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A one-dimensional iodine-bridged Pt^{II}/Pt^{IV} mixed-valence complex, *catena*-poly[[[bis(ethylenediamine)-platinum(II)]-μ-iodo-[bis(ethylenediamine)platinum(IV)]-μ-iodo] hydrogenphosphate dihydrogenphosphate iodide trihydrate]

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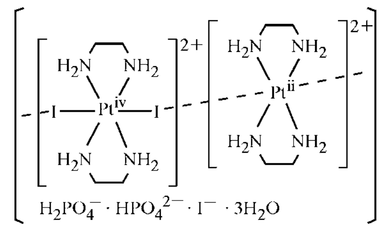
The title compound, $\{[Pt^{II}Pt^{IV}I_2(C_2H_8N_2)_4](HPO_4)(H_2PO_4)I\cdot 3H_2O\}_n$, has a chain structure composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtI_2(en)_2]^{2+}$ cations (en is ethylenediamine) stacked alternately along the *c* axis and bridged by the I atoms; a three-dimensionally valence-ordered system exists with respect to the Pt sites. The title compound also has a unique cyclic tetramer structure composed of two hydrogenphosphate and two dihydrogenphosphate ions connected by strong hydrogen bonds [O$\cdots$O = 2.522 (10), 2.567 (10) and 2.569 (11) Å]. The Pt and I atoms form a zigzag $\cdots$I—Pt^{IV}—I$\cdots$$Pt^{II}\cdots$ chain, with Pt^{IV}—I bond distances of 2.6997 (7) and 2.6921 (7) Å, interatomic $Pt^{II}\cdots$I distances of 3.3239 (8) and 3.2902 (7) Å, and Pt^{IV}—I$\cdots$$Pt^{II}$ angles of 154.52 (3) and 163.64 (3)°. The structural parameters indicating the mixed-valence state of platinum, expressed by $\delta = (Pt^{IV}-I)/(Pt^{II}-I)$, are 0.812 and 0.818 for the two independent I atoms.

Comment

The title compound, (I), is a member of the family of one-dimensional halogen-bridged mixed-valence metal complexes formulated as $[M^{II}(AA)_2][M^{IV}X_2(AA)_2]Y_4$ [M^{II}/M^{IV} = Pt^{II}/Pt^{IV}, Pd^{II}/Pd^{IV}, Ni^{II}/Ni^{IV}, Pd^{II}/Pt^{IV} and Ni^{II}/Pt^{IV}; X = Cl, Br and I; AA = $NH_2(CH_2)_2NH_2$, *etc.*; Y = ClO_4^-, HSO_4^-, X^-, *etc.*], hereafter abbreviated as *MX*-chain compounds, which are typical mixed-valence compounds belonging to class II in the classification of Robin & Day (1967). *MX*-chain compounds have been attracting much interest because of their one-dimensional mixed-valence electron systems. Unusual physical properties, such as a remarkably dichroic intense absorption band attributed to an intervalence charge-transfer (IVCT) transition from M^{II} to M^{IV} in the mixed-valence state, progressive Raman scattering in resonance with the IVCT band, and photoinduced mid-gap absorption bands due to soliton and polaron formation, are characteristics of the one-dimensional mixed-valence system.



(I)

The metal–halogen distances in crystals of *MX*-chain compounds characterize these physical properties on the basis of the mixed-valence state. The valence ordering of the metal site in the mixed-valence state is also structurally interesting because of the relation to the soliton and polaron formation as a mismatch of the valence alternation. The present X-ray crystallographic analysis of the title compound, $[Pt(en)_2][PtI_2(en)_2](HPO_4)(H_2PO_4)I\cdot 3H_2O$ (en is ethylenediamine), (I), has been performed in order to gather further structural information on these *MX*-chain compounds.

As shown in Fig. 1, the structure of (I) is built up from columns composed of square-planar $[Pt(en)_2]^{2+}$ and elongated octahedral *trans*-$[PtI_2(en)_2]^{2+}$ cations stacked alternately, bridged by the I atoms, along the *c* axis. The Pt1 and Pt2 sites are assigned to Pt^{IV} and Pt^{II}, respectively. The Pt and I atoms occupy general sites in the unit cell and form an infinite zigzag

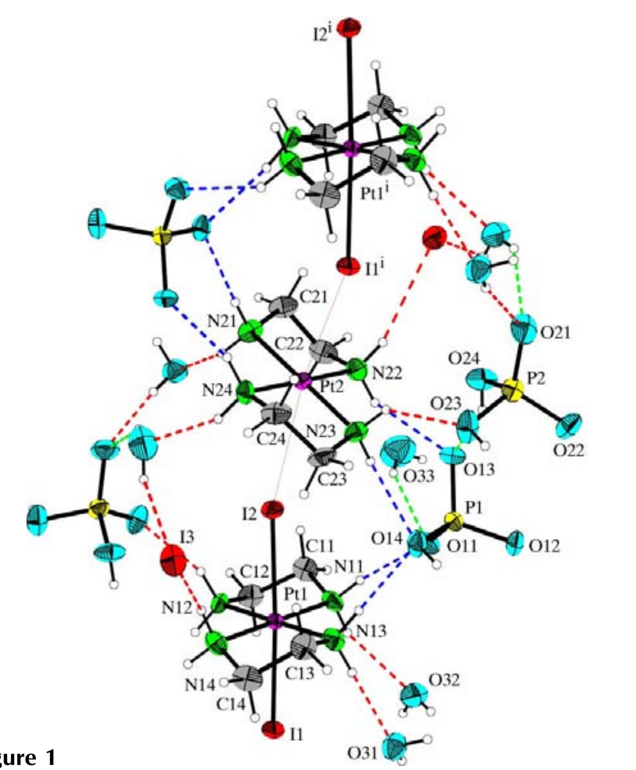


Figure 1
A view of the columnar structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds. [Symmetry code: (i) *x*, *y*, *z* + 1.]

$\cdots I-Pt^{IV}-I\cdots Pt^{II}\cdots$ chain, with $Pt^{IV}-I$ distances of 2.6997 (7) and 2.6921 (7) Å, and $Pt^{II}-I$ distances of 3.3239 (8) and 3.2902 (7) Å (Table 1).

There is no disorder of the bridging halogen atoms in (I), although the other *MX*-chain compounds have disordered structures. The I atoms are not located at the exact mid-point between two adjacent Pt atoms but at a position displaced somewhat from the mid-point to the Pt1 site. The valence ordering of the Pt site in (I) belongs to one of three different classes of the order–disorder problem described by Keller (1982); the structure of (I) can be regarded as a three-dimensionally valence-ordered structure. This type of valence ordering of the Pt site is rare. Five compounds belonging to this type were described in the review of Keller (1982). Since the publication of this review, rerefinements and re-analyses for these five compounds have shown that they belong to another class, that is, one-dimensionally valence-ordered structures with the other two directions in a disordered state; these compounds are $[Pt(tn)_2][PtX_2(tn)_2](BF_4)_4$ (tn is 1,3-propanediamine, and X = Cl and Br) and $[Pt(tn)_2][PtBr_2(tn)_2]$-$(ClO_4)_4$, re-analyzed by Cannas *et al.* (1983), and $[Pt(en)_2]$-$[PtX_2(en)_2](ClO_4)_4$ (X = Cl and Br), re-analyzed by Huckett *et al.* (1993) and Toriumi *et al.* (1993). The valence ordering of the Pt site in the majority of the *MX*-chain compounds belongs to this one-dimensionally valence-ordered structure type. On the other hand, a few *MX*-chain compounds, *viz.* $[Pt(tn)_2]$-$[PtI_2(tn)_2](ClO_4)_4$ (Cannas *et al.*, 1984) and $[Pt(NH_3)_4]$-$[PtI_2(NH_3)_4](HSO_4)_4\cdot 2H_2O$ (Tanaka *et al.*, 1986), have been reported anew as belonging to the three-dimensionally valence-ordered system to which (I) belongs.

The structural parameters indicating the mixed-valence state of the Pt atom, expressed by $\delta = (Pt^{IV}-I)/(Pt^{II}-I)$, are 0.812 and 0.818 for atoms I1 and I2, respectively. These values are much smaller than those for $[Pt(pn)_2][PtI_2(pn)_2](ClO_4)_4$ (0.937; pn is 1,2-propanediamine; Breer *et al.*, 1978), $[Pt(pn)_2]$-$[PtI_2(pn)_2]I_4$ (0.940; Endres *et al.*, 1980), $[Pt(tn)_2][PtI_2(tn)_2]$-$(ClO_4)_4$ (0.95; Cannas *et al.*, 1984) and $[Pt(en)_2][PtI_2(en)_2]$-$(ClO_4)_4$ (0.919; Endres *et al.*, 1979), and somewhat smaller than that of $[Pt(NH_3)_4][PtI_2(NH_3)_4](HSO_4)_4\cdot 2H_2O$ (0.834; Tanaka *et al.*, 1986).

Hydrogen bonds (Table 2) stabilize the columnar structure composed only of cationic complexes, as shown in Fig. 1. A $[Pt^{II/IV}(en)_2]$ unit is bound to an adjacent Pt complex unit in the column by four hydrogen-bond linkages of the type NH$\cdots$counter-anion(+ water molecule)$\cdots$HN. There are two sets of four hydrogen-bond linkages; one is composed of the N11—H11*A*$\cdots$O11—P1—O13$\cdots$H22*B*—N22, N12—H12*B*$\cdots$O22—P2—O21$\cdots$H31*A*—O31$\cdots$H21*A*—N21, N13—H13*B*$\cdots$O14$\cdots$H23*A*—N23 and N14—H14*A*$\cdots$I3$\cdots$H32*B*—O32$\cdots$H24*B*—N24 interactions, and the other is composed of the N21—H21*B*$\cdots$O12$\cdots$H12*A*—N12, N22—H22*A*$\cdots$I3$\cdots$H32*B*—O32$\cdots$H11*B*—N11, N23—H23*B*$\cdots$O23—P2—O21$\cdots$H31*B*—O31$\cdots$H13*A*—N13 and N24—H24*A*$\cdots$O11—P1—O13$\cdots$H14*B*—N14 interactions. The crystal packing is further stabilized by intercolumnar hydrogen-bond linkages, as shown in Fig. 2.

As shown in Fig. 3, a cyclic tetramer structure composed of two hydrogenphosphate ions and two dihydrogenphosphate ions is formed by strong O—H$\cdots$O hydrogen bonds [O$\cdots$O = 2.522 (10), 2.567 (10) and 2.569 (11) Å]; the O$\cdots$O distances are comparable to the average values in hydrogenphosphates (2.597 Å) and dihydrogenphosphates (2.574 Å) (Ferraris & Ivaldi, 1984). An *MX*-chain compound containing dimerized anions has already been reported; this is $[Pt(NH_3)_4]$-$[PtBr_2(NH_3)_4](HSO_4)_4$ (Tanaka *et al.*, 1982), which also has

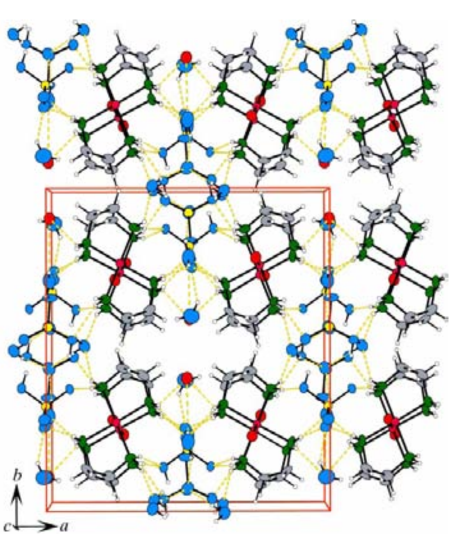


Figure 2
The crystal packing of (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

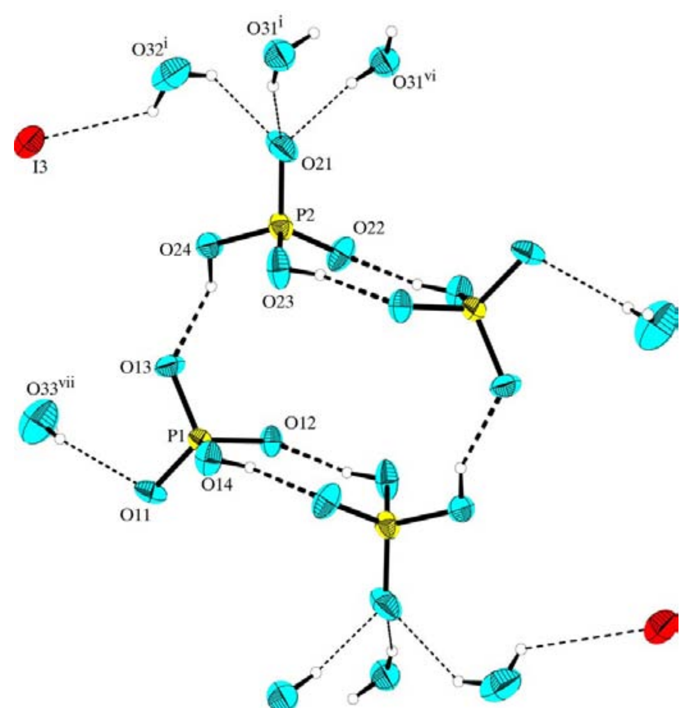


Figure 3
A view of the cyclic tetramer structure composed of two hydrogenphosphate and two dihydrogenphosphate ions, together with neighboring water molecules of crystallization and iodide ions. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $x, y, z + 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + 1, -y + 1, -z + 1$.]

strong O—H···O hydrogen bonds [2.582 (9) Å] in the dimer. The present tetramer structure of the counter-anion is the first observation in the *MX*-chain compounds to our best knowledge. In addition, the tetramers form a chain structure parallel to the Pt—I chain, connected by hydrogen bonds with the water molecules (O31).

Experimental

Compound (I) was prepared using a procedure similar to that described by Matsushita (1993). Golden plate-shaped crystals were obtained by recrystallization from an aqueous solution on slow evaporation.

Crystal data

$[Pt_2I_2(C_2H_8N_2)_4](HPO_4)(H_2PO_4)I\cdot 3H_2O$
M_r = 1258.29
Monoclinic, $P2_1/n$
a = 14.808 (1) Å
b = 16.478 (2) Å
c = 11.758 (1) Å
β = 90.84 (1)°
V = 2868.7 (5) Å^3
Z = 4
D_x = 2.913 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
θ = 10.0–15.0°
μ = 13.14 mm^{-1}
T = 295 K
Plate, gold
0.20 × 0.20 × 0.06 mm

Data collection

Rigaku AFC-5*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
T_{min} = 0.127, T_{max} = 0.501
7883 measured reflections
6603 independent reflections
4431 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.5°
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.084
S = 1.10
4491 reflections
314 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 18.1327P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.91 e Å^{-3}
$\Delta\rho_{min}$ = −2.02 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00064 (4)

Table 1
Selected geometric parameters (Å, °).

Pt1—I1	2.6997 (7)	Pt2—I1^{i}	3.3239 (8)
Pt1—I2	2.6921 (7)	Pt2—I2	3.2902 (7)
Pt1—N11	2.048 (7)	P1—O11	1.518 (7)
Pt1—N12	2.055 (8)	P1—O12	1.537 (6)
Pt1—N13	2.069 (8)	P1—O13	1.524 (7)
Pt1—N14	2.075 (8)	P1—O14	1.582 (7)
Pt2—N21	2.044 (8)	P2—O21	1.500 (8)
Pt2—N22	2.043 (8)	P2—O22	1.527 (7)
Pt2—N23	2.045 (8)	P2—O23	1.556 (7)
Pt2—N24	2.034 (8)	P2—O24	1.565 (8)
N11—Pt1—N12	83.8 (3)	N13—Pt1—I2	90.3 (2)
N11—Pt1—N13	95.2 (3)	N14—Pt1—I2	90.7 (2)
N12—Pt1—N14	97.8 (3)	I1—Pt1—I2	176.16 (3)
N13—Pt1—N14	83.2 (3)	Pt1—I1—Pt2^{ii}	154.52 (3)
N11—Pt1—I1	89.9 (2)	Pt1—I2—Pt2	163.64 (3)
N12—Pt1—I1	86.3 (2)	I2—Pt2—I1^{i}	165.88 (2)
N13—Pt1—I1	93.6 (2)	N21—Pt2—N22	83.0 (3)
N14—Pt1—I1	90.0 (2)	N21—Pt2—N24	95.6 (3)
N11—Pt1—I2	89.5 (2)	N22—Pt2—N23	97.3 (3)
N12—Pt1—I2	89.9 (2)	N23—Pt2—N24	84.1 (3)

Symmetry codes: (i) $x, y, z + 1$; (ii) $x, y, z - 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11*A*···O11	0.90	1.91	2.796 (10)	170
N11—H11*B*···O32	0.90	2.18	2.990 (12)	149
N12—H12*A*···O12^{iii}	0.90	2.11	2.987 (10)	164
N12—H12*B*···O22^{iii}	0.90	2.10	2.870 (11)	143
N13—H13*A*···O31	0.90	2.05	2.854 (12)	148
N13—H13*B*···O14	0.90	2.08	2.972 (10)	170
N14—H14*A*···I3^{iii}	0.90	2.96	3.689 (8)	139
N14—H14*B*···O13^{iii}	0.90	2.15	2.937 (11)	146
N21—H21*A*···O31^{iv}	0.90	2.24	3.002 (11)	142
N21—H21*B*···O12^{v}	0.90	2.13	3.030 (11)	176
N22—H22*A*···I3	0.90	2.92	3.686 (8)	144
N22—H22*B*···O13	0.90	2.27	3.038 (11)	143
N23—H23*A*···O14	0.90	2.26	3.132 (11)	162
N23—H23*B*···O23	0.90	2.25	2.962 (11)	136
N24—H24*A*···O11^{v}	0.90	1.98	2.846 (11)	161
N24—H24*B*···O32^{v}	0.90	2.08	2.909 (11)	153
O14—H14···O22^{vi}	0.82	1.79	2.569 (11)	159
O23—H23···O12^{vi}	0.82	1.76	2.567 (10)	167
O24—H24···O13	0.82	1.77	2.522 (10)	151
O31—H31*B*···O21^{ii}	0.82	1.93	2.731 (10)	165
O31—H31*A*···O21^{vi}	0.82	1.90	2.717 (10)	171
O32—H32*B*···I3^{ii}	0.82	2.88	3.502 (12)	134
O32—H32*A*···O21^{ii}	0.82	2.07	2.753 (13)	140
O33—H33*A*···O11^{vii}	0.82	2.11	2.824 (13)	145

Symmetry codes: (ii) $x, y, z - 1$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + 1, -y + 1, -z + 1$.

A *PLATON* (Spek, 2003) analysis of (I) pointed out the possible presence of two additional symmetry axes, *viz*. a mirror plane perpendicular to the *a* axis and an *n*-glide plane perpendicular to the *c* axis, and suggested the space group *Pmnn* (No. 58). A detailed check of the reflections observed, however, indicates that the Laue class is still 2/*m*. The R_{int} value was 0.152 if the Laue class *mmm* was assumed. A refinement in the space group *Pmnn* was attempted but could not be performed successfully. H atoms attached to C and N atoms were placed in geometrically calculated positions. H atoms of the phosphate ions were located at positions calculated on the basis of whether the P—O distances were long or short. As a result, the H atoms were attached to atoms O14, O23 and O24, which have longer P—O distances than the others. H atoms attached to atoms O31 and O32 of the water molecules were placed in positions satisfying their hydrogen-bonding geometry. Atom H33*A* of the other water molecule (O33) was also placed in a position based on the hydrogen bond between atoms O33 and O11. Atom H33*B* was placed in a position generated using a HFIX instruction, because the O33—H33*B* group does not have a hydrogen-bond acceptor. All H atoms were refined as riding (C—H = 0.97 Å, N—H = 0.90 Å and O—H = 0.82 Å), with the constraint $U_{iso}(H) = 1.5U_{eq}(C,N,O)$. The highest peak in the difference map is located 0.94 Å from atom Pt2 and the deepest hole is located 0.86 Å from atom Pt1.

Data collection: *AFC Diffractometer Control Software* (Rigaku, 1987); cell refinement: *AFC Diffractometer Control Software*; data reduction: *AFC Diffractometer Control Software* and *F2-AFC* (Matsushita, 1998); program(s) used to solve structure: *SHELX76* (Sheldrick, 1976); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1246). Services for accessing these data are described at the back of the journal.

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