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Bis(μ_2-dihydrogen phosphato-κ^2O:O')-(μ_2-hydrogen phosphato-κ^2O:O')-bis[(1,10-phenanthroline-κ^2N,N')-manganese(II)]

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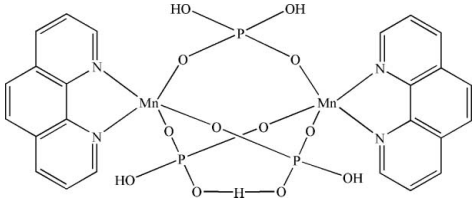
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.021; wR factor = 0.050; data-to-parameter ratio = 14.0.

In the title manganese phosphate, $[Mn_2(C_{12}H_8N_2)_2(H_{1.5}PO_4)_2(H_2PO_4)]$, a crystallographic twofold rotation axis passes through the bridging H atom and the P atom carrying two OH groups. The structure consists of distorted trigonal–bipyramidal MnO_3N_2 and tetrahedral PO_4 units linked through their vertices, giving rise to a discrete dinuclear molecular structure. The crystal structure is stabilized by intermolecular hydrogen bonds and strong π–π stacking interactions (the distance between adjacent phenanthroline rings is 3.24 Å).

Related literature

The title complex is isostructural with the previously reported zinc analogue (Ganesan *et al.*, 2003; Lin *et al.*, 2003).

For related literature, see: Chen *et al.* (2000); Zheng & Adam (1995).



Experimental

Crystal data

$[Mn_2(C_{12}H_8N_2)_2(H_{1.5}PO_4)_2(H_2PO_4)]$
M_r = 760.24
Orthorhombic, *Fdd*2
a = 40.837 (8) Å
b = 7.457 (2) Å
c = 17.424 (4) Å
V = 5306 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.21 mm^{-1}
T = 298 (2) K
0.24 × 0.21 × 0.20 mm

Data collection

Rigaku R AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.781, T_{max} = 0.785
11691 measured reflections
2965 independent reflections
2889 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.050
S = 1.15
2965 reflections
212 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Absolute structure: Flack (1983), 1389 Friedel pairs
Flack parameter: −0.001 (11)

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson,1976); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2010).

References

Chen, C.-Y., Lo, F.-R., Kao, H.-M. & Lii, K.-H. (2000). *Chem. Commun.* pp. 1061–1062.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Ganesan, S. V., Thirumurugan, A. & Natarajan, S. (2003). *Z. Anorg. Allg. Chem.* **629**, 2543–2548.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lin, Z.-E., Yao, Y.-W., Zhang, J. & Yang, G.-Y. (2003). *Dalton Trans.* pp. 3160–3164.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Zheng, Y.-Q. & Adam, A. (1995). *Z. Naturforsch. Teil B*, **50**, 1185–1194.

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supplementary materials

Acta Cryst. (2007). E**63**, m1472 [**doi:10.1107/S1600536807019332**]

Bis(μ_2-dihydrogen phosphato-κ^2O:O')(μ_2-hydrogen phosphato-κ^2O:O')bis[(1,10-phenanthroline-κ^2N,N')manganese(II)]

H.-X. Liu, X. Jiang and Y. Liang

Comment

The molecular structure of the title compound, (I), which is isostructural with the previously reported zinc analogue (Ganesan *et al.*, 2003) is illustrated in Fig 1. It consists of distorted trigonal-bipyramidal MnO_3N_2 and tetrahedral PO_4 units. The Mn(II) cation is five coordinated by three oxygen and two nitrogen atoms, with Mn–O distances in of 2.039 (2)—2.088 (1) Å and Mn–N distances in the range 2.250 (2)–2.281 (2) Å. While all the O atoms bonded to Mn are connected to P atoms, only two oxygen atoms attached to P atoms are engaged in P–O–Mn bonds and the other two are terminal ones. The P–O distances range from 1.500 (1)–1.572 (1) Å and O–P–O bond angles fall in the range of 104.71 (8)–116.5 (1)°. It is noteworthy that the hydrogen atom attached to the O(4) atom is shared by two symmetry related $H_{1.5}P(1)O_4$ groups. Such O–H–O linkages have been found in zinc carbonate (Zheng *et al.*, 1995) and also described in zinc phosphate (Lin *et al.*, 2003) and gallophosphate (Chen *et al.*, 2000).

The zero-dimensional molecular manganese phosphate is stably stacked into three-dimensional supramolecular arrays *via* strong H-bonding and π–π stacking interactions. The extensive multi-point hydrogen bonds involving the phosphate groups, forming a sheet-like structure parallel to the *bc* plane. Neighboring phen ligands from two adjacent layers exhibit a parallel stacking mode and are separated by 3.24 Å indicating significant attractive intermolecular aromatic interaction (Fig. 2).

Experimental

Compound (I) was prepared hydrothermally from a mixture of $MnCO_3$ (0.2294 g), H_3PO_4 (0.4 ml 85wt%), H_3BO_3 (0.7287 g), phen (0.3980 g) and H_2O(18 ml) in the molar ratio of 1:3:6:1:500, which was stirred for 30 min and heated at 443 K for 5 days in a Teflon-lined stainless steel autoclave (27 ml) under autogenous pressure. After cooling to room temperature, orange block-shaped crystals of (I) were obtained and washed with distilled water and dried in air. The product cannot be obtained without H_3BO_3 in the reaction system, although H_3BO_3 is absent in it.

Refinement

All H atoms bound to C were generated geometrically and refined as riding, with C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atom attached to O4 was located from the difference Fourier map and refined with U_{iso}(H) = 1.5U_{eq}(O). All other hydrogen atoms attached to O were located from the difference Fourier map and refined freely.

Figures

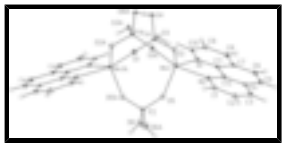

Fig. 1. The complex molecule $[(C_{12}H_8N_2Mn)_2(H_{1.5}PO_4)_2(H_2PO_4)]$ with displacement ellipsoids drawn at the 45% probability level.

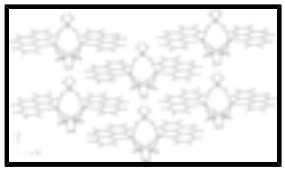

Fig. 2. View of the π–π stacking interactions between neighboring chains.

Bis(μ$_2$-dihydrogen phosphato-κ^2*O*:*O*')(μ$_2$-hydrogen phosphate-κ^2*O*:*O*')bis[(1,10-phenanthroline-κ^2*N*,*N*')manganese(II)]

Crystal data

$[Mn_2(C_{12}H_8N_2)_2(H_{1.5}PO_4)_2(H_2PO_4)]$	F_{000} = 3072
M_r = 760.24	D_x = 1.903 Mg m^{-3}
Orthorhombic, *Fdd*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: F2-2d	Cell parameters from 12033 reflections
a = 40.837 (8) Å	θ = 3.0–27.5º
b = 7.457 (2) Å	μ = 1.21 mm^{-1}
c = 17.424 (4) Å	*T* = 298 (2) K
V = 5306 (2) Å^3	Block, orange
Z = 8	0.24 × 0.21 × 0.20 mm

Data collection

Rigaku R AXIS RAPID IP diffractometer	2965 independent reflections
Radiation source: fine-focus sealed tube	2889 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.021
T = 298(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 3.0º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	*h* = −52→52
T_{min} = 0.781, T_{max} = 0.785	*k* = −8→9
11691 measured reflections	*l* = −22→22

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 5.2948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.050$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.15$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
2965 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}
212 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983)
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.001 (11)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.044642 (7)	0.13553 (4)	0.281370 (17)	0.00725 (7)
N1	0.09857 (4)	0.0839 (2)	0.26712 (9)	0.0089 (3)
N2	0.07098 (4)	0.3889 (2)	0.32082 (10)	0.0098 (3)
C1	0.05716 (5)	0.5367 (3)	0.34805 (12)	0.0118 (4)
H3A	0.0344	0.5442	0.3482	0.014*
C2	0.07522 (5)	0.6825 (3)	0.37674 (12)	0.0128 (4)
H5A	0.0646	0.7832	0.3960	0.015*
C3	0.10869 (5)	0.6737 (3)	0.37589 (12)	0.0111 (4)
H9A	0.1210	0.7688	0.3947	0.013*
C4	0.12447 (5)	0.5194 (2)	0.34630 (12)	0.0091 (4)
C5	0.15935 (5)	0.5011 (3)	0.34250 (12)	0.0119 (4)
H2A	0.1726	0.5952	0.3586	0.014*
C6	0.17320 (5)	0.3490 (3)	0.31582 (12)	0.0114 (4)
H10A	0.1959	0.3393	0.3142	0.014*
C7	0.15337 (5)	0.2018 (2)	0.28990 (12)	0.0097 (4)
C8	0.16672 (5)	0.0404 (3)	0.25998 (12)	0.0123 (4)
H8A	0.1893	0.0234	0.2584	0.015*
C9	0.14595 (5)	−0.0896 (3)	0.23344 (13)	0.0128 (4)
H11A	0.1543	−0.1949	0.2126	0.015*
C10	0.11195 (5)	−0.0634 (3)	0.23779 (11)	0.0100 (4)
H7A	0.0982	−0.1529	0.2194	0.012*
C11	0.11897 (4)	0.2161 (2)	0.29182 (11)	0.0089 (4)

C12	0.10420 (5)	0.3798 (3)	0.32039 (11)	0.0087 (4)
O1	−0.03585 (3)	0.10010 (17)	0.22335 (9)	0.0121 (3)
O2	0.01414 (3)	0.29950 (17)	0.21556 (8)	0.0109 (3)
O3	−0.03932 (3)	0.40311 (19)	0.16080 (9)	0.0115 (3)
H3	−0.0326 (7)	0.495 (4)	0.1817 (19)	0.039 (9)*
O4	−0.00937 (3)	0.15818 (18)	0.09524 (8)	0.0100 (3)
H1	0.0000	0.0000	0.0959	0.015*
P1	−0.017240 (11)	0.23433 (6)	0.17636 (3)	0.00712 (10)
O5	0.02678 (3)	0.08838 (19)	0.38875 (9)	0.0141 (3)
O6	0.01809 (4)	−0.1380 (2)	0.48733 (9)	0.0156 (3)
H2	0.0070 (8)	−0.188 (4)	0.5200 (18)	0.035 (9)*
P2	0.0000	0.0000	0.43408 (4)	0.00887 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.00656 (12)	0.00744 (12)	0.00776 (14)	−0.00075 (10)	−0.00106 (11)	0.00038 (10)
N1	0.0104 (7)	0.0097 (7)	0.0067 (9)	0.0004 (6)	−0.0003 (6)	0.0022 (6)
N2	0.0103 (8)	0.0101 (8)	0.0089 (9)	0.0003 (6)	−0.0010 (6)	0.0014 (6)
C1	0.0107 (9)	0.0132 (9)	0.0114 (10)	0.0015 (7)	0.0000 (7)	0.0010 (8)
C2	0.0172 (10)	0.0107 (9)	0.0104 (10)	0.0023 (7)	−0.0002 (8)	−0.0001 (7)
C3	0.0149 (9)	0.0093 (9)	0.0090 (10)	−0.0021 (7)	−0.0009 (8)	0.0003 (7)
C4	0.0115 (9)	0.0111 (9)	0.0048 (9)	−0.0022 (7)	−0.0017 (7)	0.0027 (7)
C5	0.0097 (9)	0.0136 (10)	0.0125 (10)	−0.0044 (7)	−0.0022 (7)	0.0021 (8)
C6	0.0070 (8)	0.0174 (9)	0.0100 (10)	−0.0011 (7)	−0.0002 (7)	0.0031 (8)
C7	0.0105 (8)	0.0126 (9)	0.0061 (9)	0.0000 (7)	0.0001 (7)	0.0032 (7)
C8	0.0089 (9)	0.0173 (10)	0.0108 (10)	0.0029 (7)	0.0017 (7)	0.0035 (8)
C9	0.0168 (10)	0.0099 (10)	0.0118 (10)	0.0040 (7)	0.0023 (8)	0.0016 (8)
C10	0.0132 (9)	0.0102 (9)	0.0066 (10)	−0.0026 (7)	−0.0006 (8)	0.0020 (7)
C11	0.0103 (9)	0.0099 (8)	0.0065 (9)	−0.0001 (6)	−0.0010 (7)	0.0021 (7)
C12	0.0090 (8)	0.0109 (9)	0.0062 (9)	−0.0011 (7)	−0.0002 (7)	0.0021 (7)
O1	0.0140 (7)	0.0090 (6)	0.0134 (8)	−0.0016 (5)	0.0023 (6)	0.0016 (6)
O2	0.0113 (7)	0.0082 (6)	0.0132 (7)	−0.0007 (5)	−0.0041 (5)	0.0020 (5)
O3	0.0106 (6)	0.0069 (6)	0.0169 (8)	0.0012 (5)	−0.0048 (5)	−0.0015 (5)
O4	0.0119 (7)	0.0100 (6)	0.0082 (7)	−0.0001 (5)	0.0009 (5)	0.0008 (5)
P1	0.0068 (2)	0.0062 (2)	0.0084 (2)	−0.00046 (16)	−0.00107 (17)	0.00098 (18)
O5	0.0138 (7)	0.0174 (7)	0.0111 (7)	−0.0058 (5)	0.0005 (6)	0.0019 (6)
O6	0.0122 (7)	0.0199 (8)	0.0147 (9)	0.0044 (5)	0.0032 (6)	0.0077 (6)
P2	0.0089 (3)	0.0111 (3)	0.0066 (3)	−0.0004 (2)	0.000	0.000

Geometric parameters (Å, °)

Mn1—O5	2.0386 (16)	C7—C11	1.409 (3)
Mn1—O1^{i}	2.0587 (14)	C7—C8	1.420 (3)
Mn1—O2	2.0884 (14)	C8—C9	1.369 (3)
Mn1—N1	2.2495 (17)	C8—H8A	0.9300
Mn1—N2	2.2805 (16)	C9—C10	1.404 (3)
N1—C10	1.329 (2)	C9—H11A	0.9300

N1—C11	1.360 (2)	C10—H7A	0.9300
N2—C1	1.326 (2)	C11—C12	1.450 (3)
N2—C12	1.358 (2)	O1—P1	1.4998 (14)
C1—C2	1.406 (3)	O1—Mn1^{i}	2.0587 (14)
C1—H3A	0.9300	O2—P1	1.5313 (13)
C2—C3	1.369 (3)	O3—P1	1.5718 (14)
C2—H5A	0.9300	O3—H3	0.82 (3)
C3—C4	1.416 (3)	O4—P1	1.5568 (15)
C3—H9A	0.9300	O4—H1	1.2402
C4—C12	1.404 (3)	O5—P2	1.5015 (14)
C4—C5	1.433 (3)	O6—P2	1.5704 (15)
C5—C6	1.350 (3)	O6—H2	0.82 (3)
C5—H2A	0.9300	P2—O5^{i}	1.5015 (14)
C6—C7	1.437 (3)	P2—O6^{i}	1.5704 (15)
C6—H10A	0.9300		
O5—Mn1—O1^{i}	103.95 (6)	C11—C7—C6	119.76 (17)
O5—Mn1—O2	113.05 (6)	C8—C7—C6	123.10 (17)
O1^{i}—Mn1—O2	97.24 (6)	C9—C8—C7	119.11 (18)
O5—Mn1—N1	114.96 (6)	C9—C8—H8A	120.4
O1^{i}—Mn1—N1	88.32 (6)	C7—C8—H8A	120.4
O2—Mn1—N1	128.57 (6)	C8—C9—C10	119.70 (18)
O5—Mn1—N2	92.01 (6)	C8—C9—H11A	120.1
O1^{i}—Mn1—N2	159.64 (6)	C10—C9—H11A	120.1
O2—Mn1—N2	87.80 (6)	N1—C10—C9	122.85 (18)
N1—Mn1—N2	73.33 (6)	N1—C10—H7A	118.6
C10—N1—C11	117.97 (16)	C9—C10—H7A	118.6
C10—N1—Mn1	125.88 (13)	N1—C11—C7	123.22 (17)
C11—N1—Mn1	116.15 (12)	N1—C11—C12	117.64 (16)
C1—N2—C12	117.95 (17)	C7—C11—C12	119.14 (17)
C1—N2—Mn1	126.56 (13)	N2—C12—C4	123.35 (18)
C12—N2—Mn1	115.34 (13)	N2—C12—C11	117.36 (17)
N2—C1—C2	123.14 (18)	C4—C12—C11	119.29 (17)
N2—C1—H3A	118.4	P1—O1—Mn1^{i}	157.83 (9)
C2—C1—H3A	118.4	P1—O2—Mn1	123.93 (8)
C3—C2—C1	118.89 (18)	P1—O3—H3	113 (2)
C3—C2—H5A	120.6	P1—O4—H1	113.7
C1—C2—H5A	120.6	O1—P1—O2	113.10 (8)
C2—C3—C4	119.83 (18)	O1—P1—O4	110.90 (8)
C2—C3—H9A	120.1	O2—P1—O4	110.36 (8)
C4—C3—H9A	120.1	O1—P1—O3	109.76 (8)
C12—C4—C3	116.82 (17)	O2—P1—O3	107.63 (8)
C12—C4—C5	120.03 (17)	O4—P1—O3	104.71 (8)
C3—C4—C5	123.15 (18)	P2—O5—Mn1	144.99 (10)
C6—C5—C4	120.84 (18)	P2—O6—H2	117 (2)
C6—C5—H2A	119.6	O5^{i}—P2—O5	116.52 (13)
C4—C5—H2A	119.6	O5^{i}—P2—O6	111.46 (8)
C5—C6—C7	120.93 (17)	O5—P2—O6	104.82 (8)

C5—C6—H10A	119.5	$O5^{i}$—P2—$O6^{i}$	104.82 (8)
C7—C6—H10A	119.5	O5—P2—$O6^{i}$	111.46 (8)
C11—C7—C8	117.12 (17)	O6—P2—$O6^{i}$	107.57 (12)

Symmetry codes: (i) −*x*, −*y*, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···$O2^{ii}$	0.82 (3)	1.81 (3)	2.624 (2)	172 (3)
O4—H1···$O4^{iii}$	1.240	1.240	2.480 (2)	179
O6—H2···$O4^{iv}$	0.82 (3)	1.87 (3)	2.665 (2)	166 (3)

Symmetry codes: (ii) −*x*, −*y*+1, *z*; (iii) −*x*, −*y*, *z*; (iv) *x*, *y*−1/2, *z*+1/2.

Fig. 1

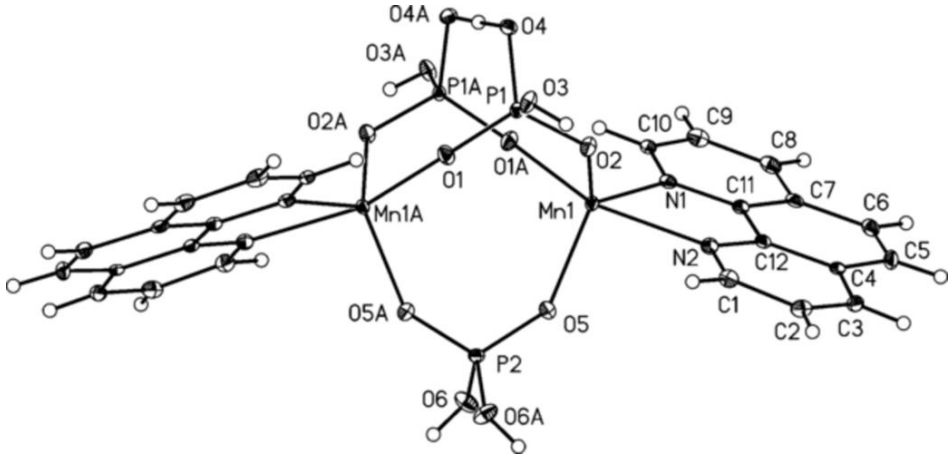
O4A
O4
O3A
P1A
P1
O3
O2A
O1
O1A
O2
C10
C9
C8
C11
C7
C6
C5
C4
C3
C2
C1
N1
N2
C12
Mn1A
Mn1
O5A
O5
P2
O6
O6A

Fig. 2