

rather coplanar with the principal plane I [interplanar angle 2 (1)°].

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Structure of a Bromo-Bridged One-Dimensional Pd^{II}–Pd^{IV} Mixed-Valence Complex, *catena*- μ -Bromo-bis(ethylenediamine)palladium(II,IV) Diperchlorate, [Pd(C₂H₈N₂)₂][PdBr₂(C₂H₈N₂)₂](ClO₄)₄

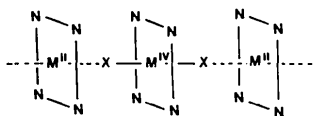
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Abstract. $M_r = 1010.80$, orthorhombic, *Imcb*, $a = 10.814$ (1), $b = 13.608$ (2), $c = 9.663$ (4) Å, $V = 1422.0$ (3) Å³, $Z = 2$, $D_x = 2.38$, $D_m = 2.39$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 4.677$ mm⁻¹, $F(000) = 988$, room temperature, $R = 0.038$, $wR = 0.050$ for 1016 observed reflections [$|F_o| > 3\sigma(F_o)$]. The crystal comprises linear chains, ...Pd^{II}...Br–Pd^{IV}–Br, parallel to the a axis, where tetragonal [PdBr₂(en)₂]²⁺ and square-planar [Pd(en)₂]²⁺ units are stacked alternately with bromo bridges. The Pd^{IV}–Br and Pd^{II}...Br distances along the chain are 2.496 (1) and 2.911 (1) Å, respectively. The ratio between Pd^{IV}–Br and Pd^{II}...Br distances is 0.86, which is larger than that of the chloro analog (0.77).

Introduction. Halogen-bridged one-dimensional M^{II} – M^{IV} mixed-valence complexes ($M = \text{Pt, Pd and Ni}$) having the structure



have attracted much interest from the viewpoint of low-dimensional compounds (Miller & Epstein,

1976). Their solid-state physical properties such as electronic absorption and emission spectra, and electrical conductivity, have been studied as functions of bridged halogens, metals, in-plane ligands and counter anions (Matsumoto, Yamashita & Kida, 1978a; Hamaue, Aoki, Yamashita & Kida, 1981; Yamashita, Matsumoto & Kida, 1978; Yamashita, Nonaka, Kida, Hamaue & Aoki, 1981; Tanino & Kobayashi, 1983; Yamashita & Ito, 1984). For an understanding of the physical properties, structural parameters along the linear chain are of fundamental importance. In this paper, we describe the structure of the title compound. Recently, the structure of its chloro analog, [Pd(en)₂][PdCl₂(en)₂](ClO₄)₄, was reported (Beauchamp, Layek & Theophanides, 1982).

Experimental. Golden needles elongated along the a axis recrystallized from dilute perchloric acid. D_m by flotation in CHBr₃/CHCl₃. Crystal 0.50 × 0.30 × 0.22 mm. Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions by least-squares fit of 50 2θ values ($25^\circ < 2\theta < 30^\circ$). Intensities in the range $2\theta < 65^\circ$ measured with θ – 2θ scan technique. h 0→16, k 0→20, l 0→14. Three reference reflections monitored periodically showed no significant intensity deterioration. 2933 unique reflections measured. Intensity data corrected for Lorentz–polarization factors and for absorption. Structure solved by conventional heavy-atom method and refined

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on $|F|$ by block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H (from ΔF maps). Positional disorder of perchlorate ions observed and taken into consideration in the refinement. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1974). Weighting scheme $w = [\sigma_{\text{count}}^2 + (0.015|F_o|)^2]^{-1}$ employed. $\Delta/\sigma < 0.5$, $-1.3 < \Delta\rho < 0.8 \text{ e \AA}^{-3}$. No correction for secondary extinction. Calculations carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICSIII (Sakurai & Kobayashi, 1979).

Discussion. Atomic parameters are listed in Table 1.* The crystal structure of $[\text{Pd}(\text{en})_2][\text{PdBr}_2(\text{en})_2](\text{ClO}_4)_4$ along with the atomic numbering system is shown in Fig. 1. Relevant bond distances and angles are given in Table 2. The crystal is isomorphous with the chloro analog and its structure is essentially similar to those of Pt analogs (Matsumoto, Yamashita & Kida, 1978*b*; Matsumoto, Yamashita, Ueda & Kida, 1978; Yamashita, Ito, Toriumi & Ito, 1983). As shown in Fig. 1, the square-planar four-coordinate Pd^{II} and the octahedral six-coordinate Pd^{IV} units, both of which have a 2+ charge, are stacked alternately in the direction of the a axis, constructing linear chains of $\dots\text{Pd}^{\text{II}}\dots\text{Br}-\text{Pd}^{\text{IV}}-\text{Br}$ segments. The neighboring Pd^{II} and Pd^{IV} units in the chain are linked by two hydrogen bonds between NH groups of the ligand and O of the perchlorate ions $[\text{NH}\dots\text{O} = 3.025(6) \text{ \AA}]$. No significant interactions among the chains are observed.

As has been observed previously for most $M^{\text{II}}-M^{\text{IV}}$ mixed-valence complexes of this type, the bridging Br atoms are positionally disordered. The Br atom occupies two positions on the C_2 axis equidistant from the midpoint ($2/m$ site) between two Pd atoms with an occupancy factor of 0.25, the two positions being $0.416(2) \text{ \AA}$ apart. Because of the disorder, the oxidation states of the Pd atoms cannot be identified and all the Pd sites comprise $\frac{1}{2}\text{Pd}^{\text{II}} + \frac{1}{2}\text{Pd}^{\text{IV}}$ as in the chloro analog (Beauchamp, Layek & Theophanides, 1982). The shorter Pd-Br distance of $2.496(1) \text{ \AA}$ corresponds to the distance between the Pd^{IV} and Br atoms, whereas the longer one $[2.911(1) \text{ \AA}]$ is for the $\text{Pd}^{\text{II}}\dots\text{Br}$ separation. No positional disorder was found for the ethylenediamine moieties. Thus, the molecular dimensions of the $\text{Pd}(\text{en})_2$ moiety in the Pd^{II} and Pd^{IV} units are crystallographically the same (Yamashita, Ito, Toriumi & Ito, 1983).

* List of anisotropic thermal parameters for non-hydrogen atoms, atomic parameters for H atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42077 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The distance between Pd^{II} and Pd^{IV} atoms along the chain $[5.407(1) \text{ \AA}]$ is slightly longer (*ca* 0.05 \AA) than that in the chloro-bridged analog. The $\text{Pd}^{\text{IV}}-\text{X}$ bond distance in the bromo complex is longer by 0.172 \AA than that in the chloro analog $[2.324(3) \text{ \AA}]$, whereas the $\text{Pd}^{\text{II}}\dots\text{X}$ in the former is slightly shorter than that in the latter $[3.033(3) \text{ \AA}]$. The ratios between the $\text{Pd}^{\text{IV}}-\text{X}$ and $\text{Pd}^{\text{II}}\dots\text{X}$ bond distances are 0.86 and 0.77 for the bromo- and chloro-bridged complexes, respectively, suggesting that the difference of the oxidation states between Pd^{II} and Pd^{IV} atoms in the bromo-bridged

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) for non-hydrogen atoms

$$B_{\text{eq}} = \frac{1}{3} \sum_i \beta_i \mathbf{a}_i \cdot \mathbf{a}_i$$

	x	y	z	Occupancy factor	B_{eq}
Pd	2500	0	0	0.25	1.5
Br	4808 (1)	0	0	0.25	2.3
N	2485 (2)	-1006 (2)	-1582 (3)	1.00	2.4
C	2801 (3)	-494 (4)	-2890 (4)	1.00	3.1
Cl	5000	3041 (2)	690 (2)	0.30	2.5
Cl'	5000	2893 (2)	972 (3)	0.20	2.6
O(1)	3909 (2)	2638 (4)	175 (4)	1.00	5.2
O(2)	5000	4036 (5)	427 (11)	0.30	5.4
O(3)	5000	2891 (11)	2162 (9)	0.30	9.3
O(2')	5000	3797 (9)	1660 (19)	0.20	6.8
O(3')	5000	2139 (13)	1994 (18)	0.20	9.8

Table 2. Bond distances (\AA) and angles ($^\circ$) within the complex cation with their *e.s.d.*'s (in parentheses)

Pd-Br	2.496 (1)	Br-Pd-N	90.45 (7)
Pd...Br'	2.911 (1)	N-Pd-N ^{II}	83.7 (1)
Pd-N	2.052 (3)	Pd-N-C	108.7 (2)
N-C	1.484 (5)	N-C-C ^{II}	108.8 (3)
C-C ^{II}	1.495 (7)		

Key to symmetry operations: (i) $-x, y, z$; (ii) $\frac{1}{2}-x, -y, z$.

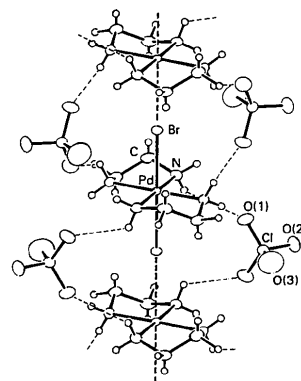


Fig. 1. Portion of the infinite chain along a with surrounding ClO_4^- ions. The disordered perchlorate ion with minor occupancy factor is omitted for clarity. The thick and thin dashed lines represent the $\text{Pd}^{\text{II}}\dots\text{Br}$ bond and the hydrogen bond, respectively.

complex is much reduced compared with that in the chloro-bridged complex. This result is consistent with the spectral and conductivity data reported previously (Aoki, Hamaue, Kida, Yamashita, Takemura, Furuta & Kawamori, 1982).

Interestingly, the bond-distance ratios of the chloro- and bromo-bridged Pd complexes, [Pd(en)₂][PdX₂(en)₂](ClO₄)₄, are comparable to those of the chloro- and bromo-bridged Pt analogs, respectively, whereas the spectral and conductivity data of the chloro and bromo Pd complexes are nearly equal to those of the bromo and iodo Pt analogs, respectively (Aoki *et al.*, 1982).

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Structure of Di- μ -chloro-tetrachlorobis(tetrahydrofuran)-[μ -(dimethyl sulfide)]-diniobium(Nb–Nb), [Nb₂Cl₆(C₄H₈O)₂(C₂H₆S)], and Di- μ -chloro-tetrachlorobis(tetrahydrofuran)-[μ -(dimethyl sulfide)]-ditantalum(Ta–Ta), [Ta₂Cl₆(C₄H₈O)₂(C₂H₆S)]

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Abstract. [NbCl₂(THF)]₂(μ -Cl)₂(μ -SMe₂): M_r = 604.88, triclinic, $P\bar{1}$, a = 8.104 (1), b = 16.669 (5), c = 7.917 (4) Å, α = 101.28 (3), β = 95.21 (3), γ = 81.24 (2)°, V = 1034 (1) Å³, Z = 2, D_x = 1.942 Mg m⁻³, Mo $K\alpha$, λ = 0.71073 Å, μ = 1.94 mm⁻¹, $F(000)$ = 596, T = 298 K, R = 0.0575 for 1816 ($I \geq 3\sigma$) reflections. [TaCl₂(THF)]₂(μ -Cl)₂(μ -SMe₂): M_r = 780.96, triclinic, $P\bar{1}$, a = 8.122 (2), b = 16.663 (4), c = 7.932 (1) Å, α = 101.44 (2), β = 95.56 (2), γ = 81.18 (2)°, V = 1037 (1) Å³, Z = 2, D_x = 2.502 Mg m⁻³, Mo $K\alpha$, λ = 0.71073 Å, μ = 11.30 mm⁻¹, $F(000)$ = 724, T = 298 K, R = 0.0293 for 2886 ($I \geq 3\sigma$) reflections. The metal–metal bond lengths are: Nb=Nb 2.684 (2) and Ta=Ta 2.6695 (5) Å. The structures of these two confacial-bioctahedral complexes are isomorphous and correspond with the structures of similar Nb and Ta complexes previously studied. The metal–Cl and

metal–S bond lengths fall into a very narrow range, even when different *trans* ligands are present.

Introduction. Niobium and tantalum in their oxidation states of III exhibit a remarkable tendency to form dimeric complexes (Cotton & Walton, 1982; Rocklage, Turner, Fellmann & Schrock, 1982; Templeton, Dorman, Clardy & McCarley, 1978). There are two general types of geometry that these complexes adopt: edge-sharing bioctahedron or confacial bioctahedron (Cotton & Roth, 1983; Sattelberger, Wilson & Huffman, 1982; Cotton & Najjar, 1981; Templeton & McCarley, 1978; Cotton & Hall, 1980). There are indications that in the confacial-bioctahedral complexes, $M_2X_6(L_1)_2(\mu-L_2)$, M = Nb and Ta, X = Cl and Br and $L_1 = L_2$ = tetrahydrothiophene (THT) or SMe₂, the terminal ligands (L_1) are more labile than the bridging ones (L_2) and are easily replaced (Cotton, Falvello & Najjar, 1982; Cotton & Hall, 1980; Keen & Brown, 1982). We have further

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