(CH_3O_4S)_2(H_2O)_4]$, $M_r = 318{\cdot}55$, monoclinic, $P2_1/c$, $a = 10{\cdot}658$ (2), $b = 7{\cdot}717$ (1), $c = 21{\cdot}449$ (3) Å, $\beta = 92{\cdot}02$ (2)°, $V = 1763$ Å^3, $Z = 6$, $D_x = 1{\cdot}800$ g cm^{-3}, Mo $K\alpha$ (graphite-monochromated), $\lambda = 0{\cdot}70926$ Å, $\mu = 5{\cdot}56$ cm^{-1}, $F(000) = 996$, $T = 295$ K, 3102 unique reflections, 2382 with $I > 3\sigma(I)$, final $R = 0{\cdot}039$ for 2364 reflections. (II) $C_3H_{21}AlO_{18}S_3$, $[Al(H_2O)_6]^{3+}.3CH_3O_4S^-$, $M_r = 468{\cdot}34$, monoclinic, $P2_1/n$, $a = 10{\cdot}821$ (1), $b = 22{\cdot}503$ (4), $c = 14{\cdot}439$ (3) Å, $\beta = 91{\cdot}58$ (2)°, $V = 3514$ Å^3, $Z = 8$, $D_x = 1{\cdot}770$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 5{\cdot}54$ cm^{-1}, $F(000) = 1952$, $T = 295$ K, 4850 unique reflections, 1170 with $I > 2\sigma(I)$, final $R = 0{\cdot}080$. The structures are similar in that they contain water coordinated to the metal, but they are distinctly different from the corresponding hydroxymethanesulfonate salts of the remaining Group I and Group II metals which contain no coordinated water.

Introduction. The structures of the hydroxymethanesulfonate salts of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and NH_4^+ have recently been determined (Owen, 1982). In order to complete this series of Group I and Group II salts, the structure of the Mg^{II} salt has now been determined. In addition, the structure of the Al^{III} salt has also been determined for comparison. There have been only a few reports of crystal-structure determinations of organometallic compounds that contain both aluminium and oxygen and which involve relatively simple organic ligands (Hon & Pfluger, 1973; McClelland, 1975; Taylor, 1978; Boardman, Small & Worall, 1983; Simonsen & Bechtel, 1980; Bulc, Golic & Siftar, 1976, 1982; Mooy, Krieger, Heijdenrijk & Stam, 1974). All of these reported compounds have the organic ligand hexacoordinated to Al^{III} and were similar to the expected compounds of Cr^{III} and Fe^{III}. In the hydroxymethanesulfonate salt of Al^{III}, however, the organic ligand is not coordinated to the metal.

Experimental. A crystalline sample of the Mg^{II} salt (I) was prepared by routine methods, but the preparation of the Al^{III} salt (II) proved more difficult. A single large crystal (0·5 × 0·5 × 1·5 cm) of the

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aluminium salt was eventually prepared by bubbling SO_2 into an aqueous solution of CH_2O. This solution was warmed to drive off excess SO_2 and then aged $Al(OH)_3$ was stirred into it until no more would dissolve. The product was a white powder, soluble in water. Multiple recrystallizations, in a desiccator, of solutions of the powder produced one crystal on one occasion only. Though there were many subsequent attempts to repeat the recrystallization, none were successful even when seeded with a fragment of the one crystal.

For both salts, Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 reflections with $\theta = 10–14°$. ω–2θ scans, ω-scan width $(1·0 + 0·35\tan\theta)°$ at $1·0–3·3° \text{min}^{-1}$, extended 25% on each side for background measurement, three standard reflections showed negligible variation in intensity, intensities reduced to a standard scale (Cameron & Cordes, 1979), Lp corrections applied, no corrections for absorption. The structures were solved by Patterson methods from which the S- and metal-atom positions were obtained. The remaining non-H atoms were located from subsequent difference-Fourier syntheses. Scattering factors for neutral atoms were those recorded in *International Tables for X-ray Crystallography* (1974) and were corrected for the real part of anomalous dispersion. Computer programs used were *SHELX76* (Sheldrick, 1976) for (I), *CRYSTALS* (Carruthers & Watkin, 1979) for (II) and *CHEMGRAF* (Davies, 1983).

(I): Crystal dimensions $0·20 \times 0·25 \times 0·30$ mm, intensities for $\theta < 23°$; *hkl*: -12 to 12, 0 to 9, 0 to 25; 3654 reflections measured, 3102 unique ($R_{\text{int}} = 0·036$) and 2382 considered observed with $I > 3\sigma(I)$. All H-atom positions were determined from a difference-Fourier synthesis and allowed to refine. The H-atom positions on two of the water molecules were constrained to prevent unreasonable geometry. Anisotropic refinement (on F) of the non-H atoms and isotropic refinement of the H atoms employed a 3-block-matrix least-squares method, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0·019|F_o|^2]^{-1}$. The refinement converged at $R = 0·039$, $wR = 0·040$ for 2364 observed reflections, 237 parameters, 18 reflections omitted because of suspected extinction, $(\Delta/\sigma)_{\max} = 0·6$, max. and min. heights in the final difference-Fourier map = 0·71 and $-0·73$ e Å^{-3}, no correction for extinction.

(II): Crystal diffracts poorly, large cube (edge ~0·35 mm) was cut from the one original crystal (see above). Care was taken to ensure that the large crystal was completely bathed in the X-ray beam. The analysis of the original data lasted many months. When the structure had been solved, an attempt was made to secure additional data, but although the crystal did not decompose noticeably during the data collection, it was found that, in the interval, both the crystal fragment that had been irradiated and the remnant of the original crystal had turned to powder. All efforts to prepare additional crystals of the compound have been unsuccessful with powders resulting from every attempt.

Intensities for $\theta < 23°$; *hkl*: -11 to 11, 0 to 24, 0 to 15; 5651 reflections measured, 4850 unique ($R_{\text{int}} = 0·066$) and 1170 considered observed with $I > 2\sigma(I)$. Only the methylene and hydroxyl H-atom positions could be determined from a difference-Fourier synthesis. These atoms were placed and only allowed to ride on the atoms to which they were bonded. It was not possible to locate any of the H atoms belonging to the water molecules, probably the result of a paucity of observed data. Only 24% of the reflections had $I > 2\sigma(I)$, 88% for the magnesium compound. Anisotropic refinement of the non-H atoms and refinement of individual isotropic temperature factors on the H atoms used a 3-block-matrix least-squares method and converged at $R = 0·080$, $wR = 0·083$, weight = $[\sigma^2(F_o)]^{-1}$, for 1170 unique observed reflections, 490 parameters; $(\Delta/\sigma)_{\max} = 0·2$; max. peak height in the final difference-Fourier map = 0·84 e Å^{-3}, no correction for extinction. The same atomic positions gave $R = 0·099$ for 1739 reflections with $I > \sigma(I)$. The final R value is high; this is probably caused in part by the poor quality of the data ($R_{\text{int}} = 0·066$) and also by the fact that the water H atoms (4·9% of total scattering material) have not been located or taken into account. The parameters quoted for this compound must therefore be treated with caution. The results are included for completeness to record, at least, the gross structural details of the compound and the ligand environment of the Al^{3+}.

Discussion. Atomic positional parameters are listed in Table 1 for (I) and Table 2 for (II). Selected bond lengths for both complexes are given in Table 3.* The magnesium salt contains one and a half unique molecular units, with one of the Mg atoms at a centre of inversion, which gives the formula $[Mg(H_2O)_4(HOCH_2SO_3)_2]$. Four water molecules and an O atom from each of the —SO_3 groups form a regular octahedron about the Mg^{2+}. The Mg—O bond lengths (Table 2) are similar for all ligands. The molecules making up the asymmetric unit are shown in Fig. 1. There is an extensive hydrogen-bonding network linking the molecules. Table 4 lists the H···O contacts. With the exception of the O atoms bonding the sulfonate ligands to Mg, all O atoms in the salt

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* Lists of anisotropic thermal parameters, H-atom positions, interatomic distances, bond angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52217 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters and equivalent isotropic thermal parameters* (Å^2) *for* (I) *with e.s.d.'s in parentheses*

$U_{eq} = (U_1U_2U_3)^{1/3}$.

	x	y	z	U_{eq}
Mg(1)	0·17298 (6)	0·51563 (10)	0·33551 (3)	0·0212
Mg(2)	0·5	0·0	0·5	0·0208
O(11)	0·0255 (2)	0·5594 (3)	0·27462 (8)	0·0355
O(12)	0·3200 (1)	0·4818 (2)	0·4026 (1)	0·0418
O(13)	0·2349 (2)	0·3088 (2)	0·2838 (1)	0·0380
O(14)	0·1181 (2)	0·7254 (2)	0·38614 (9)	0·0342
O(15)	0·5478 (2)	0·2487 (2)	0·4693 (1)	0·0424
O(16)	0·3589 (2)	−0·0074 (3)	0·43273 (8)	0·0384
S(1)	0·30229 (5)	0·83457 (6)	0·25613 (3)	0·0196
O(21)	0·2893 (2)	0·6621 (2)	0·283428 (9)	0·0322
O(22)	0·1966 (1)	0·8811 (3)	0·2152 (1)	0·0414
O(23)	0·3341 (2)	0·9660 (2)	0·30268 (9)	0·0335
O(24)	0·4100 (2)	0·7151 (2)	0·15576 (9)	0·0345
C(1)	0·4359 (2)	0·8172 (3)	0·2085 (1)	0·0253
S(2)	0·03286 (5)	0·18315 (6)	0·40650 (2)	0·0187
O(31)	0·0604 (2)	0·3592 (2)	0·38721 (9)	0·0316
O(32)	0·0263 (2)	0·0599 (2)	0·35535 (8)	0·0323
O(33)	0·1176 (7)	0·1259 (2)	0·45788 (8)	0·0323
O(34)	−0·1286 (2)	0·2974 (2)	0·4867 (1)	0·0435
C(2)	−0·1217 (2)	0·1903 (3)	0·4355 (1)	0·0307
S(3)	0·36072 (5)	0·22567 (8)	0·60975 (3)	0·0222
O(41)	0·3723 (1)	0·0973 (2)	0·55989 (8)	0·0266
O(42)	0·3637 (2)	0·1438 (3)	0·67084 (9)	0·0378
O(43)	0·4469 (1)	0·3672 (3)	0·6044 (1)	0·0520
O(44)	0·1859 (2)	0·3793 (2)	0·5403 (1)	0·0477
C(3)	0·2058 (2)	0·3101 (3)	0·6003 (1)	0·0334

are involved in hydrogen bonds to O atoms in adjacent molecules. This results in a complex three-dimensional network of hydrogen bonding.

The structure of the aluminium salt contains six unique hydroxymethanesulfonate anions and three unique Al^{3+} cations (two of these are at centres of inversion), giving the formula $[\mathrm{Al(H_2O)_6}].(\mathrm{HOCH_2SO_3})_3.(\mathrm{Al_{1/2}.Al_{1/2}})(\mathrm{H_2O})_6(\mathrm{HOCH_2SO_3})_3$. As shown in Fig. 2, all three of the Al^{3+} ions are surrounded by a regular octahedron of O atoms from the six water molecules, with discrete anions packing around the cations. As with the magnesium salt there appears to be an extensive hydrogen-bonding network. Table 5 lists the O···O contact distances, all of which are in the range 2·53–2·85 Å. From these distances each of the sulfonate O atoms appears to be hydrogen bonded to one water O atom and each of the hydroxyl O atoms is hydrogen bonded to one water O atom and also to another sulfonate group. Each water O atom also appears to be involved in at least two hydrogen bonds. The structure of the aluminium salt bears some similarity to the structure of the chloride (El Saffar & Malcahy, 1971) and the nitrate (Herpin & Sundarsanan, 1965) where the cation is surrounded by a regular octahedron of water molecules, but differs from the oxalate (Taylor, 1978) and acetylacetone (Hon & Pfluger, 1973; McClelland, 1975) where the Al^{3+} ion is coordinated to the strongly chelating ligands.

The structures of the series of hydroxymethanesulfonate salts (Owen, 1982) from Li^+–Cs^+, Mg^{2+}–Ba^{2+} and Al^{3+} have now been completed. All of these salts were crystallized from an aqueous

Table 2. *Atomic positional parameters and equivalent isotropic thermal parameters* (Å^2) *for* (II) *with e.s.d.'s in parentheses*

Atom *W* refers to the O atom of water ligands.

$U_{eq} = (U_1U_2U_3)^{1/3}$.

	x	y	z	U_{eq}
Al(1)	0·5123 (7)	0·2548 (3)	−0·0249 (5)	0·0360
Al(2)	0·5	0·5	0·5	0·0148
Al(3)	0·0	0·5	0·0	0·0260
S(1)	0·4321 (6)	0·1990 (3)	0·6201 (5)	0·0390
S(2)	0·4223 (6)	0·4389 (3)	0·1417 (5)	0·0379
S(3)	0·5928 (5)	0·3131 (3)	0·3392 (4)	0·0286
S(4)	0·7814 (6)	0·0973 (3)	0·2743 (4)	0·0335
S(5)	0·4181 (6)	−0·0508 (3)	0·1451 (5)	0·0364
S(6)	0·3164 (6)	0·1497 (3)	0·2573 (5)	0·0377
O(11)	0·393 (2)	0·1396 (10)	0·628 (1)	0·0520
O(12)	0·379 (2)	0·2273 (8)	0·537 (1)	0·0396
O(13)	0·411 (2)	0·2334 (9)	0·703 (1)	0·0298
C(11)	0·597 (2)	0·2982 (14)	0·610 (2)	0·0373
O(14)	0·620 (2)	0·1695 (10)	0·521 (1)	0·0441
O(21)	0·367 (2)	0·4858 (7)	0·079 (1)	0·0313
O(22)	0·412 (2)	0·4533 (8)	0·239 (1)	0·0452
O(23)	0·372 (1)	0·3802 (7)	0·115 (1)	0·0115
C(21)	0·588 (2)	0·4398 (13)	0·120 (2)	0·0208
O(24)	0·608 (2)	0·4209 (7)	0·030 (2)	0·0361
O(31)	0·603 (2)	0·3007 (10)	0·242 (1)	0·0510
O(32)	0·644 (2)	0·3696 (9)	0·363 (1)	0·0458
O(33)	0·641 (2)	0·2679 (9)	0·399 (1)	0·0452
C(31)	0·428 (3)	0·3174 (14)	0·360 (2)	0·0322
O(34)	0·409 (1)	0·3541 (8)	0·453 (1)	0·0318
O(41)	0·787 (2)	0·0494 (9)	0·208 (2)	0·0451
O(42)	0·906 (2)	0·1246 (10)	0·291 (2)	0·0636
O(43)	0·727 (2)	0·0814 (10)	0·357 (1)	0·0511
C(41)	0·686 (2)	0·1554 (12)	0·227 (2)	0·0187
O(44)	0·739 (2)	0·1766 (8)	0·149 (2)	0·0452
O(51)	0·369 (1)	−0·1132 (7)	0·144 (1)	0·0231
O(52)	0·412 (2)	−0·0233 (11)	0·237 (2)	0·0111
O(53)	0·359 (2)	−0·0123 (8)	0·072 (2)	0·0424
C(51)	0·579 (2)	−0·0598 (14)	0·119 (2)	0·0320
O(54)	0·599 (2)	−0·0854 (8)	0·036 (1)	0·0465
O(61)	0·256 (2)	0·2032 (9)	0·288 (2)	0·0556
O(62)	0·406 (2)	0·1262 (9)	0·323 (1)	0·0424
O(63)	0·370 (2)	0·1588 (9)	0·165 (1)	0·0482
C(61)	0·194 (3)	0·0945 (10)	0·247 (2)	0·0319
O(64)	0·103 (1)	0·1176 (9)	0·182 (1)	0·0257
W(11)	0·550 (1)	0·2585 (7)	−0·148 (1)	0·0184
W(12)	0·472 (1)	0·2523 (8)	0·103 (1)	0·0344
W(13)	0·381 (1)	0·2019 (7)	−0·046 (1)	0·0275
W(14)	0·641 (1)	0·3067 (7)	0·004 (1)	0·0289
W(15)	0·616 (1)	0·1887 (8)	−0·010 (1)	0·0335
W(16)	0·405 (1)	0·3219 (8)	−0·040 (1)	0·0336
W(21)	0·530 (2)	0·5003 (9)	0·373 (1)	0·0392
W(22)	0·641 (1)	0·5509 (9)	0·525 (1)	0·0354
W(23)	0·607 (2)	0·4339 (7)	0·516 (1)	0·0389
W(31)	−0·054 (2)	0·5033 (8)	0·123 (1)	0·0367
W(32)	−0·101 (1)	0·4321 (7)	−0·017 (1)	0·0267
W(33)	−0·134 (2)	0·5491 (8)	−0·039 (1)	0·0348

Table 3. *Selected bond lengths* (Å) *for* (I) *and* (II) *with e.s.d.'s in parentheses*

(*a*) Compound (I)			
Mg(1)—O(11)	2·036 (2)	Mg(1)—O(31)*	2·054 (2)
Mg(1)—O(12)	2·106 (2)	Mg(2)—O(15)	2·098 (2)
Mg(1)—O(13)	2·065 (2)	Mg(2)—O(16)	2·048 (2)
Mg(1)—O(14)	2·046 (2)	Mg(2)—O(41)*	2·047 (2)
Mg(1)—O(21)*	2·041 (2)		
(*b*) Compound (II)†			
Al(1)—*W*(11)	1·835 (15)	Al(2)—*W*(21)	1·87 (2)
Al(1)—*W*(12)	1·91 (2)	Al(2)—*W*(22)	1·935 (15)
Al(1)—*W*(13)	1·87 (2)	Al(2)—*W*(23)	1·89 (2)
Al(1)—*W*(14)	1·86 (2)	Al(3)—*W*(31)	1·887 (15)
Al(1)—*W*(15)	1·88 (2)	Al(3)—*W*(32)	1·893 (15)
Al(1)—*W*(16)	1·91 (2)	Al(3)—*W*(33)	1·897 (15)

* O atom from hydroxymethanesulfonate ligand.

† Atom *W* refers to the O atom of water ligands.

medium, but only the Mg^{2+} and Al^{3+} salts described above are heavily hydrated. Both forms of the Na^+ salt and the Ca^{2+}, Sr^{2+} and Ba^{2+} salts contain only a single water molecule in the asymmetric unit. The remaining salts of this series are anhydrous. Clearly, then, the structures of the Mg^{2+} and Al^{3+} salts fall in a separate category from the others and are themselves structurally similar.

In biological systems, replacement of essential metals in complexes by other foreign metals can seriously affect the function of that complex in the organism. The above results suggest that Al^{3+} may be able to replace Mg^{2+} in some aqueous organic ligand systems without too much disruption of the structure.

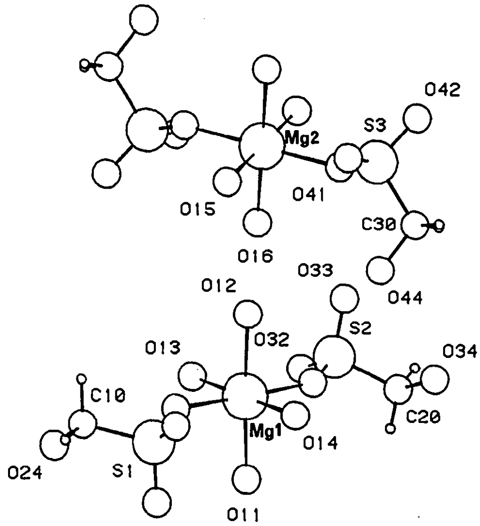

Fig. 1. The two independent molecules of (I). Mg(2) is on a centre of inversion.

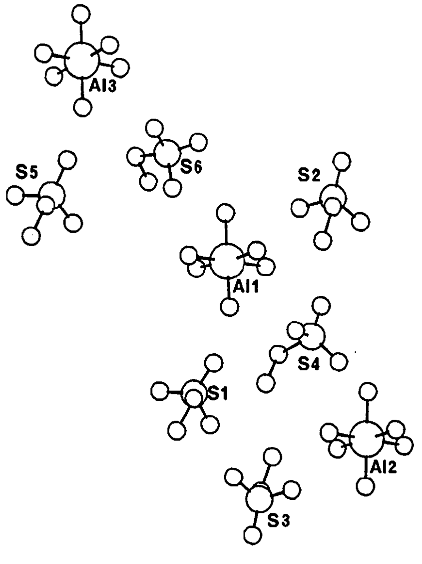

Fig. 2. The three independent cations and six independent anions of the asymmetric unit of (II). Al(2) and Al(3) are on centres of inversion.

Table 4. *Hydrogen-bonding* H···O *contact distances* (Å) *for* (I)

The H atoms are numbered so that the first two digits correspond to the numbering of the O atoms to which they are bonded, *e.g.* O(11) is bonded to H(111) and H(112).

Contact	Distance	Symmetry position of O atom		
H(111)···O(22)	1·91	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
H(112)···O(32)	2·31	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
H(121)···O(43)	1·96	$1-x$,	$1-y$,	$-z$
H(131)···O(23)	2·10	x,	$1+y$,	z
H(132)···O(42)	1·99	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
H(141)···O(32)	1·94	x,	$-1+y$,	z
H(151)···O(24)	1·80	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
H(152)···O(34)	2·49	$-1+x$,	y,	z
H(161)···O(33)	2·01	x,	y,	z
H(162)···O(23)	2·10	x,	$1+y$,	z
H(24)···O(42)	1·96	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
H(34)···O(44)	1·82	$-x$,	$1-y$,	$1-z$
H(44)···O(33)	1·83	x,	y,	z

Table 5. *Hydrogen-bonding* O···O *contact distances* (Å) *for* (II)

Atom *W* refers to the O atom of water ligands.

Contact	Distance	Symmetry position of second O atom		
O(11)···*W*(32)	2·65	$\frac{1}{2}+x$,	$\frac{1}{2}+y$,	$\frac{1}{2}+z$
O(12)···*W*(14)	2·71	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(12)···O(34)	2·72	x,	y,	z
O(13)···*W*(11)	2·65	x,	y,	$1+z$
O(13)···O(44)	2·85	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(14)···*W*(33)	2·73	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
O(14)···O(33)	2·85	x,	y,	z
O(21)···*W*(33)	2·69	$-x$,	$1-y$,	$-z$
O(21)···O(24)	2·64	$1-x$,	$1-y$,	$-z$
O(22)···*W*(21)	2·53	x,	y,	z
O(23)···*W*(16)	2·63	x,	y,	z
O(24)···*W*(14)	2·62	x,	y,	z
O(31)···*W*(12)	2·65	x,	y,	z
O(32)···*W*(23)	2·69	x,	y,	z
O(33)···*W*(13)	2·79	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(34)···*W*(22)	2·67	$1-x$,	$1-y$,	$1-z$
O(41)···*W*(21)	2·57	$1\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
O(42)···*W*(16)	2·72	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(42)···O(64)	2·69	$1+x$,	y,	z
O(43)···*W*(31)	2·59	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
O(44)···*W*(15)	2·63	x,	y,	z
O(51)···*W*(15)	2·58	$1-x$,	$-y$,	$-z$
O(52)···*W*(31)	2·58	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
O(53)···*W*(22)	2·59	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
O(53)···O(54)	2·74	$1-x$,	$-y$,	$-z$
O(54)···*W*(13)	2·63	$1-x$,	$-y$,	$-z$
O(61)···*W*(11)	2·59	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(62)···*W*(32)	2·66	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
O(63)···*W*(12)	2·55	x,	y,	z
O(64)···*W*(23)	2·66	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$

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Bis-μ-[methylenebis(diphenylphosphine)]-dinitratodisilver(I) Dichloroform Solvate

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Abstract. $[Ag_2(NO_3)_2(C_{25}H_{22}P_2)_2].2CHCl_3$, $[Ag(NO_3)(Ph_2PCH_2PPh_2)]_2.2CHCl_3$, $M_r = 1347{\cdot}2$, triclinic, $P\bar{1}$, $a = 11{\cdot}232\,(1)$, $b = 12{\cdot}085\,(1)$, $c = 10{\cdot}844\,(1)$ Å, $\alpha = 98{\cdot}81\,(1)$, $\beta = 100{\cdot}06\,(1)$, $\gamma = 88{\cdot}19\,(1)°$, $V = 1432\,(1)$ Å^3, $D_x = 1{\cdot}562$ Mg m^{-3} for $Z = 1$ (dimer), Mo $K\bar{\alpha}$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}065$ mm^{-1}, $F(000) = 676$, $T = 295\,(2)$ K, $R = 0{\cdot}028$ for 5133 observed reflections. The title compound exists as a centrosymmetric dimer in which two diphosphine ligands bridge two Ag atoms thereby forming an eight-membered ring. The ring adopts a staggered conformation with significant bending at the Ag atoms; Ag—P 2·452 (1) and 2·422 (1) Å, P—Ag—P 149·4 (1)°. The two nitrate anions each weakly chelate an Ag atom with Ag—O bond distances of 2·659 (3) and 2·652 (3) Å so that the Ag atoms are tetracoordinated.

Introduction. There are several studies in the literature concerning the interaction of silver(I) salts with the diphosphine bis(diphenylphosphine)methane (hereafter dppm) (Dean, Vittal & Srivastava, 1987; Obendorf, Probst, Peringer, Falk & Müller, 1988). Crystal structures are available for the 1:1 (*i.e.* 1 Ag : 1 dppm) complexes $[Ag_2(dppm)_2(NO_3)_2]$, $[Ag_4(dppm)_4(NO_3)_2][PF_6]_2$ (Ho & Bau, 1983) and $[Ag_3(dppm)_3Br_2]Br$ (Schubert, Neugebauer & Aly, 1980). A recent report of the chloro analogue of the latter compound has also appeared, namely $[Ag_3(dppm)_3Cl_2][Ph_2Sn(NO_3)_2Cl]$ (Franzoni, Pelizzi, Predieri, Tarasconi, Vitali & Pelizzi, 1989). In the dinuclear structure of $[Ag_2(dppm)_2(NO_3)_2]$, the P—Ag—P angles were found to be non-linear [138·3 (1)°] such that the eight-membered ring adopted the unusual conformation in which the two methylene C atoms were eclipsed (Ho & Bau, 1983). In the tetranuclear species $[Ag_4(dppm)_4(NO_3)_2][PF_6]_2$, which arises as a result of bridging nitrate groups, the two $[Ag_2(dppm)_2]$ units were also found to adopt the less usual conformation (Ho & Bau, 1983). A third structural type is found in the trinuclear cations $[Ag_3(dppm)_3Br_2]^+$ and $[Ag_3(dppm)_3Cl_2]^+$ in which each edge of a triangle of Ag atoms is bridged by a dppm ligand; the two coordinated halide atoms each cap a triangular face leading to a coordination polyhedron based on a trigonal bipyramid (Schubert *et al.*, 1980; Franzoni *et al.*, 1989). This communication reports the crystallographic characterization of a second isomer of $[Ag_2(dppm)_2(NO_3)_2]$ isolated as its chloroform solvate in which the $[Ag_2(dppm)_2]$ units are found to adopt the more usual staggered conformation.

Experimental. The title compound was prepared by mixing equimolar quantities of $AgNO_3$ (Johnson Matthey) and dppm (Strem) in aqueous ethanol. The resultant precipitate was recrystallized from a chloroform/373–393 K petroleum spirit solution at room temperature. Crystals were obtained as a $CHCl_3$ solvate and were found to be stable to light but decomposed on exposure to air presumably as a result of solvent loss. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; $\omega{:}2\theta$ scan technique. Cell parameters on crystal 0·34 ×

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