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catena-Bis(phosphinato)(2,2'-bipyridyl)manganese(II)

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Abstract. $C_{10}H_{12}MnN_2O_4P_2$, $C2/c$; $a = 16.827$ (15), $b = 10.745$ (20), $c = 7.170$ (5) Å, $\beta = 91.46$ (3)°, $Z = 4$, $D_x = 1.75$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 105.3$ cm⁻¹. The crystal contains chains along *c*. Each six-coordinate Mn atom is bonded to a bipyridyl ligand and is linked through two bridging phosphinate groups to each of the Mn atoms related to it by the *c* glide.

Introduction. The title compound was studied during an investigation of the structural role of the phosphinate anion, $H_2PO_2^-$, in a number of salts. It was obtained by the method of Sala-Pala, Kergoat & Everchais (1972) as yellow laths elongated along *c*. Equi-inclination multifilm Weissenberg photographs of the levels $h0-l$ and $hk0-6$ were recorded from two crystals each $0.1 \times 0.2 \times 0.5$ mm, and were scanned by the SRC Microdensitometer Service, Rutherford Laboratory. The systematic absences indicated the space group *Cc* or *C2/c*. The intensities were corrected for absorption. The structure was solved by the heavy-atom method. Refinement was initiated in space group *Cc*, and was continued in *C2/c* after the diad axis had become apparent. A difference synthesis at $R = 0.065$ showed

Table 2. Interatomic distances (Å) and angles (°)

Mn—O(1)	2.170 (4)	N—C(5)	1.334 (7)
Mn—O(2 ^l)	2.140 (4)	C(1)—C(2)	1.404 (7)
Mn—N	2.311 (4)	C(2)—C(3)	1.378 (8)
P—O(1)	1.494 (4)	C(3)—C(4)	1.370 (8)
P—O(2)	1.489 (4)	C(4)—C(5)	1.384 (8)
N—C(1)	1.342 (7)	C(1)—C(1 ⁱⁱ)	1.497 (10)
O(1)—Mn—O(2 ^l)	90.2 (2)	Mn—N—C(5)	123.1 (4)
O(1)—Mn—O(1 ⁱⁱ)	175.4 (2)	C(1)—N—C(5)	118.3 (5)
C(2 ⁱⁱⁱ)—Mn—O(2 ⁱⁱⁱ)	107.3 (2)	N—C(1)—C(2)	122.0 (5)
O(1)—Mn—N	87.2 (2)	C(1)—C(2)—C(3)	118.1 (5)
O(2 ^l)—Mn—N	90.9 (2)	C(2)—C(3)—C(4)	120.0 (5)
N—Mn—N ⁱⁱ	70.8 (2)	C(3)—C(4)—C(5)	118.4 (5)
O(2 ⁱⁱⁱ)—Mn—N	161.6 (2)	C(4)—C(5)—N	123.1 (5)
O(1)—P—O(2)	119.5 (2)	N—C(1)—C(1 ⁱⁱ)	116.1 (5)
Mn—N—C(1)	118.6 (4)	C(2)—C(1)—C(1 ⁱⁱ)	122.0 (5)

Distances between atoms in adjacent chains

P—C(2^{iv}) 3.77 (1) O(1)—C(2^{iv}) 3.37 (1) C(1)—C(2^{iv}) 3.47 (1)

Symmetry code

(i) $x, -y, \frac{1}{2} + z$
 (ii) $-x, y, \frac{1}{2} - z$

(iii) $-x, -y, -z$
 (iv) $x, 1 - y, \frac{1}{2} + z$

Table 1. Atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0	1536 (1)	2500
P	1037 (1)	993 (1)	-1349 (2)
O(1)	367 (2)	1606 (4)	-377 (6)
O(2)	988 (2)	-357 (3)	-1803 (7)
N	770 (3)	3290 (4)	3012 (6)
C(1)	430 (3)	4412 (5)	2798 (7)
C(2)	849 (3)	5520 (5)	3156 (8)
C(3)	1643 (3)	5435 (6)	3655 (9)
C(4)	1996 (3)	4291 (5)	3847 (9)
C(5)	1536 (3)	3241 (6)	3530 (8)

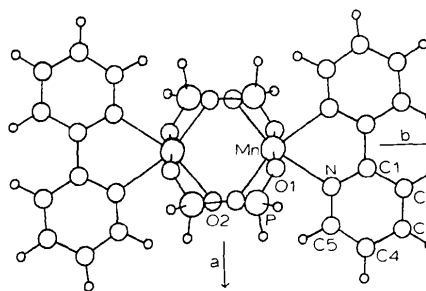


Fig. 1. Axial (*c*) projection of one chain.

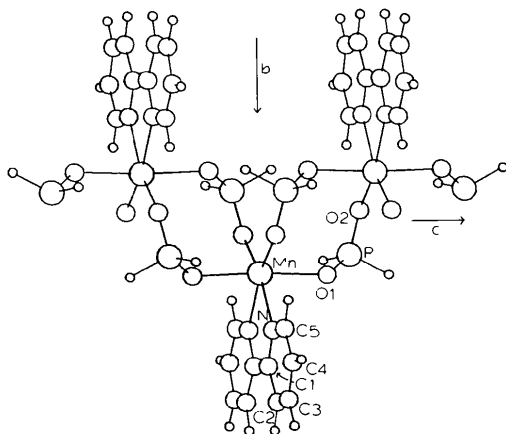


Fig. 2. Part of one chain: *a*-axis projection.

peaks close to the expected positions of all H atoms, at 1.38 and 1.42 Å from P and 0.98 to 1.15 Å from C; as these were of similar height to the stronger 'noise' peaks, the H atoms were included at calculated positions in the last cycles ($d_{\text{P-H}}$ 1.40, $d_{\text{C-H}}$ 1.05 Å, U_{H} 0.05 Å²). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.051$ with unit weights (87 parameters, 922 unique reflections above background); and, with a small decrease in all standard deviations, at $R = 0.054$, $R_w = 0.062$ by application of the weighting factor $w = 1/(1 + 0.0077F^2)$. The final atomic coordinates are given in Table 1;* derived distances and angles in Table 2. G. M. Sheldrick's *SHELX* 76 system was used in all calculations.

Discussion. Each Mn atom is linked through a double Mn–O–P–O–Mn bridge to each of the glide-related Mn atoms, so that a chain polymer extends along *c* (Figs. 1 and 2). The bipyridyl ligand completes the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33075 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

distorted octahedral coordination to Mn. The two chains through each cell are related by the *C*-centring operation. There are no abnormally short interchain contacts (Table 2). The ability of the H_2PO_2^- ion to act as a bridging ligand between cations, through either one or both O atoms, has been noted previously (Matsuzaki & Iitaka, 1969; Ionov, Aslanov, Rybakov & Porai-Koshits, 1973). This property, together with the apparent inability of H_2PO_2^- to act as a chelating ligand and the size and rigidity of the essentially planar bipyridyl, accounts for the present structure. The dimensions of H_2PO_2^- (Table 2) are normal (Williams, 1966; Matsuzaki & Iitaka, 1969; Galigné & Dumas, 1973); the mean observed P–H distance (1.40 Å, not refined) equals the covalent-radius sum. The bond lengths in the MnN_2O_4 group are also normal. The inter-ring distance [C(1)–C(1ⁱⁱ)] in 2,2'-bipyridyl is near the upper end of the range of distances found in numerous studies of bipyridyl complexes (Camus, Marsich & Nardin, 1977) but is close to the distance in the free ligand (1.50 Å; Merritt & Schroeder, 1956). The greatest distance of a ring atom from the mean plane of a pyridyl ring is 0.015 Å [C(2), the atom most closely involved in interchain contacts] and the Mn atom lies 0.043 Å from this plane. The dihedral angle between the rings is 4.5°. No C or N atom is more than 0.041 Å from the mean plane of the whole ligand, the normal to which is inclined at 15° to the chain (*c*) axis.

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