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Structure of a Pt^{II}–Pt^{IV} Mixed-Valence Complex, Bis(ethylenediamine)platinum(II)-bis(ethylenediamine)diiodoplatinum(IV) Perchlorate, $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$*

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Abstract. $[Pt(C_2H_8N_2)_2]^{2+}.[Pt(C_2H_8N_2)_2I_2]^{2+}.4ClO_4^-$, $C_4H_{16}N_4Pt^{2+}.C_4H_{16}I_2N_4Pt^{2+}.4ClO_4^-$, monoclinic, $Z = 2$, $a = 16\cdot914\,(2)$, $b = 11\cdot640\,(2)$, $c = 7\cdot429\,(1)$ Å, $\beta = 98\cdot48\,(1)$°, $V = 1446\cdot8\,(4)$ Å^3, $D_x = 2\cdot907$, $D_m = 2\cdot87$ Mg m^{-3}, $\mu = 12\cdot17$ mm^{-1}. Only continuous and diffuse layer lines are observed corresponding to odd values of k; the subcell for which $b = 5\cdot820\,(1)$ Å has space group $C2$. The structure is interpreted in terms of chains of alternately arranged square-planar $[Pt(en)_2]^{2+}$ and tetragonal-bipyramidal $[Pt(en)_2I_2]^{2+}$ units, the disorder arising from a stacking mistake involving displacement of the chain by one-half of the repeating unit. The oxidation number of each Pt atom can be assigned on the basis of the Pt–I distances. However, judging from the ratios of the Pt^{IV}–I and Pt^{II}–I distances, the difference of the oxidation states between Pt^{II} and Pt^{IV} atoms is much reduced compared with those of the chloro and bromo analogs.

Introduction. In the previous study in this series, we determined the crystal structures of $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$ and $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$, and showed that these complexes contain infinite chains ($\cdots Pt^{II}\cdots X$–Pt^{IV}–$X\cdots$) comprising alternately arranged tetragonal-bipyramidal $[Pt(tn)_2X_2]^{2+}$ and square-planar $[Pt(tn)_2]^{2+}$ units, where tn denotes trimethylenediamine and X represents Cl or Br. The ratios of the Pt^{IV}–X and Pt^{II}–X bond distances are 0·76, 0·86 and 0·87 for $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$ and $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$, respectively, implying that the difference in the oxidation states between Pt^{II} and Pt^{IV} atoms is much reduced in the bromo analogs compared to that in the chloro analog (Matsumoto, Yamashita & Kida, 1978*b*). This suggests that the difference in the oxidation states between Pt^{II} and Pt^{IV} atoms is much reduced in the iodo analog. Accordingly, in this study we have carried out the X-ray crystallographic analysis of $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$, in order to elucidate the oxidation states of platinum atoms in the mixed-valence Pt^{II}–Pt^{IV} compounds.

Golden lustrous platy crystals of the title compound were obtained from dilute perchloric acid solution (Matsumoto, Yamashita & Kida, 1978*a*). Crystals exhibited a remarkable dichroism: they are dark-brown with polarized light along the b axis and light-brown with polarized light perpendicular to the b axis. Rotation and Weissenberg photographs about the b axis showed normal sharp reflections on even layers but only diffuse and continuous reflections on odd layers. These reflections are indexed with respect to the subcell for which b is halved ($b = 5\cdot820$ Å). In the subcell unit, the iodine atoms have half-weight. The dimensions of the single crystal used for the intensity measurements were $0\cdot1 \times 0\cdot54 \times 0\cdot24$ mm. Intensity data were collected on a Syntex $P\bar{1}$ four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. 850 independent reflections within a range of $2\theta < 52°$ were collected by the θ–2θ scan technique with a variable scan rate of 4·0–24·0° min^{-1}. 738 reflections with $I > 3\cdot00\sigma(I)$ were considered as observed and were used for the analysis. Lorentz and polarization corrections were applied for the data. Corrections for the absorption effect were made (Busing & Levy, 1957).

The structure was solved by a combination of minimum-function and heavy-atom methods. Systematic subcell absences found on the Weissenberg photographs were consistent with space groups $C2$, Cm or $C2/m$. Of these, $C2$ was selected on the basis of the restriction on the crystal packing of the counter ions and the conformation of the ethylenediamine, and was later confirmed in the course of the structure determination. The positions of all non-hydrogen atoms were obtained from the minimum-function maps. Block-diagonal least-squares refinement of the atomic coordinates and isotropic thermal parameters was carried out, and the discrepancy indices $R_1 = \sum||F_o| - |F_c||/|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$

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* Studies on Mixed-Valence Complexes of Platinum and Palladium. III.

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were 9·06 and 11·27% respectively. The refinement then proceeded with anisotropic temperature factors for the Pt, I and Cl atoms, and the final discrepancy indices were $R_1 = 5{\cdot}41$ and $R_2 = 6{\cdot}57\%$. A final difference Fourier synthesis showed no significant feature. In the least-squares procedure, the weighting scheme was $w = (1{\cdot}5 + 0{\cdot}067|F_o|)^{-1}$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on the FACOM M-190 computer in the Computer Center of Kyushu University with *UNICS* II (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). Atomic coordinates with respect to the subcell are listed in Table 1, I(1) and I(2) being given half-weight.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic temperature factors of the non-hydrogen atoms*

The atomic parameters are given with respect to the subcell unit for which b is halved ($b = 5{\cdot}820$ Å).

	x	y	z	B (Å^2)
Pt	0	0	0	1·39
I(1)	0	5353 (20)	0	2·36*
I(2)	0	4684 (16)	0	2·33*
Cl	1407 (3)	5083 (40)	4740 (8)	3·34
O(1)	829 (12)	7093 (43)	4626 (28)	3·3 (3)
O(2)	1023 (13)	3030 (41)	4624 (32)	3·4 (4)
O(3)	1933 (16)	5285 (95)	6389 (38)	7·1 (7)
O(4)	1836 (13)	5340 (80)	3183 (31)	5·1 (5)
N(1)	1153 (9)	321 (54)	1381 (22)	2·2 (3)
N(2)	537 (9)	236 (70)	−2246 (19)	1·7 (2)
C(1)	1721 (18)	−603 (45)	59 (42)	3·0 (5)
C(2)	1453 (17)	583 (57)	−1732 (39)	3·7 (6)

* Occupancy 0·5.

Table 2. *Bond distances* (Å) *and angles* (°)

Pt$^{(i)}$–I(1)	2·704 (11)	N(2)–C(2)	1·55 (3)
Pt–I(1)	3·115 (11)	C(1)–C(2)	1·50 (4)
Pt$^{(i)}$–I(2)	3·039 (9)	Cl–O(1)	1·51 (2)
Pt–I(2)	2·726 (9)	Cl–O(2)	1·35 (3)
Pt–N(1)	2·07 (1)	Cl–O(3)	1·40 (2)
Pt–N(2)	2·01 (1)	Cl–O(4)	1·46 (2)
N(1)–C(1)	1·56 (3)		

(i) Symmetry operation $x, -1 + y, z$.

I(1)–Pt–N(1)	95·1 (9)	N(1)–C(1)–C(2)	105 (2)
I(1)–Pt–N(2)	93·0 (11)	N(2)–C(2)–C(1)	108 (2)
I(2)–Pt–N(1)	84·8 (9)	O(1)–Cl–O(2)	112 (1)
I(2)–Pt–N(2)	86·0 (11)	O(1)–Cl–O(3)	107 (2)
N(1)–Pt–N(2)	84 (1)	O(1)–Cl–O(4)	105 (2)
Pt–N(1)–C(1)	106 (2)	O(2)–Cl–O(3)	111 (3)
Pt–N(2)–C(2)	111 (2)	O(2)–Cl–O(4)	109 (2)
		O(3)–Cl–O(4)	110 (1)

Hydrogen bonds	
O(1)–N(1)$^{(i)}$	3·16 (2)
O(1)–N(1)$^{(ii)}$	3·05 (2)
O(2)–N(1)$^{(iii)}$	2·91 (2)
O(2)–N(2)$^{(iv)}$	3·04 (2)

Symmetry code*	
(i)	$x, 1 + y, z$
(ii)	$x, 1 + y, 1 + z$
(iii)	x, y, z
(iv)	$x, y, 1 + z$

* With respect to the subcell.

Discussion. The molecular structure of $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$ and the atom-numbering scheme utilized for the description of the molecule are shown in Fig. 1. Bond distances and angles with their estimated standard deviations are listed in Table 2.

The structures of a number of similar mixed-valence compounds of Pt or Pd have been studied (Brosset, 1948; Hall & Williams, 1958; Ryan & Rundle, 1961; Craven & Hall, 1961, 1966; Wallen, Brosset & Vannerberg, 1962; Brown & Hall, 1976; Matsumoto, Yamashita & Kida, 1978*b*), and in every case the odd layer lines about the chain axis were diffuse and continuous, except for our three complexes $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$ and $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ (Matsumoto, Yamashita & Kida, 1978*b*). In the case of Reihlen's green salt $[Pt(ea)_4][PtBr_2(ea)_4]Br_4.4H_2O$ (ea = ethylamine), Brown & Hall (1976) explained the diffuse and continuous odd layer lines on the assumption that stacking mistakes displace the chain by one-half of the repeat unit. Accordingly, in the present compound the disorder may also be attributed to stacking mistakes similar to those assumed for Reihlen's green, as shown in Fig. 2. These stacking mistakes only cause disorder of the iodine atoms, which may exert little effect on the stacking energy of the crystal. By analogy with the

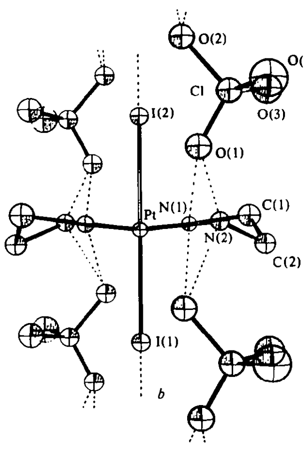

Fig. 1. A perspective drawing of the molecule. The thermal ellipsoids are drawn at the 30% probability level.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34199 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chloro and bromo analogs, we regarded the linear chain as consisting of alternately arranged tetragonal-bipyramidal $[Pt(en)_2I_2]^{2+}$ and square-planar $[Pt(en)_2]^{2+}$ units, where 2·704 (11), 2·726 (9) Å and 3·115 (11), 3·039 (9) Å are assigned as the Pt^{IV}—I and Pt^{II}—I distances respectively. The thermal parameters of N(1), N(2), C(1) and C(2) are normal. Therefore, the dimensions and conformation of the Pt^{II} and Pt^{IV} species should be the same except for the Pt—I bond; this is because such differences between the Pt^{II} and Pt^{IV} species would result in high thermal parameters in the average subcell structure.

The distances N(1)—O(1), N(1)—O(2), N(2)—O(1), and N(2)—O(2) indicate that there are hydrogen bonds between these atoms. These hydrogen bonds should contribute to the formation of the infinite chain, as was observed for the chloro and bromo analogs.

The ratio of the Pt^{IV}—I and Pt^{II}—I distances is 0·93, which is much higher than the ratios of the Pt^{IV}—halogen and Pt^{II}—halogen distances reported for the bromo (0·86, 0·87) and chloro (0·76) analogs (Matsumoto, Yamashita & Kida, 1978*b*). The above results imply that the difference in the oxidation states between Pt^{IV} and Pt^{II} atoms is reduced in the order: chloro, bromo and iodo analogs.

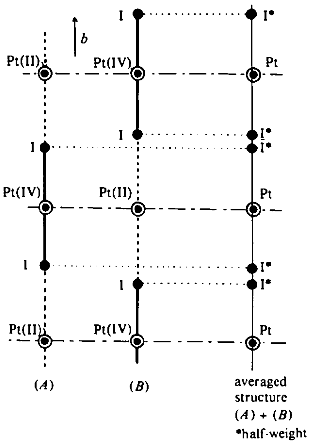

Fig. 2. An illustration of the disorder along **b**.

Recently, we evaluated the quantitative values of the oxidation states of these complexes from the X-ray photoelectron spectra (ESCA), and confirmed that the ESCA results were consistent with the above structural results (Yamashita, Matsumoto & Kida, 1978).

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Tetrakis(*N*,*N'*-diethylthiourea)cobalt(II) Diperchlorate

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Abstract. $[Co(C_5H_{12}N_2S)_4](ClO_4)_2$, $C_{20}H_{48}Cl_2CoN_8O_8S_4$, orthorhombic, *Pbcn*, $a = 19{\cdot}447$ (4), $b = 13{\cdot}939$ (4), $c = 14{\cdot}360$ (5) Å, $Z = 4$, $D_o = 1{\cdot}36$ (1), $D_c = 1{\cdot}342$ Mg m^{-3}. The structure contains discrete $Co[S{=}C(NHCH_2CH_3)_2]_4^{2+}$ ions with point symmetry 2. Each Co atom is ligated by four S atoms having a

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