HUNTER, W. N., MUIR, K. W. & SHARP, D. W. A. (1985). *Acta Cryst.* C**41**, 1750–1752.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

MANOJLOVIĆ-MUIR, LJ. & MUIR, K. W. (1974). *Inorg. Chim. Acta*, **10**, 47–49.

TORRENS, H. (1977). PhD Thesis, Univ. of Glasgow.

Acta Cryst. (1986). C**42**, 963–968

Structures of One-Dimensional Pd^{II}–Pd^{IV} Mixed-Valence Complexes, $[Pd^{II}L][Pd^{IV}Cl_2L]Y_4$ ($Y = ClO_4$ and PF_6), and Their Parent Pd^{II} and Pd^{IV} Complexes, $[Pd^{II}L](ClO_4)_2$ and $[Pd^{IV}Cl_2L](NO_3)_2.HNO_3.H_2O$, with 1,4,8,11-Tetraazacyclotetradecane (L)

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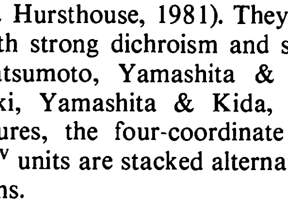
Abstract. Molecular and crystal structures of the title compounds, $[Pd^{II}L](ClO_4)_2$ (1), $[Pd^{IV}Cl_2L](NO_3)_2.HNO_3.H_2O$ (2), $[Pd^{II}L][Pd^{IV}Cl_2L](ClO_4)_4$ (3), and $[Pd^{II}L][Pd^{IV}Cl_2L](PF_6)_4$ (4), have been determined by single-crystal X-ray diffraction at room temperature, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å. Crystal data are: for (1), $C_{10}H_{24}Cl_2N_4O_8Pd$, $M_r = 505{\cdot}65$, orthorhombic, *Pbnm*, $a = 13{\cdot}337$ (2), $b = 14{\cdot}492$ (3), $c = 9{\cdot}746$ (2) Å, $U = 1883{\cdot}8$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}30$ mm^{-1}, $F(000) = 1024$, $R = 0{\cdot}054$, $wR = 0{\cdot}066$ for 1824 observed reflections; for (2), $C_{10}H_{27}Cl_2N_7O_{10}Pd$, $M_r = 582{\cdot}69$, triclinic, $P\bar{1}$, $a = 9{\cdot}549$ (1), $b = 16{\cdot}034$ (1), $c = 7{\cdot}863$ (1) Å, $\alpha = 86{\cdot}59$ (1), $\beta = 111{\cdot}51$ (1), $\gamma = 103{\cdot}27$ (1)°, $U = 1089{\cdot}6$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}78$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}15$ mm^{-1}, $F(000) = 592$, $R = 0{\cdot}023$, $wR = 0{\cdot}035$ for 5730; for (3), $C_{20}H_{48}Cl_6N_8O_{16}Pd_2$, $M_r = 1082{\cdot}20$, monoclinic, $C2/c$, $a = 17{\cdot}649$ (12), $b = 9{\cdot}738$ (8), $c = 11{\cdot}067$ (8) Å, $\beta = 91{\cdot}33$ (6)°, $U = 1901$ (3) Å^3, $Z = 2$, $D_x = 1{\cdot}89$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}43$ mm^{-1}, $F(000) = 1092$, $R = 0{\cdot}041$, $wR = 0{\cdot}061$ for 1708; for (4), $C_{20}H_{48}Cl_2F_{24}N_8P_4Pd_2$, $M_r = 1264{\cdot}25$, monoclinic, $P2_1/m$, $a = 9{\cdot}978$ (5), $b = 11{\cdot}638$ (4), $c = 9{\cdot}917$ (3) Å, $\beta = 117{\cdot}17$ (2)°, $U = 1024{\cdot}6$ (7) Å^3, $Z = 1$, $D_x = 2{\cdot}05$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}30$ mm^{-1}, $F(000) = 626$, $R = 0{\cdot}055$, $wR = 0{\cdot}080$ for 2299. The coordination geometry of (1) is of the square-planar type with an average Pd–N distance of 2·051 (7) Å, whereas (2) is a six-coordinate complex of the *trans*-$PdCl_2N_4$ type with mean Pd–N and Pd–Cl lengths of 2·062 (4) and 2·303 (1) Å, respectively. In (3) and (4), the four-coordinate Pd^{II} and six-coordinate Pd^{IV}, both of which have a 2+ charge, are stacked alternately in the direction of the needle axis, constructing linear chains of $\cdots Cl–Pd^{IV}–Cl\cdots Pd^{II}\cdots$ segments. Neighboring Pd^{II} and Pd^{IV} units are connected by hydrogen bonds, $NH\cdots X\cdots HN$ ($X = O$ for 3 and $X = F$ for 4). In both (3) and (4), the bridging Cl atoms are statistically disordered and all Pd sites comprise $\frac{1}{2}Pd^{II} + \frac{1}{2}Pd^{IV}$. Average coordination bond distances in the chain structures are: Pd–N = 2·055 (5) Å for (3) and 2·049 (8) Å for (4); Pd^{IV}–Cl = 2·319 (3) Å for (3) and 2·309 (3) Å for (4); $Pd^{II}\cdots Cl$ = 3·219 (3) Å for (3) and 3·514 (3) Å for (4). In all the complexes, the macrocyclic ligand L adopts the same, most stable, chelate ring conformation, the two six- and two five-membered rings being in chair and *gauche* forms, respectively. Structural changes upon the formation of the one-dimensional linear chain structure are discussed.

Introduction. Recently much interest has been attracted to one-dimensional M^{II}–M^{IV} mixed-valence complexes of Pt, Pd and Ni from the viewpoint of the chemistry and physics of low-dimensional compounds (Miller & Epstein, 1976; Yamashita, Nonaka, Kida, Hamaue & Aoki, 1981; Aoki, Hamaue, Kida, Yamashita, Takemura, Furuta & Kawamori, 1982; Clark, Kurmoo, Galas & Hursthouse, 1981). They show lustrous deep color with strong dichroism and semiconducting behavior (Matsumoto, Yamashita & Kida, 1978*a*; Hamaue, Aoki, Yamashita & Kida, 1981). In the crystal structures, the four-coordinate M^{II} and six-coordinate M^{IV} units are stacked alternately, constructing linear chains.



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In compounds of this type, the ratio between M^{IV}–X and $M^{II}\cdots X$ distances strongly affects physical properties along the chain, the degree of which depends on the kind of metals, bridging halogens, counter anions, or in-plane ligands. It has been pointed out that, as the ratio approaches unity, the difference between the oxidation states of M^{II} and M^{IV} decreases. This is evidenced by electronic spectra, X-ray photoelectron spectra, and electrical conductivities (Matsumoto, Yamashita & Kida, 1978*b*; Matsumoto, Yamashita, Ueda & Kida, 1978; Matsumoto, Yamashita, Kida & Ueda, 1979; Hamaue, Aoki, Yamashita & Kida, 1981; Yamashita, Matsumoto, & Kida, 1978). When the ratio is unity, that is, when X is located midway between the metals, every metal atom becomes equivalent, *i.e.* tervalent, and the compound should show metallic behavior.

In the present study, the crystal structures of the title compounds have been determined in order to compare the structural parameters of the chain structures with those of the discrete component complexes. To our knowledge, no study from such a standpoint has been reported for one-dimensional complexes of this type. A preliminary report on the syntheses and structural characterization of the present compounds appeared elsewhere (Yamashita, Ito, Toriumi & Ito, 1983).

Experimental. Mixed-valence complexes and parent complexes synthesized by methods described previously (Yamashita, Ito, Toriumi & Ito, 1983); single crystals of (1) and (3) grown from dilute perchloric acid solution, (2) and (4) from aqueous solutions containing HNO_3 and $NaPF_6$, respectively.

Rigaku AFC-5 automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}71073$ Å), θ–2θ scan technique. Conditions for the intensity measurements: for (1), colorless tabular crystals, dimensions $0{\cdot}28 \times 0{\cdot}26 \times 0{\cdot}24$ mm, $2\theta_{max} = 60°$, $h\,0\rightarrow18$, $k\,0\rightarrow20$, $l\,0\rightarrow13$, number of measured reflections = 3040, number of observed reflections $[|F_o| > 3\sigma(|F_o|)] = 1824$, $R_{int}(F) = 0{\cdot}005$ for three equivalent reflections; for (2) [in same order as for (1)], yellow tabular crystals, $0{\cdot}55 \times 0{\cdot}55 \times 0{\cdot}50$ mm, 60°, $h\,-14\rightarrow13$, $k\,0\rightarrow24$, $l\,-11\rightarrow11$, 7230, 5757, 0·005 for 406; for (3), lustrous green needles with (001) elongated, $0{\cdot}40 \times 0{\cdot}18 \times 0{\cdot}18$ mm, 60°, $h\,-24\rightarrow24$, $k\,0\rightarrow13$, $l\,-15\rightarrow15$, 6400, 1708, 0·032 for 1708; for (4), lustrous brown needles with (010) elongated, $0{\cdot}64 \times 0{\cdot}44 \times 0{\cdot}36$ mm, 60°, $h\,0\rightarrow14$, $k\,0\rightarrow16$, $l\,-13\rightarrow12$, 3286, 2299, 0·015 for 126. A crystal of (2) was shaped by a thin paraffin-coated knife and inserted into a thin-walled glass capillary to prevent deterioration of the crystal. Crystals of (3) and (4) coated with a thin layer of epoxy resin. Three reference reflections monitored periodically showed no significant intensity deterioration for each crystal.

Intensity data corrected for Lorentz–polarization factors; absorption corrections made with a numerical Gaussian integration method (6 × 6 × 6 grids); unit-cell dimensions determined by a least-squares method based on 50 θ values ($12° < \theta < 15°$) for (1), (2) and (4), and 47 θ values ($10° < \theta < 14°$) for (3).

All structures solved and refined on $|F|$ by standard Patterson, Fourier, and block-diagonal least-squares techniques with anisotropic thermal parameters for non-H atoms and isotropic for H; scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974), those for H from Stewart, Davidson & Simpson (1965); effects of anomalous dispersion for non-H atoms were corrected. Weighting scheme: $w = [\sigma^2_{count} + (0{\cdot}015|F_o|)^2]^{-1}$, σ_{count} standard deviation of F_o calculated from counting statistics. Crystal-structure analyses successfully made by applying centrosymmetric space groups for all crystals. $\Delta/\sigma < 0{\cdot}5$. No correction for secondary extinction.

Except for compound (1), difference syntheses permitted location of all H atoms, including H atom of HNO_3 for (2), and their positional and isotropic thermal parameters were refined.

In the initial stages of structure analyses for (3) and (4), positional disorder of Cl atoms on the $\cdots$Cl—Pd^{IV}—Cl$\cdots Pd^{II}\cdots$ linear chains was found in Patterson and Fourier maps. The Cl atom in (3) was disordered at two sites related by the twofold axis on $(0,y,\frac{1}{4})$, and again Cl in (4) was disordered at two sites related by the mirror plane on $y = \frac{1}{4}$. Difference syntheses for (1), (3), and (4) also revealed orientational disorder of the counter anions [ClO_4 for (1) and (3), PF_6 for (4)], and their positional and anisotropic thermal parameters were refined.

In the final stage of the refinement for (2), it was revealed that 27 strong, low-angle reflections were seriously affected by a secondary-extinction effect. To improve the accuracy of atomic parameters, they were excluded in the final refinement.

Peaks in the final difference Fourier maps: for (1), $-0{\cdot}7 < \Delta\rho < 2{\cdot}0$ e Å^{-3}; for (2), $-0{\cdot}8 < \Delta\rho < 0{\cdot}5$ e Å^{-3}; for (3), $-1{\cdot}3 < \Delta\rho < 1{\cdot}5$ e Å^{-3}; for (4), $-1{\cdot}0 < \Delta\rho < 2{\cdot}2$ e Å^{-3}. Atomic parameters for non-H atoms in compounds (1)–(4) are given in Tables 1–4.*

All calculations carried out on HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS*III (Sakurai & Kobayashi, 1979).

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, atomic parameters for hydrogen atoms, and perspective drawings of crystal structures for (1) and (2), have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42869 (71 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Fig. 1 shows the atom-numbering scheme. Perspective drawings of the complex cations in (1), (2) and (3) are presented in Figs. 2–4, respectively. Bond distances and angles except for those of counter anions are listed in Table 5. Hydrogen-bond parameters are given in Table 6.

$[\mathrm{Pd^{II}}L](\mathrm{ClO_4})_2$ (1). The crystal consists of discrete $[\mathrm{Pd}L]^{2+}$ and $\mathrm{ClO_4^-}$. The $\mathrm{Pd^{II}}$ ion is surrounded by four N atoms of the macrocyclic ligand in a square-planar fashion with an average distance of 2·051 (7) Å. The $\mathrm{Pd^{II}}$ is located on a mirror plane passing through Pd, C(6), and C(13). The macrocyclic ligand adopts the most stable ring conformations; six-membered rings take a chair form and five-membered rings are in a *gauche* conformation. The bond lengths and angles within the ligand are normal (Ito, Sugimoto, Toriumi & Ito, 1981; Bosnich, Mason, Pauling, Robertson & Tobe, 1965).

Table 1. *Fractional coordinates* ($\times 10^4$, *for* Pd $\times 10^5$) *and equivalent isotropic thermal parameters* (Å^2) *for* $[\mathrm{Pd}L](\mathrm{ClO_4})_2$ (1)

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}
Pd	20559 (4)	12314 (4)	25000	3·6
N(1)	1248 (6)	1818 (5)	4072 (7)	9·0
N(4)	2843 (4)	653 (4)	4081 (7)	7·5
C(2)	1473 (9)	1330 (6)	5357 (8)	9·7
C(3)	2589 (10)	1190 (6)	5349 (9)	10·5
C(5)	3918 (5)	562 (5)	3860 (10)	8·7
C(6)	4166 (9)	43 (8)	2500	11·5
C(13)	−44 (9)	2501 (10)	2500	11·6
C(14)	194 (5)	1939 (7)	3825 (10)	9·3
Cl(1)	3623 (2)	3599 (1)	2500	6·4
Cl(2)	2047 (2)	3731 (2)	7500	10·7
O(1)	4212 (7)	2796 (5)	2500	10·3
O(2)*	2992 (8)	3609 (6)	3639 (14)	13·8
O(3)*	4254 (8)	4361 (7)	2500	12·8
O(4)	2492 (10)	2890 (6)	7500	13·4
O(5)	1436 (6)	3821 (5)	6326 (11)	15·6
O(6)*	2784 (18)	4486 (9)	7500	22·5
O(2′)*	3918 (20)	4267 (17)	3533 (32)	9·9
O(3′)*	2687 (26)	3618 (37)	2500	16·2
O(6′)*	2895 (24)	4170 (25)	7500	8·6

* Occupancies for the disordered atoms are 0·8 for O(2), O(3), and O(6), and 0·2 for O(2′), O(3′), and O(6′).

Table 2. *Fractional coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* (Å^2) *for non-hydrogen atoms for* $[\mathrm{PdCl_2}L](\mathrm{NO_3})_2.\mathrm{HNO_3}.\mathrm{H_2O}$ (2)

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}
Pd(*a*)	0	0	0	1·9
Pd(*b*)	0	50000	50000	2·0
Cl(*a*)	14365 (5)	8676 (3)	25602 (5)	3·1
Cl(*b*)	6758 (5)	59575 (3)	29819 (6)	3·3
N(*a*1)	4736 (15)	10063 (8)	−16066 (18)	2·4
N(*a*4)	19425 (15)	−3172 (9)	−1062 (19)	2·7
N(*b*1)	12396 (17)	59268 (9)	70246 (19)	2·9
N(*b*4)	20491 (16)	46024 (9)	57328 (20)	2·9
C(*a*2)	15915 (20)	8030 (11)	−23381 (24)	3·1
C(*a*3)	27805 (19)	4455 (11)	−7967 (27)	3·2
C(*a*5)	29200 (20)	−6638 (13)	15920 (28)	3·6
C(*a*6)	20079 (23)	−14395 (14)	22181 (30)	4·0
C(*a*7)	8903 (21)	−12478 (12)	30240 (24)	3·3
C(*b*2)	27041 (23)	56570 (12)	81338 (26)	3·9
C(*b*3)	32878 (21)	53067 (13)	68582 (30)	3·8
C(*b*5)	23728 (24)	42950 (14)	41852 (31)	4·1
C(*b*6)	10806 (27)	35842 (14)	30616 (31)	4·5
C(*b*7)	−3949 (28)	38618 (13)	18656 (27)	4·2
N(*n*1)	51613 (18)	26563 (12)	77799 (24)	4·1
N(*n*2)	73047 (18)	17317 (10)	28067 (21)	3·5
N(*n*3)	25668 (18)	31379 (10)	−7306 (22)	3·3
O(*n*1)	44086 (17)	20915 (9)	64224 (20)	4·4
O(*n*2)	52830 (22)	23873 (12)	92965 (23)	6·2
O(*n*3)	56415 (23)	33901 (12)	74371 (25)	6·6
O(*n*4)	72423 (16)	23953 (9)	35427 (19)	3·8
O(*n*5)	62888 (19)	10716 (10)	25920 (25)	5·3
O(*n*6)	84243 (19)	17658 (11)	23444 (27)	5·5
O(*n*7)	22814 (17)	25465 (8)	3199 (18)	3·8
O(*n*8)	20716 (18)	29754 (9)	−24043 (19)	4·2
O(*n*9)	33001 (19)	38525 (9)	−854 (23)	5·2
O(*w*)	46329 (17)	26983 (10)	35815 (20)	4·3

Table 3. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *for non-hydrogen atoms for* $[\mathrm{Pd}L][\mathrm{PdCl_2}L](\mathrm{ClO_4})_4$ (3)

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}
Pd	0	0	0	1·9
Cl(1)*	56 (2)	−30 (4)	2095 (2)	2·7
N(1)	−985 (3)	−1112 (5)	126 (4)	2·4
N(4)	−699 (3)	1686 (5)	21 (4)	2·4
C(2)	−1621 (3)	−164 (7)	−146 (7)	3·6
C(3)	−1460 (4)	1173 (7)	441 (6)	3·5
C(5)	−417 (4)	2871 (6)	715 (5)	3·1
C(6)	361 (4)	3340 (7)	298 (6)	3·6
C(7)	1016 (4)	2411 (7)	620 (6)	3·4
Cl(2)	6665 (1)	1321 (2)	2430 (2)	3·9
O(1)	6803 (4)	905 (8)	1218 (6)	7·9
O(2)*	6183 (5)	2476 (10)	2446 (7)	6·2
O(3)*	6685 (7)	398 (12)	3341 (10)	8·1
O(4)	7350 (6)	1890 (16)	2848 (10)	15·5
O(2′)*	5894 (12)	1703 (29)	2352 (21)	7·9
O(3′)*	6239 (16)	236 (23)	2811 (24)	7·7

* Occupancies for the disordered atoms are 0·5 for Cl(1), 0·7 for O(2) and O(3), and 0·3 for O(2′) and O(3′).

Table 4. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *for non-hydrogen atoms for* $[\mathrm{Pd}L][\mathrm{PdCl_2}L](\mathrm{PF_6})_4$ (4)

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}
Pd	0	0	0	2·3
Cl*	41 (3)	1982 (2)	−90 (3)	3·3
N(1)	−1906 (6)	69 (4)	−2032 (6)	3·8
N(4)	−1453 (7)	80 (4)	939 (7)	3·8
C(2)	−3213 (7)	−139 (6)	−1689 (9)	5·0
C(3)	−2905 (8)	447 (8)	−245 (9)	5·0
C(5)	−922 (8)	720 (6)	2377 (8)	4·5
C(6)	590 (10)	353 (8)	3523 (8)	5·3
C(7)	1878 (8)	629 (7)	3258 (7)	4·8
P(1)	3252 (3)	2500	−2337 (3)	4·1
P(2)	6457 (3)	2500	−5500 (3)	5·1
F(11)	4843 (9)	2500	−2134 (14)	11·5
F(12)	2764 (11)	2500	−4085 (8)	10·7
F(13)	1714 (11)	2500	−2445 (17)	15·7
F(14)	3755 (19)	2500	−652 (12)	18·7
F(15)	3204 (7)	1156 (4)	−2381 (8)	10·5
F(21)	7634 (12)	2500	−3753 (9)	11·8
F(22)	4767 (8)	2500	−6446 (17)	15·4
F(23)*	8289 (14)	2500	−5185 (20)	12·1
F(24)*	5736 (22)	2500	−7360 (16)	9·7
F(25)*	6840 (13)	3708 (9)	−5849 (14)	8·8
F(26)*	5613 (19)	1568 (10)	−4812 (17)	10·3
F(27)*	6363 (20)	3828 (14)	−5295 (22)	6·4
F(28)*	7773 (68)	3247 (27)	−5654 (49)	23·0

* Occupancies for the disordered atoms are 0·5 for Cl, 0·6 for F(23), 0·4 for F(24), 0·5 for F(25) and F(26), and 0·25 for F(27) and F(28), respectively.

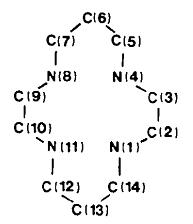

Fig. 1. Atom numbering scheme for 1,4,8,11-tetraazacyclotetradecane (*L*). This numbering scheme is used for all the compounds studied irrespective of the presence of crystallographic symmetry elements.

$[Pd^{IV}Cl_2L](NO_3)_2.HNO_3.H_2O$ (2). The crystal consists of discrete $[PdCl_2L]^{2+}$, NO_3^-, HNO_3 and H_2O, which are linked by hydrogen bonds (Table 6). There are two crystallographically independent cations in a unit cell; their structures are essentially the same. Each Pd^{IV} ion sits at a center of symmetry and is surrounded octahedrally by four N atoms of the macrocyclic ligand in a single plane with an average

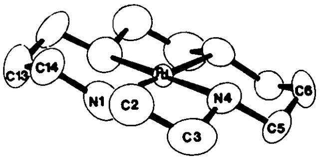

Fig. 2. Perspective drawing of $[Pd^{II}L]^{2+}$ in (1).

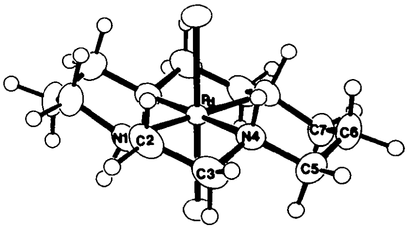

Fig. 3. Perspective drawing of $[Pd^{IV}Cl_2L]^{2+}$ in (2).

Table 5. *Bond distances* (Å) *and angles* (°) *within the complex cations with their e.s.d.'s* (*in parentheses*)

	$[PdL](ClO_4)_2$ (1)	$[PdCl_2L](NO_3)_2.HNO_3.H_2O$ (2*a*)	(2*b*)	$[PdL][PdCl_2L](ClO_4)_4$ (3)	$[PdL][PdCl_2L](PF_6)_4$ (4)
Pd^{IV}–Cl	–	2·303 (1)	2·302 (1)	2·319 (3)	2·309 (3)
$Pd^{II}\cdots$Cl	–	–	–	3·219 (3)	3·514 (3)
Pd–N(1)	2·057 (7)	2·060 (1)	2·058 (1)	2·055 (5)	2·046 (5)
Pd–N(4)	2·044 (7)	2·064 (2)	2·066 (2)	2·054 (5)	2·052 (8)
N(1)–C(2)	1·470 (11)	1·486 (3)	1·497 (3)	1·479 (8)	1·510 (12)
N(4)–C(3)	1·499 (11)	1·490 (2)	1·482 (2)	1·516 (8)	1·451 (8)
N(1)–C(14)	1·437 (10)	1·485 (2)	1·485 (3)	1·510 (8)	1·474 (10)
N(4)–C(5)	1·455 (9)	1·483 (2)	1·496 (3)	1·467 (8)	1·477 (9)
C(2)–C(3)	1·502 (18)	1·515 (2)	1·501 (4)	1·480 (10)	1·486 (13)
C(5)–C(6)	1·560 (11)	1·514 (3)	1·509 (3)	1·529 (10)	1·478 (10)
C(6)–C(7)	1·559 (13)	1·518 (4)	1·528 (3)	1·504 (10)	1·460 (14)
Cl–Pd–N(1)	–	89·28 (4)	87·59 (4)	86·7 (2)	87·0 (1)
Cl–Pd–N(4)	–	91·91 (4)	91·33 (5)	90·6 (2)	90·1 (2)
N(1)–Pd–N(4)	83·0 (3)	84·70 (6)	84·74 (6)	84·9 (2)	85·0 (3)
N(1)–Pd–N(11)	96·3 (3)	–	–	–	–
N(1)–Pd–N(8)	179·2 (3)	–	–	–	–
N(4)–Pd–N(8)	97·8 (3)	–	–	–	–
Pd–N(1)–C(2)	109·2 (6)	106·72 (10)	106·65 (12)	107·2 (4)	106·4 (4)
Pd–N(4)–C(3)	107·0 (5)	106·72 (11)	106·91 (13)	106·1 (4)	107·3 (6)
Pd–N(1)–C(14)	116·0 (6)	115·80 (11)	115·65 (11)	115·1 (4)	115·6 (4)
Pd–N(4)–C(5)	115·5 (5)	115·78 (13)	115·32 (11)	116·0 (4)	116·4 (5)
C(2)–N(1)–C(14)	113·7 (8)	114·01 (14)	113·80 (15)	113·2 (5)	116·2 (5)
C(3)–N(4)–C(5)	113·1 (7)	114·27 (12)	113·80 (16)	113·0 (5)	114·7 (6)
N(1)–C(2)–C(3)	105·3 (8)	107·81 (16)	108·58 (15)	108·9 (5)	108·9 (5)
N(4)–C(3)–C(2)	107·4 (8)	107·72 (13)	108·27 (17)	108·5 (5)	109·6 (7)
N(1)–C(14)–C(13)	113·7 (8)	112·16 (16)	111·62 (17)	110·9 (5)	112·1 (6)
N(4)–C(5)–C(6)	112·2 (7)	111·80 (13)	112·26 (20)	111·9 (5)	112·8 (7)
C(5)–C(6)–C(7)	116·4 (9)	115·05 (19)	115·10 (19)	116·1 (6)	118·1 (7)
C(12)–C(13)–C(14)	111·8 (10)	–	–	–	–

Table 6. *Hydrogen-bond distances* (Å) *with their e.s.d.'s* (*in parentheses*)

Key to symmetry operations: (i) *x*, *y*, *z*; (ii) 1−*x*, −*y*, −*z*; (iii) 1−*x*, 1−*y*, 1−*z*; (iv) *x*, *y*, 1+*z*; (v) 0·5−*x*, −0·5+*y*, 0·5−*z*; (vi) 0·5−*x*, 0·5−*y*, −*z*; (vii) −1+*x*, 0·5−*y*, *z*; (viii) −*x*, −*y*, *z*.

$[PdCl_2L](NO_3)_2.HNO_3.H_2O$ (2)	
$N(a1)\cdots O(n7)^{i}$	2·818 (2)
$N(a4)\cdots O(n6)^{ii}$	2·877 (3)
$N(b1)\cdots O(n4)^{iii}$	2·842 (2)
$N(b4)\cdots O(n8)^{iv}$	2·915 (2)
$O(n1)\cdots O(w)^{i}$	2·445 (2)
$O(n4)\cdots O(w)^{i}$	2·657 (3)
$O(n7)\cdots O(w)^{i}$	2·698 (2)

$[PdL][PdCl_2L](ClO_4)_4$ (3)	
$N(1)\cdots O(2)^{v}$	3·046 (9)
$N(4)\cdots O(2)^{vi}$	2·956 (9)
$N(4)\cdots O(2')^{vi}$	3·07 (3)

$[PdL][PdCl_2L](PF_6)_4$ (4)	
$N(1)\cdots F(21)^{vii}$	3·226 (7)
$N(1)\cdots F(27)^{vii}$	3·16 (2)
$N(4)\cdots F(15)^{viii}$	3·074 (11)

distance of 2·062 (4) Å, and by two Cl atoms occupying the axial positions with an average distance of 2·303 (1) Å. The macrocyclic ligand in (2) again adopts the same most stable ring conformation as that in (1). Two NO_3^- ions and an HNO_3 are linked to a water molecule by strong hydrogen bonds (Table 6), forming a cluster anion $[NO_3H\cdots O(H\cdots O_3N)_2]^{2-}$.

$[Pd^{II}L][Pd^{IV}Cl_2L](ClO_4)_4$ (3). Fig. 4 shows a portion of the infinite chain along the *c* axis of crystal (3). There is only one crystallographically independent Pd atom, which sits on a center of symmetry and is surrounded by four N atoms of the macrocyclic ligand in a square-planar geometry with an average distance of 2·055 (5) Å. Neighboring Pd units are related by a twofold axis that is perpendicular to the chain axis and passes through midpoints between the two Pd atoms and between the perchlorate ions.

As has been observed previously for most M^{II}–M^{IV} mixed-valence compounds of this type, the bridging Cl atoms are positionally disordered. The Cl atom occupies two positions which are related by the twofold axis. These positions are equidistant from the midpoint between two Pd atoms with an occupancy factor of 0·5 and are 0·923 (3) Å apart. From the analogy with the structure of Wolffram's red salt (Craven & Hall, 1961), it can be considered that the four-coordinate Pd^{II} and six-coordinate Pd^{IV} units are stacked alternately in the crystal, constructing linear chains as shown in the structural formula. Because of the disordered structure, the oxidation states of the Pd atoms cannot be identified and all the Pd sites comprise $\frac{1}{2}Pd^{II} + \frac{1}{2}Pd^{IV}$. The shorter Pd—Cl distance [2·319 (3) Å] corresponds to the distance between Pd^{IV} and Cl atoms, whereas the longer one [3·219 (3) Å] is for the separations of the Pd^{II} and Cl atoms. The ratio between the Pd^{IV}–Cl and $Pd^{II}\cdots$Cl is 0·72.

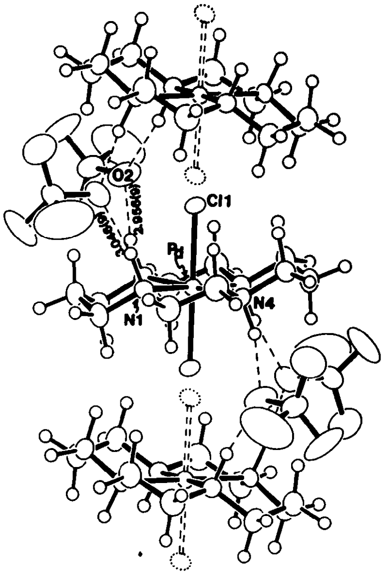

Fig. 4. Perspective drawing of the infinite chain of $\cdots$Cl—Pd^{IV}—Cl$\cdots Pd^{II}\cdots$ along **c** in (3), together with the hydrogen-bond parameters. Disordered perchlorate oxygens with minor occupancies are omitted for clarity. The dashed spheres and bonds represent the disordered positions of the Pd—Cl bonds. The dashed lines correspond to the hydrogen bonds.

The 14-membered macrocyclic ligands in the Pd^{II} and Pd^{IV} units in (3) adopt the most stable ring conformation just as in (1) and (2). The successive macrocycles are, however, rotated by approximately 180° about the chain axis. Neighboring Pd^{II} and Pd^{IV} units are linked by two hydrogen bonds, NH$\cdots$O$\cdots$HN [2·956 (9), 3·046 (9) Å].

No positional disorder is observed for the atoms in the [Pd*L*] moiety, which suggests similar molecular dimensions between $Pd^{II}L$ and $Pd^{IV}L$ units.

$[Pd^{II}L][Pd^{IV}Cl_2L](PF_6)_4$ (4). The crystal structure of this compound is essentially the same as that of (3), consisting of a chain of $\cdots$Cl—Pd^{IV}—Cl$\cdots Pd^{II}\cdots$ segments and counter anions. Neighboring Pd^{II} and Pd^{IV} units are linked by hydrogen bonds, NH$\cdots$F$\cdots$HN [3·074 (11), 3·226 (7) Å]. A Pd atom resides again at a center of symmetry. But two [Pd*L*] units bridged by the hydrogen bonds are related in this case by a mirror plane that is perpendicular to the chain axis and passes through midpoints between the two Pd atoms and between two P atoms of PF_6^- ions. Thus successive macrocycles are rotated exactly by 180° about the chain axis. The bridging Cl atoms are again disordered in the same manner as in (3). All the Pd atom sites comprise $\frac{1}{2}Pd^{II} + \frac{1}{2}Pd^{IV}$. The Pd^{IV}—Cl distances in (3) and (4) are nearly equal to each other, while the $Pd^{II}\cdots$Cl distance in (4) [3·514 (3) Å] is much longer than that in (3) (see below). The ratio between Pd^{IV}–Cl and $Pd^{II}\cdots$Cl distances is 0·66.

It was found that compounds (3) and (4) have a linear chain structure and are Wolffram's red salt analogues (Craven & Hall, 1961). Their chemical and physical properties such as lustrous deep color, diamagnetism, and electrical conductivity (Yamashita, Ito, Toriumi & Ito, 1983) are consistent with those expected for the structures found.

A result which deserves particular emphasis in the present study is that it became possible to compare coordination bond lengths of Pd in various oxidation states and to compare structural parameters of the chain structure with those in the discrete component complexes. All the present compounds have the same in-plane ligand (*L*), which adopts the same overall ring conformation in (1)–(4). Table 7 collates the averaged coordination bond lengths and angles. Interestingly, the Pd–N distances in (1)–(4) are very similar to one another, irrespective of the oxidation states and coordination number of Pd, either in the chain structures or in the discrete complexes. This fact along with the similarity of geometrical features of the [Pd*L*]

Table 7. *Averaged coordination bond distances* (Å) *and angles* (°) *with their e.s.d.'s* (*in parentheses*)

	[Pd*L*](ClO$_4$)$_2$ (1)	[PdCl$_2$*L*](NO$_3$)$_2$.HNO$_3$.H$_2$O (2)	[Pd*L*][PdCl$_2$*L*](ClO$_4$)$_4$ (3)	[Pd*L*][PdCl$_2$*L*](PF$_6$)$_4$ (4)
Pd^{IV}–Cl	–	2·303 (1)	2·319 (3)	2·309 (3)
Pd^{II}···Cl	–	–	3·219 (3)	3·514 (3)
Pd–N	2·051 (7)	2·062 (4)	2·055 (5)	2·049 (8)
Cl–Pd–N(1)	–	88·4 (8)	86·7 (2)	87·0 (1)
Cl–Pd–N(2)	–	91·6 (3)	90·6 (2)	90·1 (2)
N–Pd–N(5*)†	83·0 (3)	84·77 (6)	84·9 (2)	85·0 (3)
Pd–N–C(5*)	108·1 (11)	106·75 (11)	106·7 (6)	106·9 (6)
Pd–N–C(6*)	115·8 (6)	115·6 (2)	115·6 (5)	116·0 (5)

† Abbreviations: 5*, five-membered ring; 6*, six-membered ring.

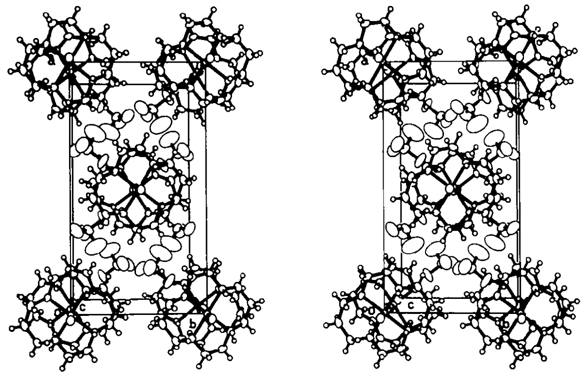

Fig. 5. Stereoscopic view of the crystal structure of (3) along **c**.

moieties is surely responsible for the positional disorder of the bridging Cl$^-$ ions found in (3) and (4).

The Pd^{IV}–Cl distances in the chain structures [2·319 (3) Å for (3) and 2·309 (3) Å for (4)] are very slightly longer than that of the discrete complex [2·303 (1) Å], indicating an electronic interaction along the chains. But the difference is surprisingly small.

Fig. 5 shows the crystal structure of (3) viewed along the *c* axis. One chain consists of alternately stacked Pd^{II} and Pd^{IV} units and ClO$_4^-$. Each ClO$_4^-$ is associated with one chain but does not interact strongly with the neighboring chains. The packing cohesions among the chains are mainly weak electrostatic interactions. The situation is essentially the same in (4), since the features of the crystal structure of (4) are almost the same as (3). An appreciable difference in the crystal structures of (3) and (4) is the Pd^{II}···Pd^{IV} separations along the chain, or Pd^{II}···Cl distances. These distances in (3) are much shorter than those in (4) [Pd^{II}···Pd^{IV} = 5·533 (4) Å for (3) and 5·819 (2) Å for (4); Pd^{II}···Cl = 3·219 (3) Å for (3) and 3·514 (3) Å for (4)].

All the observed facts suggest that there is statistical disorder in the arrangement of the chains. The packing disorder among the chains seems to be observed as the positional disorder of the bridging Cl$^-$ ions.

The ratio of the Pd^{IV}–Cl to Pd^{II}···Cl distance was found to be 0·72 for (3) and 0·66 for (4), respectively. The values indicate that the electronic interaction along the chain is stronger in (3). This is consistent with the data for electrical conductivities and electronic spectra (Yamashita, Ito, Toriumi & Ito, 1983).

When the present linear-chain complexes (3) and (4) are compared with a recently reported ethylenediamine analogue, [Pd(en)$_2$][PdCl$_2$(en)$_2$](ClO$_4$)$_4$ (Beauchamp, Layek & Theophanides, 1982), the electronic interactions along the chain in the ethylenediamine complex are stronger than those in (3) and (4) in view of the distance ratios and electronic spectral data (Matsumoto, Yamashita & Kida, 1978*a*).

References

Aoki, R., Hamaue, Y., Kida, S., Yamashita, M., Takemura, T., Furuta, Y. & Kawamori, A. (1982). *Mol. Cryst. Liq. Cryst.* **81**, 301–309.

Beauchamp, A. L., Layek, D. & Theophanides, T. (1982). *Acta Cryst.* B**38**, 1158–1164.

Bosnich, B., Mason, R., Pauling, P. J., Robertson, G. B. & Tobe, M. L. (1965). *Chem. Commun.* pp. 97–98.

Clark, R. J. H., Kurmoo, M., Galas, A. M. R. & Hursthouse, M. B. (1981). *Inorg. Chem.* **20**, 4206–4212.

Craven, B. M. & Hall, D. (1961). *Acta Cryst.* **14**, 475–480.

Hamaue, Y., Aoki, R., Yamashita, M. & Kida, S. (1981). *Inorg. Chim. Acta*, **54**, L13–L14.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Ito, T., Sugimoto, M., Toriumi, K. & Ito, H. (1981). *Chem. Lett.* pp. 1477–1478.

Matsumoto, N., Yamashita, M. & Kida, S. (1978*a*). *Bull. Chem. Soc. Jpn*, **51**, 2334–2337.

Matsumoto, N., Yamashita, M. & Kida, S. (1978*b*). *Bull. Chem. Soc. Jpn*, **51**, 3514–3518.

Matsumoto, N., Yamashita, M., Kida, S. & Ueda, I. (1979). *Acta Cryst.* B**35**, 1458–1460.

Matsumoto, N., Yamashita, M., Ueda, I. & Kida, S. (1978). *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **11**, 209–216.

Miller, J. S. & Epstein, A. J. (1976). *Prog. Inorg. Chem.* **20**, 1–154.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77 (in Japanese).

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Yamashita, M., Ito, H., Toriumi, K. & Ito, T. (1983). *Inorg. Chem.* **22**, 1566–1568.

Yamashita, M., Matsumoto, N. & Kida, S. (1978). *Inorg. Chim. Acta*, **31**, L381–L382.

Yamashita, M., Nonaka, Y., Kida, S., Hamaue, Y. & Aoki, R. (1981). *Inorg. Chim. Acta*, **52**, 43–46.