Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1317). Services for accessing these data are described at the back of the journal.

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Poly[mercury(II)-μ-4,4′-bipyridine-di-μ-bromo]

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Abstract

The title compound, $[HgBr_2(C_{10}H_8N_2)]_n$, was obtained by mixing equimolar ethanolic solutions of mercuric bromide and 4,4′-bipyridine (4,4′-bipy). The bipy ligand acts as a linear bifunctional bridge forming a planar $\{-[Hg(4,4'\text{-bipy})]-\}_n$ belt in the direction of the *a* axis. The remaining mercury coordination sites are occupied by Br^- ions which link Hg centres in neighbouring belts *via* double bridges to form extended two-dimensional layers.

Comment

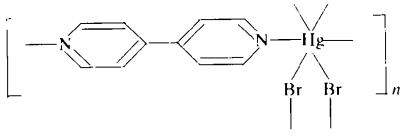
There has been significant interest recently in metal complexes containing 4,4′-bipyridine (4,4′-bipy). The rod-like rigidity of this ligand leads to metal complexes which are often extended solids with topological structures. Three types of polymer structure formed by 4,4′-bipy can be summarized as follows:

(i) each metal ion is connected by two bridging 4,4′-bipy ligands to form one-dimensional $[M(4,4'\text{-bipy})]_n$ polymeric chains, for example, $\{[Ni(4,4'\text{-bipy})(C_5H_9OS_2)_2]\cdot 2CCl_4\}_n$ (Gable *et al.*, 1985), $[Cd(4,4'\text{-bipy})(C_4H_{17}OS_2)_2]_n$ (Abrahams *et al.*, 1990), $[Cu(4,4'\text{-bipy})(H_2O)_2(ClO_4)_2]_n\cdot n(4,4'\text{-bipy})$ (Chen *et al.*, 1996), $[Cu(4,4'\text{-bipy})(2,2'\text{-bipy})(ClO_4)_2]_n$ (Chen *et al.*, 1992) and $[Co(NCS)_2(H_2O)_2(4,4'\text{-bipy})]\cdot(4,4'\text{-bipy})$ (Lu *et al.*, 1997). In the last two of these, the one-dimensional chains are connected by hydrogen bonding involving uncoordinated 4,4′-bipy, resulting in a two-dimensional structure.

(ii) Mutually interpenetrating two-dimensional sheets of [Cu(4,4′-bipy)Cl] were synthesized by Yaghi & Li (1995) and two-dimensional layers were found in $\{[Cd(4,4'\text{-bipy})_2](NO_3)_2\}_n$ (Fujita *et al.*, 1994) and $[Co(NCS)_2(4,4'\text{-bipy})_2]\cdot 2[(CH_3CH_2)_2O]$ (Lu *et al.*, 1997), in which the metal ion was coordinated by four bridging 4,4′-bipy ligands. Infinite square-grid two-dimensional cationic sheets of composition $[Cd(H_2O)_2(4,4'\text{-bipy})_2]_n^{2n+}$ were observed in $[Cd(H_2O)_2(4,4'\text{-bipy})_2]PF_6\cdot 2(4,4'\text{-bipy})\cdot 4H_2O$ (Robson *et al.*, 1992).

(iii) Three-dimensional structures with super-diamond-type nets are observed in $[Cu(4,4'\text{-bipy})_{1.5}]NO_3\cdot 1.25H_2O$ (Yaghi & Li, 1995) and $[Cu(4,4'\text{-bipy})_2(PF_6)]$ (MacGillivray *et al.*, 1994), the extent of interpenetration leaving extended channels through the structure. However, in $[Zn(4,4'\text{-bipy})_2(SiF_6)]\cdot 2H_2O$ (Gable *et al.*, 1990), there are no accessible voids. Moreover, the complex $[Ag(4,4'\text{-bipy})_2(CF_3SO_3)]_n$ (Carlucci *et al.*, 1994) is also of this type. Three-dimensional structures with large square channels are found in $[Zn(4,4'\text{-bipy})_2(SiF_6)]_n\cdot DMF$ (Subramanian & Zaworotko, 1995) and $[Zn_2(4,4'\text{-bipy})(PO_3F)_2]$ (Halasyamani *et al.*, 1997). The three-dimensional framework of $[Ag(4,4'\text{-bipy})]NO_3$ (Robinson & Zaworotko, 1995) is assembled from T-shaped cationic building blocks.

The title compound, (I), belongs to type (ii). The Hg^{II} ion is coordinated by two N atoms from two different 4,4′-bipy ligands and by four Br^- ligands (Fig. 1). The N_2Br_4 coordination about mercury is close to octahedral (Table 2).



(I)

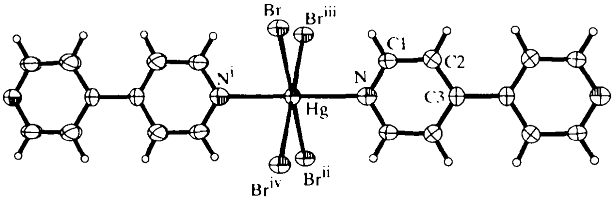


Fig. 1. View of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability. [Symmetry codes: (i) $-x, y, z$; (ii) $x, -y, -z$; (iii) $x, y, -z$; (iv) $x, -y, z$.]

The Hg atom sits on a crystallographic *mmm* site (Table 1), with the pyridine rings lying perpendicular to [001], and the bridging bromide with a mirror plane perpendicular to the *b* axis.

The two pyridine rings of each 4,4′-bipy ligand are coplanar, being related by an inversion centre at ($\frac{1}{2}$,0,0). Planes of Hg atoms lie 6.280 (2) Å apart. Adjacent 4,4′-bipy ligands are separated by the *c*-axis translation of 3.945 (1) Å.

The infinite $\{-[Hg(4,4'\text{-bipy})]-\}_n$ chains extending along the *a* axis are linked by doubly bridging bromide chains extending along the *c* axis, resulting in two-dimensional layers in the *ac* plane (Fig. 2).

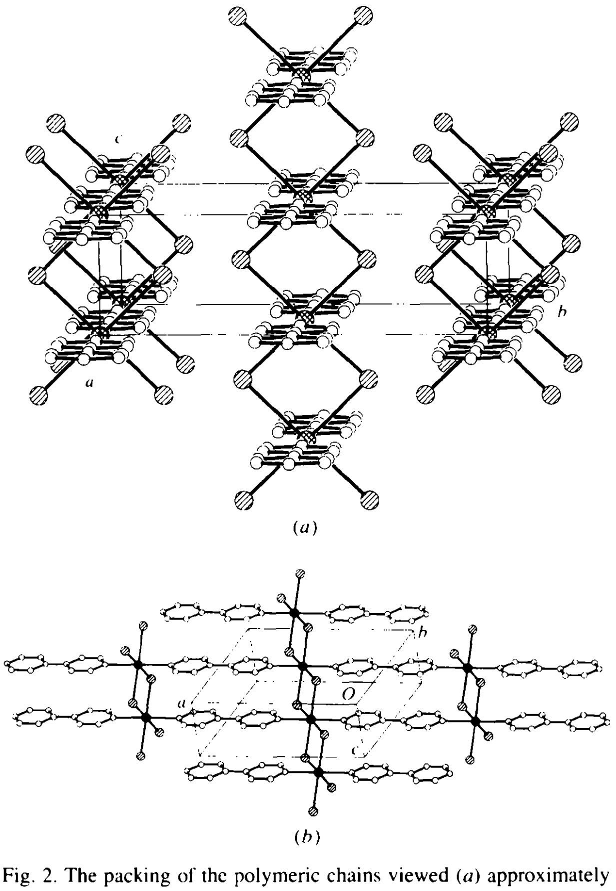


Fig. 2. The packing of the polymeric chains viewed (*a*) approximately along the *a* axis and (*b*) approximately along the *b* axis.

Experimental

[$HgBr_2(4,4'\text{-bipy})]_n$ was obtained by reaction of $HgBr_2$ and 4,4′-bipy (molar ratio 1:1) in ethanol. A single crystal suitable for X-ray single-crystal analysis was obtained by diffusing a clear ethanolic solution of $HgBr_2$ (obtained by filtering a saturated ethanolic solution of $HgBr_2$) through ethylene glycol (3 ml) into an ethanolic solution of 4,4′-bipy (0.1 *M*). After a few days, a colourless crystal was retrieved from the ethanol/ethylene glycol interface.

Crystal data

[$HgBr_2(C_{10}H_8N_2)$]
$M_r = 516.58$
Orthorhombic
Cmmm
$a = 11.688\ (2)$ Å
$b = 12.561\ (4)$ Å
$c = 3.945\ (1)$ Å
$V = 579.1\ (3)$ Å^3
$Z = 2$
$D_x = 2.962$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 11.59\text{–}16.37°$
$\mu = 20.087$ mm^{-1}
$T = 296$ K
Needle
0.40 × 0.05 × 0.04 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1989)
$T_{min} = 0.292$, $T_{max} = 0.434$
358 measured reflections
358 independent reflections
340 reflections with $I > 4\sigma(I)$
$\theta_{max} = 25.9°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = -4 \rightarrow 0$
3 standard reflections every 300 reflections intensity variation: 1.9%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.038$
$S = 1.25$
340 reflections
29 parameters
H-atom parameters constrained
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -1.40$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Guassian isotropic
Extinction coefficient: 1.43×10^{-6}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg	0	0	0	0.0233 (4)
Br	0	0.16237 (9)	1/2	0.0260 (6)
N	0.2010 (9)	0	0	0.027 (5)
C1	0.2578 (9)	0.0876 (7)	0	0.054 (6)
C2	0.3746 (9)	0.0908 (7)	0	0.060 (7)
C3	0.4360 (9)	0	0	0.023 (5)

Table 2. *Selected geometric parameters (Å, °)*

Hg---N	2.35 (1)	Hg · Br	2.837 (1)
N^{i}—Hg—N	180	Br—Hg—Br^{ii}	88.08 (4)
N—Hg—Br	90.03 (2)	Br—Hg—Br^{iii}	180
N—Hg—Br^{ii}	89.99 (2)	Br^{i}—Hg—Br^{iii}	180

Symmetry codes: (i) $-x, y, z$; (ii) $x, y, -z$; (iii) $x, -y, -z$.

The major residual difference electron-density features lie 0.96 Å from the Hg atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: local programs.

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Bis(dihydrogen phosphato-*O*)[(1*RS*,4*RS*,8*SR*,11*SR*)-1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) monohydrate

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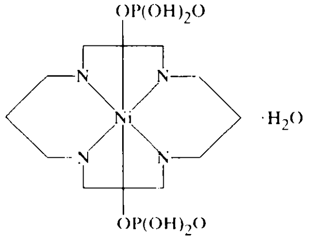
Abstract

The Ni^{II} ion in the title compound, $[Ni(H_2PO_4)_2(C_{10}H_{24}N_4)]\cdot H_2O$, is six-coordinate in a distorted square-bipyramidal environment. Four N atoms from the tetraaza-macrocycle are in a square-planar arrangement [average Ni—N distance = 2.071 (2) Å] and two O atoms, one from each dihydrogen phosphate ion, are axial [average Ni—O distance = 2.144 (2) Å]. The structure of the title complex forms a three-dimensional framework, which delimits intersecting *b*-axis and *c*-axis tunnels. Two types of hydrogen bonds, O—H···O and N—H···O, ensure the cohesion and stability of the molecular packing.

Comment

The title compound belongs to the family of 14-membered macrocyclic amines. Their coordination behavior with transition metals has been widely studied both chemically and crystallographically, but the reported crystal structures of macrocyclic amines and their salts are rather few in number. The crystal structure of bis(dihydrogen phosphato-*O*)(1,4,8,11-tetraazacyclotetradecane-κ^4N)nickel(II) monohydrate, (I), is composed of nickel complex molecules. Each complex is connected to six others by means of hydrogen bonding, strong enough to form a three-dimensional framework, which delimits intersecting tunnels where water molecules are located (Fig. 1). The coordination geometry around the Ni^{II} ion is slightly distorted square bipyramidal with four equatorial N atoms and two axial O atoms, one



(I)

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