de direction moyenne parallèle à **c** (Fig. 2), lesquels sont reliés *via* les atomes d'oxygène O(3) et O(4) par les molécules d'eau pour former des couches de plan moyen parallèle à *bc* (Fig. 1). Ces couches sont alternativement reliées entre elles par ces mêmes molécules d'eau au moyen de liaisons hydrogène et par les atomes de plomb (Fig. 1).

Toutes les liaisons hydrogène sont intermoléculaires. La molécule d'eau joue un rôle très important dans la cohésion de la structure. Chacun de ses atomes d'hydrogène, H(1*W*) et H(2*W*), échange une liaison hydrogène assez lâche [O(*W*)···O(4) = 2,799 (8) Å et O(*W*)···O(C1^{ii}) = 2,860 (8) Å] avec respectivement O(4) et O(C1^{ii}), tandis que l'atome d'oxygène O(*W*), en coordination tétraédrique, échange deux liaisons hydrogène plus courtes [O(*W*)···O(3) = 2,708 (8) Å et O(*W*)···O(6^{iii}) = 2,652 (8) Å] avec respectivement H(O3) et H(O6^{iii}). La molécule d'eau est donc liée à quatre anions $HEDP^{2-}$ par liaison monodentée. Réciproquement chaque coordinat $HEDP^{2-}$ est relié à quatre molécules d'eau.

En définitive, cette structure est constituée de feuillets bidimensionnels parallèles au plan *bc* selon la séquence: $\cdots$—$(HEDP)_\infty$—$(Pb)_\infty$—$(HEDP)_\infty$—$(H_2O)_\infty$—$(HEDP)_\infty$—$(Pb)_\infty$—$\cdots$.

La conformation des anions $HEDP^{2-}$ est telle que les groupes PO_3 sont en position éclipsée et qu'ils admettent un pseudo plan de symétrie défini par C(1), C(2) et O(C1). Pour chaque PO_3 on relève deux liaisons P—O courtes [1,506 (5) et 1,507 (2) Å pour P(1); 1,499 (5) et 1,513 (5) Å pour P(2)] dont les atomes d'oxygène [O(1) et O(2), O(4) et O(5)] sont accepteurs de liaison hydrogène et (ou) entrent dans le polyèdre de coordination du plomb et une liaison longue [P(1)—O(3) = 1,570 (5) Å; P(2)—O(6) = 1,581 (5) Å] concernant les atomes d'oxygène de groupements hydroxyles. Il en résulte que chaque groupe phosphonate conserve un proton conférant dans le cas présent à l'acide hydroxyéthylidènediphosphonique un comportement de diacide, alors que dans le cas de la structure de $[Rb\{C(CH_3)(OH)(P_2O_6H_3)\}].2H_2O$ (Charpin, Lance, Nierlich, Vigner, Lee, Silvestre et Nguyen Quy Dao, 1988) il avait été observé un comportement de monoacide.

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Structure of μ-Iodo-bis[μ-tetraethyl diphosphonate(III)]-bis[tricarbonylmanganese(I)] Triiodide

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Abstract. $[Mn_2I(CO)_6(C_8H_{20}O_5P_2)_2]I_3$, $M_r = 1301{\cdot}94$, orthorhombic, $P2_12_12_1$, $a = 18{\cdot}027$ (4), $b = 17{\cdot}788$ (4), $c = 13{\cdot}657$ (3) Å, $V = 4379$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}975$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0{\cdot}71073$ Å), $\mu = 3{\cdot}54$ mm^{-1}, $F(000) = 2488$, $T = 291$ K, final $R = 0{\cdot}049$ for 2613 observed reflections and 433 variables. The complex cation consists of two *fac*-$Mn(CO)_3$ moieties bridged by the I atom and by the two phosphite ligands to give an *A*-type structure. The Mn—I, Mn—C and Mn—P distances are 2·688–2·678 (3), 1·79–1·92 (2) and 2·262–2·279 (6) Å respectively, and Mn—I—Mn is 114·4 (1)°.

Introduction. The determination of the structure of the present compound, whose preparation has already been described (Riera, Ruiz, Tiripicchio & Tiripicchio Camellini, 1986), was carried out to confirm the stereochemistry of the complex cation. The spectroscopic data, especially those from infrared

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spectroscopy (C—O stretching vibrations, ν_{CO}), suggested an *A*-type structure such as that shown in the Fig. 1 (the three bridges are placed in a face of the octahedron around each Mn atom), as has finally been confirmed by the present X-ray diffraction study. However, the above IR spectroscopic data did not totally exclude the possibility of a *B*-type structure (in which both P atoms on each manganese are mutually *trans*) (see Fig. 1).

Experimental. A crystal of about 0·1 × 0·1 × 0·1 mm was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12°$) and refined by least-squares method. Intensities were collected, using the Ω–2θ scan technique, up to $\theta = 25°$ in the *hkl* range from (0,0,0) to (21,20,16). Three reflections were measured every two hours as orientation and intensity control, no significant intensity decay was observed. 4321 reflections were measured, 2613 of which were assumed as observed applying the condition $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied.

The structure was solved locating all the I and Mn atoms, and three of the four P atoms, with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); the other atoms were found by Fourier synthesis with *SHELX*76 (Sheldrick, 1976).

The structure was refined by full-matrix least squares, using *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0{\cdot}00035|F_o|^2]^{-1}$.

All non-H atoms, except C(85), were anisotropically refined. Due to a disorder problem, C(85) was isotropically refined in two sites, C(85*A*) and C(85*B*), with occupation factor 0·5. Only the H atoms of CH_2 groups, except for C(8), were included in the refinement in their geometrical positions with overall isotropic temperature factor (final value $U = 0{\cdot}15$).

The final *R* was 0·049 ($wR = 0{\cdot}047$). Maximum shift/e.s.d. was 0·157 for U_{22} of C(3). The final difference Fourier map showed a residual electron density between −1·31 and 0·68 e Å^{-3}. The values of *f*, *f*′ and *f*″ were taken from *International Tables for X-ray Crystallography* (1974).

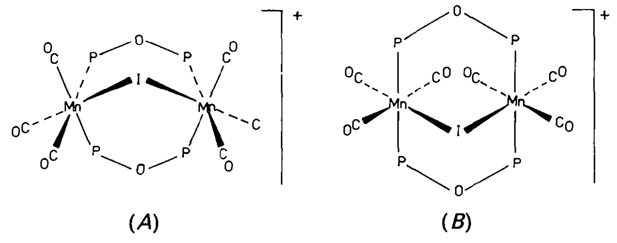

Fig. 1. Possible *'a priori'* structures of the complex cation.

Table 1. *Fractional positional and thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq} (Å^2 × 10^2)
I2	0·30599 (10)	0·89674 (10)	0·66698 (14)	7·84 (7)
I3	0·21658 (9)	0·87300 (9)	0·84368 (13)	6·87 (6)
I4	0·12307 (11)	0·85066 (12)	1·01724 (16)	9·42 (8)
I1	0·30534 (7)	0·55305 (7)	0·48026 (10)	4·24 (4)
Mn1	0·37315 (17)	0·43146 (16)	0·40510 (22)	3·74 (10)
Mn2	0·39801 (16)	0·66011 (17)	0·54385 (22)	3·70 (10)
P1	0·4287 (3)	0·4184 (3)	0·5540 (4)	4·00 (18)
P2	0·4792 (3)	0·4846 (3)	0·3499 (5)	4·23 (20)
P3	0·4708 (3)	0·5762 (3)	0·6253 (4)	3·83 (19)
P4	0·4625 (3)	0·6484 (3)	0·4025 (4)	4·28 (22)
O10	0·4784 (7)	0·4899 (7)	0·5885 (9)	3·8 (5)
O20	0·5045 (7)	0·5686 (7)	0·3785 (10)	5·0 (5)
O1	0·4858 (7)	0·3518 (7)	0·5559 (11)	5·5 (6)
O2	0·3807 (7)	0·4093 (8)	0·6523 (10)	5·6 (5)
O3	0·4806 (11)	0·4899 (11)	0·2326 (12)	9·1 (9)
O4	0·5504 (7)	0·4409 (8)	0·3787 (12)	6·3 (6)
O5	0·5529 (7)	0·5999 (8)	0·6242 (11)	5·3 (5)
O6	0·4447 (8)	0·5690 (8)	0·7372 (10)	5·3 (5)
O7	0·5260 (7)	0·7039 (8)	0·3855 (13)	6·6 (6)
O8	0·4113 (8)	0·6623 (9)	0·3101 (10)	6·1 (6)
C11	0·3283 (12)	0·4586 (12)	0·2824 (17)	5·1 (8)
O11	0·3000 (10)	0·4732 (10)	0·2136 (11)	8·1 (7)
C12	0·2896 (12)	0·3788 (12)	0·4373 (14)	4·4 (8)
O12	0·2373 (8)	0·3469 (10)	0·4522 (12)	7·2 (7)
C13	0·4133 (12)	0·3415 (13)	0·3598 (16)	5·3 (8)
O13	0·4367 (10)	0·2897 (9)	0·3245 (13)	7·8 (8)
C21	0·3402 (11)	0·7296 (12)	0·4792 (18)	5·0 (8)
O21	0·3064 (9)	0·7742 (9)	0·4365 (11)	7·3 (7)
C22	0·3358 (11)	0·6666 (11)	0·6530 (17)	4·2 (8)
O22	0·2991 (8)	0·6721 (8)	0·7190 (11)	6·1 (6)
C23	0·4580 (11)	0·7338 (13)	0·5843 (15)	4·4 (8)
O23	0·4945 (8)	0·7825 (9)	0·6136 (13)	7·1 (7)
C1	0·5365 (12)	0·3359 (13)	0·6386 (19)	7·1 (11)
C15	0·5676 (16)	0·2612 (14)	0·6253 (21)	9·5 (12)
C2	0·3253 (14)	0·3488 (16)	0·6758 (26)	10·5 (15)
C25	0·3196 (20)	0·3274 (18)	0·7699 (17)	10·9 (16)
C3	0·5290 (23)	0·478 (3)	0·1637 (27)	25 (4)
C35	0·5559 (23)	0·4312 (25)	0·1065 (27)	16·4 (22)
C4	0·6250 (14)	0·4659 (16)	0·3855 (25)	9·8 (13)
C45	0·6799 (18)	0·4048 (24)	0·3887 (28)	14·9 (19)
C5	0·6175 (12)	0·5612 (14)	0·6666 (18)	7·1 (10)
C55	0·6880 (14)	0·5992 (16)	0·6445 (22)	10·1 (12)
C6	0·4694 (16)	0·5188 (14)	0·8158 (17)	7·9 (12)
C65	0·4100 (18)	0·5150 (19)	0·8901 (24)	12·0 (16)
C7	0·5980 (13)	0·6999 (14)	0·4085 (25)	9·0 (13)
C75	0·6379 (15)	0·7780 (16)	0·4165 (26)	10·6 (15)
C8	0·4427 (16)	0·6708 (16)	0·2078 (19)	9·4 (12)
C85*A*	0·391 (3)	0·728 (4)	0·166 (5)	10·1 (19)
C85*B*	0·380 (3)	0·662 (4)	0·134 (5)	9·9 (20)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mn1—Mn2	4·509 (4)	Mn1—C11	1·923 (23)
I1—Mn1	2·688 (3)	Mn1—C12	1·828 (21)
I1—Mn2	2·678 (3)	Mn1—C13	1·862 (23)
Mn1—P1	2·279 (6)	Mn2—C21	1·842 (22)
Mn1—P2	2·262 (6)	Mn2—C22	1·869 (22)
Mn2—P3	2·278 (6)	Mn2—C23	1·787 (22)
Mn2—P4	2·263 (7)		

I2—I3—I4	178·3 (1)	C12—Mn1—C13	87·7 (10)
Mn1—I1—Mn2	114·4 (1)	I1—Mn2—P3	93·0 (2)
I1—Mn1—P1	86·6 (2)	I1—Mn2—P4	88·8 (2)
I1—Mn1—P2	100·1 (2)	I1—Mn2—C21	88·2 (7)
I1—Mn1—C11	86·6 (7)	I1—Mn2—C22	85·9 (6)
I1—Mn1—C12	86·9 (7)	I1—Mn2—C23	178·1 (7)
I1—Mn1—C13	174·3 (7)	P3—Mn2—P4	93·5 (2)
P1—Mn1—P2	88·2 (2)	P3—Mn2—C21	178·8 (7)
P1—Mn1—C11	171·3 (7)	P3—Mn2—C22	89·8 (7)
P1—Mn1—C12	95·5 (7)	P3—Mn2—C23	88·9 (7)
P1—Mn1—C13	92·2 (7)	P4—Mn2—C21	86·8 (8)
P2—Mn1—C11	87·7 (7)	P4—Mn2—C22	173·9 (7)
P2—Mn1—C12	172·3 (7)	P4—Mn2—C23	91·2 (7)
P2—Mn1—C13	85·4 (7)	C21—Mn2—C22	90·1 (9)
C11—Mn1—C12	89·5 (9)	C21—Mn2—C23	89·9 (10)
C11—Mn1—C13	95·1 (10)	C22—Mn2—C23	94·0 (10)

Final positional and thermal parameters, for non-H atoms, are given in Table 1.* A selection of the molecular geometry data is collected in Table 2. The geometry and the crystallographic numbering scheme of the cation complex is given in Fig. 2. The geometrical calculations were performed with *PARST* (Nardelli, 1983), and Fig. 2 was drawn with *PLUTO* (Motherwell, 1976).

Discussion. The complex cation consists of two *fac*-$Mn(CO)_3$ moieties bridged by the I atom and by the two tetraethyl diphosphonate (tedip) ligands in an *A*-type structure. Each metal displays a distorted octahedral coordination with three carbonyl groups and one iodine and two phosphorus in the remaining positions (see Fig. 2 and Table 2). Application of the EAN rule to the Mn atoms requires no direct *M*—*M* bond, which is an accord with the very long Mn(1)—Mn(2) distance, 4·509 (4) Å.

The bond lengths Mn(1)—I(1) 2·688 (3) Å, Mn(2)—I(1) 2·678 (3) Å, Mn—C(carbonyl) 1·787 (22)–1·923 (23) Å, and Mn—P 2·279 (6)–2·262 (6) Å, and the bond angle Mn(1)—I(1)—Mn(2) 114·4 (1)° are in the range expected, and show a good match with the results obtained for the closely related cationic complex $[Mn_2(\mu\text{-}I)(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)][BF_4]$ (Riera *et al.*, 1986). In this cation the bond lengths Mn—I are 2·689 (3) and 2·666 (2) Å, and the bond angle Mn—I—Mn is 113·9 (1)°. The distances Mn—P are 2·350 (4) and 2·361 (4) Å, and those between Mn and C(carbonyls) are in the range 1·78 (1)–1·87 (1) Å. All these values match satisfactorily with the results for our structure, given in Table 2.

In the literature there are no other cationic complexes of iodine-bridged dimanganese, except for those obtained by one of us (V. Riera and collaborators), but the structures of those complexes have not been determined by X-ray diffraction.

A neutral diiodine-bridged dimanganese complex, $[Mn_2(\mu\text{-}I)_2(CO)_6(\mu\text{-}P_2Ph_4)]$, has been studied by X-rays (Calderazzo, Poli, Vitali, Korp, Bernal, Pelizzi, Atwood & Hunter, 1983). In this compound the distances Mn—I are in the range 2·698 (2)–2·725 (2) Å, the distances Mn—P are 2·355 (3) and 2·369 (3) Å and the distances Mn—C are in the range 1·77 (1)–1·83 (1) Å. Some of these bond lengths are slightly longer with respect to those in the present structure, which could be due to the cationic character of our complex. However, the differences in the Mn—I—Mn angles are considerable [90·26 (5)° and 90·84 (5)° in the neutral complex].

Binuclear cationic iodine-bridged complexes are known for other metals, for instance [(μ-iodo)-bis-[dicarbonyl-η-cyclopentadienyliron(I)] tetrafluoroborate(III), with an Fe—I—Fe angle of 110·8 (1)° (Cotton, Frenz & White, 1973). These authors point out that 'presumably the tendency of the bridging I atoms would be to form bonds at or near an angle of 90° so as to optimize the employment of its *p* orbitals,' and they attribute the greater magnitude of the angle to steric demands. Our complex would be another example of this type.

The triiodide anion shows the expected linear arrangement, I2—I3—I4 angle 178·3 (1)°.

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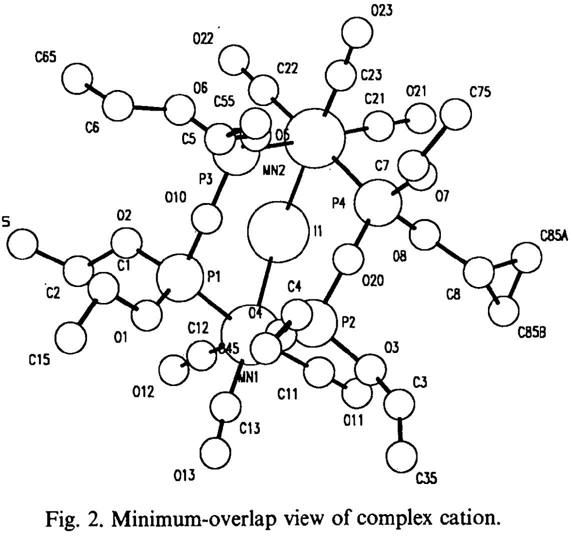

Fig. 2. Minimum-overlap view of complex cation.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52554 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.