stretching modes with increasing of pressure observed for $Pt(dmg)_2$ (Hara & Nicol, 1978; Tkacz & Drickamer, 1986) indicates the shortening of these bond distances. Some bonds are unreasonably long at high pressures. This seems to be a result of the poor accuracy of the determinations at high pressures.

Relationship between the molecular structure and physical properties

The drastic decrease of the electrical resistance and the red shift in the absorption peak at 16 300 cm^{-1} is interpreted in terms of the decrease of Pt—Pt separation within a chain as the pressure rises. A powder X-ray diffraction measurement (Shirotani & Suzuki, 1986) shows that the Pt—Pt distance decreases monotonically up to 13·0 GPa. The strong intermolecular metal—ligand $d\pi$–π^* or ligand—ligand π–π^* interactions within a chain and C—H···O interactions between chains may play an important role in the reverse behavior observed for the electrical resistance at high pressures.

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Mixed-Valence Linear-Chain Complexes: X-ray Structural Characterization of a $Pd^{II}/Pd^{IV}Br_2$ Chain and of Three Mixed-Metal Chains, $[NiPt(en)_4Cl_2]^{4+}$, $[PdPt(pn)_4Cl_2]^{4+}$ and $[NiPt(pn)_4Cl_2]^{4+}$, all as Perchlorate Salts

By Robin J. H. Clark, Vincent B. Croud* and Rachel J. Wills

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, England

and Paul A. Bates, Helen M. Dawes and Michael B. Hursthouse

Chemistry Department, Queen Mary College, University of London, Mile End Road, London E1 4NS, England

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Abstract

The X-ray crystal structures of the mixed-valence linear-chain complexes $[Pd(en)_2][Pd(en)_2Br_2](ClO_4)_4$ (1), $[Ni(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (2), $[Pd(pn)_2][Pt(pn)_2Cl_2](ClO_4)_4$ (3) and $[Ni(pn)_2][Pt(pn)_2Cl_2](ClO_4)_4$ (4), where en = 1,2-ethanediamine and pn = 1,2-propanediamine, are reported. Crystal data are as follows: (1) bis(1,2-ethanediamine)palladium(II) dibromobis(1,2-ethanediamine)palladium(IV) tetra-

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* Present address: Borax Research Ltd, Cox Lane, Chessington, Surrey KT9 1SJ, England.

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perchlorate, $[Pd(C_2H_8N_2)_2][Pd(C_2H_8N_2)_2Br_2](ClO_4)_4$, $M_r = 1010{\cdot}8$, orthorhombic, *Iba*2, $a = 9{\cdot}651$ (1), $b = 13{\cdot}586$ (2), $c = 10{\cdot}774$ (3) Å, $V = 1412{\cdot}7$ (5) Å^3, $Z = 2$, $D_x = 2{\cdot}38$ g cm^{-3}, μ(Mo $K\alpha$) = $43{\cdot}8$ cm^{-1}, $F(000) = 988$, $R = 0{\cdot}039$ for 756 observed data and 117 parameters; (2) bis(1,2-ethanediamine)nickel(II) dichlorobis(1,2-ethanediamine)platinum(IV) tetraperchlorate, $[Ni(C_2H_8N_2)_2][Pt(C_2H_8N_2)_2Cl_2](ClO_4)_4$, $M_r = 962{\cdot}91$, orthorhombic, *Iba*2, $a = 9{\cdot}580$ (1), $b = 13{\cdot}631$ (2), $c = 10{\cdot}744$ (1) Å, $V = 1402{\cdot}9$ (3) Å^3, $Z = 2$, $D_x = 2{\cdot}28$ g cm^{-3}, μ(Mo $K\alpha$) = $61{\cdot}8$ cm^{-1}, $F(000) = 944$, $R = 0{\cdot}032$ for 853 observed data and 117 parameters; (3) bis(1,2-propanediamine)palladium(II) dichlorobis(1,2-propanediamine)platinum(IV) tetraperchlorate, $[Pd(C_3H_{10}N_2)_2][Pt(C_3H_{10}N_2)_2Cl_2](ClO_4)_4$, $M_r = 1066{\cdot}7$, orthorhombic, *Pbam*, $a = 19{\cdot}387$ (6), $b = 7{\cdot}747$ (1), $c = 5{\cdot}496$ (2) Å, $V = 825{\cdot}4$ (4) Å^3, $Z = 1$, $D_x = 2{\cdot}15$ g cm^{-3}, μ(Mo $K\alpha$) = $50{\cdot}81$ cm^{-1}, $F(000) = 522$, $R = 0{\cdot}029$ for 567 observed data and 76 parameters; (4) bis(1,2-propanediamine)nickel(II) dichlorobis(1,2-propanediamine)platinum(IV) tetraperchlorate, $[Ni(C_3H_{10}N_2)_2][Pt(C_3H_{10}N_2)_2Cl_2](ClO_4)_4$, $M_r = 1019{\cdot}02$, orthorhombic, *Pbam*, $a = 19{\cdot}360$ (6), $b = 7{\cdot}756$ (3), $c = 5{\cdot}466$ (6) Å, $V = 820{\cdot}7$ (6) Å^3, $Z = 1$, $D_x = 2{\cdot}06$ g cm^{-3}, μ(Mo $K\alpha$) = $54{\cdot}4$ cm^{-1}, $F(000) = 504$, $R = 0{\cdot}039$ for 564 observed data and 76 parameters. λ(Mo $K\alpha$ = $0{\cdot}71069$ Å, $T = 291$ K for all measurements. The square-planar bis(diamine) metal moieties are linearly but asymmetrically bridged by halogen atoms; change of chlorine to bromine leads to a reduction in the asymmetry and a decrease in the semiconductor band gap. Whilst change in the M^{II} site to a lighter metal (*e.g.* Pt to Pd or Ni) does not radically change the $M^{IV}\cdots M^{II}$ distance, it does lead to an increase in the band gap.

Introduction

Extensive spectroscopic, structural and conductivity studies of complexes with empirical formulae $Pt(LL)_2X(ClO_4)_2$ have shown them to be mixed-valence linear-chain semiconductors of the type $[Pt(LL)_2][Pt(LL)_2X_2](ClO_4)_4$, where LL = 1,2-ethanediamine (en) or 1,2-propanediamine (pn) and X = Cl, Br, or I (Matsumoto, Yamashita, Ueda & Kida, 1978; Cannas, Marongiu, Martin & Keller, 1983; Clark, 1984). These complexes consist of linear chains of nearly planar $Pt(LL)_2$ units which are bridged asymmetrically in the chain direction by halide ions. The heavier halide ions sit nearer to the midpoint between successive Pt atoms, thus reducing the distinction between the oxidation states. The chains are parallel and ordered within a given chain; however, the crystal periodicity in the directions perpendicular to the chain is destroyed by a random relationship between any chain and its immediately adjacent chains.

Recent spectroscopic studies have pointed to the existence of analogous palladium mixed-valence complexes and also of mixed-metal complexes of the sort $[M(LL)_2][M'(LL)_2X_2](ClO_4)_4$, where M = Ni or Pd, M' = Pt, X = Cl, Br or I, and LL = en or pn (Clark, Croud & Wills, 1988; Clark & Croud, 1985, 1986). The complex $[Pd(en)_2][Pd(en)_2Cl_2](ClO_4)_4$ has recently been structurally characterized (Beauchamp, Layek & Theophanides, 1982) whilst the structure of the corresponding bromide, our compound (1), was reported whilst our work was in progress (Martin, Keller & Muller, 1985). This paper is concerned with the characterization of three mixed-metal complexes, $[Ni(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (2), $[Pd(pn)_2][Pt(pn)_2Cl_2](ClO_4)_4$ (3) and $[Ni(pn)_2][Pt(pn)_2Cl_2](ClO_4)_4$ (4). We report also our results on the complex $[Pd(en)_2][Pd(en)_2Br_2](ClO_4)_4$ (1), since they contribute significantly to a long-running debate as to the true space group adopted by the isostructural (en) complexes. Our studies were made primarily in order to examine the effect of change of amine, halide and metal ion on the geometry of the metal-halide chain and the magnitude of the band gap.

Experimental

Preparation

Complex (1) was prepared as described by Clark, Croud & Kurmoo (1983), complex (2) as described by Clark & Croud (1986), complex (3) as described by Clark & Croud (1985), and complex (4) as described by Clark *et al.* (1988), in which papers the appropriate analyses are given.

Crystallography

Acicular crystals of all four complexes were examined photographically before diffractometer measurements and all four showed features noticed in previous work – namely diffuseness in the generally weak odd layers along the needle axes. Indeed, for compounds (3) and (4) these layers were so weak and diffuse that, in the subsequent diffractometric work, no localized diffraction maxima could be detected, leading to a cell repeat in the chain direction of approximately one-half of the equivalent dimension for compounds (1) and (2), see below. Diffractometer measurements (Enraf–Nonius CAD-4, $\theta/2\theta$ scans, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å) were made in each case following detailed procedures (Jones, Hursthouse, Malik & Wilkinson, 1979). The crystals were all mounted with the needle axis, c, approximately parallel to the diffractometer φ axis. Details of the intensity measurements and refinements are given in Table 1.

It is pertinent to note that our investigations have given results for complexes (1) and (2) which are in

Table 1. *Details of intensity measurements and structure refinements*

	(1)	(2)	(3)	(4)
Crystal dimensions (mm)	0·10 × 0·10 × 0·45	0·20 × 0·25 × 0·48	0·13 × 0·35 × 0·63	0·05 × 0·05 × 0·38
θ range (°) for cell determination	7·77–14·93	7·87–14·91	10·21–14·96	9·47–15·65
Scan width (°)	0·8 + 0·35tanθ	0·8 + 0·35tanθ	0·85 + 0·35tanθ	0·8 + 0·35tanθ
Intensity standards	3 4 5, 4 4 4	2 4 8, 1 2 9	0 5 1, 1 3 5	0 3 5, 0 3 5
	4 4 6	1 2 9	2 2 8	2 2 10
Decay (%)	3	4	5	4
θ range (°)	2·0–30·0	2·0–30·0	1·5–25·0	1·5–25·0
Index range h	0→13	0→13	0→23	0→23
k	0→19	0→19	0→9	0→9
l	0→15	0→15	0→6	0→6
Total unique data	1081	1074	808	806
Total observed $[F_o > 3\sigma(F_o)]$	756	853	567	564
Min., max. absorption correction*	0·91, 1·0	0·81, 1·0	0·92, 1·0	0·79, 1·0
No. of parameters	117	117	76	76
Weighting scheme parameter g†	0·0008	0·0008	0·0002	0·0003
Max. (Δ/σ)‡	1·5	1·1	0·001	0·006
Difference map residual $\Delta\rho$ (e Å^{-3})	−1·71	−0·93	−0·44	−0·72
	0·79	0·75	0·62	0·99
S	3·035	2·292	2·312	3·183
Final R	0·039	0·032	0·029	0·039
Final wR	0·040	0·034	0·027	0·036

* North, Phillips & Mathews (1968).

† Weights = $(\sigma^2 + gF_o^2)^{-1}$.

‡ High Δ/σ and $\Delta\rho$ relate to perchlorate O atoms which still show evidence of disorder.

agreement with those of Martin *et al.* (1985) in their determination of structure (1), with clear indications that space group *Iba*2 is correct. Refinement in this space group gave R, R_w values of 0·039, 0·051 for complex (1) [Martin *et al.* (1985) obtained 0·048, 0·056 for a comparable data set] and 0·32, 0·045 for complex (2). In the latter complex the metal site was represented by equal proportions of Pt and Ni, which were also tied to a single set of displacement-factor coefficients. For both structures, the chain halogen atoms, which formally occupy two symmetry-unrelated positions, were refined with tied z coordinates to avoid correlation problems. The resulting displacement ellipsoids are quite reasonable and we consider validate this procedure. Beauchamp *et al.* (1982) have described the analogous Pd$^{\rm II}$/Pd$^{\rm IV}$ chloro complex in space group *Ibam*, whilst Matsumoto *et al.* (1978) have described the structure of the Pt$^{\rm II}$/Pt$^{\rm IV}$ chloro complex in space group *I*222.

For complexes (3) and (4), which also form an isostructural pair, there is again a space-group problem. Matsumoto *et al.* (1978) determined the structure of the analogous Pt$^{\rm II}$/Pt$^{\rm IV}$ chloride and assumed the space group $P22_12_1$. Cannas *et al.* (1983) determined the structure of the analogous bromide and found systematic absences consistent with space groups *Pba*2 or *Pbam*, but were unable to distinguish between the two. Our results agree with those of Cannas *et al.* (1983) in that the presence of a and b glides is confirmed. Refinement of the structure of complex (3) in *Pba*2, which requires the metal atom to occupy a site of symmetry 2 and thus restricts the relative conformations of the two pn ligands to be the same, gave a final R value of 0·026. Space group *Pbam*, which requires disorder of the ligand arrangement to simulate the $2/m$ symmetry required, and which could involve mixing of chiral or centrosymmetric isomers, gave an R value of 0·029. Similar differences (0·062, 0·064) were found by Cannas *et al.* (1983) for their structure. In that high displacement in the c-axis direction was apparent for the ring C atoms in *Pba*2, we marginally prefer to adopt the centrosymmetric space group. All results presented for compounds (3) and (4) refer to this choice. It is to be noted, however, that the alternative space-group possibilities do not affect the determination of the geometry of the metal-halogen chain.

All computations were made using *SHELX* (Sheldrick, 1976) and *PARST* (Nardelli, 1983), and diagrams drawn using *SNOOPI* (Davies, 1983), on a VAX 11/750 computer. Scattering-factor data were taken from *International Tables for X-ray Crystallography* (1974). Final atomic fractional coordinates are given in Tables 2–5.*

Results and discussion

These structure determinations have given models analogous to those previously found for related complexes. Linear chains of $M^{\rm II}\cdots X\text{—}M^{\rm IV}\text{—}X\cdots$ units, with 'equatorial' bis(diamine), eclipsed N_4 coordination, are aligned along the c axes of the unit cells. The chains are disordered so that each metal site is an equal mixture of $M^{\rm II}$ and $M^{\rm IV}$ ions, and the halide ions half occupy two neighbouring, off-centre sites, see Figs. 1 and 2. This common feature in these linear-chain complexes has been discussed in detail in a number of other papers, and will not be repeated here. Our main objective is to explore the influence that the use of

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51396 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $[\mathrm{Pd}(en)_2][\mathrm{Pd}(en)_2\mathrm{Br}_2](\mathrm{ClO}_4)_4$ (1)

U_{eq} according to Hamilton (1959).

	x	y	z	U_{eq}
Pd	0	0	0	17·0 (2)
Br(1)	0	0	2297 (2)	35·1 (6)
Br(2)	0	0	−2297 (2)	35·1 (6)
Cl	4205 (2)	2015 (2)	2503 (9)	40·3 (6)
N(1)	1547 (16)	−1044 (10)	60 (12)	19 (2)
N(2)	1629 (16)	955 (12)	119 (14)	30 (3)
C(1)	2835 (18)	−417 (13)	307 (17)	30 (3)
C(2)	2933 (19)	575 (13)	−348 (20)	33 (3)
O(1)	4835 (13)	2360 (8)	1394 (9)	39 (2)
O(2)	4808 (26)	2377 (22)	3543 (21)	112 (4)
O(3)	3496 (28)	1144 (18)	2561 (50)	99 (3)
O(4)	2961 (21)	2755 (19)	2368 (38)	89 (3)
O(3*A*)	4630 (16)	959 (9)	2439 (32)	43 (3)
O(4*A*)	2817 (17)	1954 (17)	2599 (38)	74 (3)

Table 3. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $[\mathrm{Ni}(en)_2][\mathrm{Pt}(en)_2\mathrm{Cl}_2](\mathrm{ClO}_4)_4$ (2)

U_{eq} according to Hamilton (1959).

	x	y	z	U_{eq}
M*	0	0	0	17·2 (1)
Cl(1)	0	0	2154 (3)	29·1 (7)
Cl(2)	0	0	−2154 (3)	29·1 (6)
Cl(3)	4182 (2)	2018 (1)	2494 (6)	42·3 (4)
N(1)	1485 (12)	−1021 (7)	−11 (13)	36 (2)
N(2)	1571 (9)	956 (6)	35 (14)	29 (2)
C(1)	2845 (13)	−453 (10)	281 (11)	36 (2)
C(2)	2904 (15)	534 (10)	−376 (12)	41 (2)
O(1)	4811 (10)	2345 (7)	1398 (9)	50 (2)
O(2)	4749 (17)	2386 (14)	3551 (21)	115 (3)
O(3)	3271 (20)	1229 (10)	2415 (21)	88 (2)
O(4)	3041 (14)	2808 (12)	2353 (24)	89 (2)
O(3*A*)	4625 (14)	947 (7)	2547 (30)	58 (2)
O(4*A*)	2798 (12)	1939 (15)	2588 (29)	82 (2)

* $M = 0{\cdot}5\mathrm{Ni} + 0{\cdot}5\mathrm{Pt}$.

Table 4. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $[\mathrm{Pd}(pn)_2][\mathrm{Pt}(pn)_2\mathrm{Cl}_2](\mathrm{ClO}_4)_4$ (3)

U_{eq} according to Hamilton (1959).

	x	y	z	U_{eq}
M*	0	0	0	24·7 (2)
Cl(1)	0	0	4215 (7)	38 (1)
Cl(2)	1158 (2)	5852 (4)	5000	47·4 (8)
O(1)	1603 (6)	4409 (17)	5000	109 (5)
O(2)	1558 (5)	7425 (14)	5000	90 (4)
O(3)	747 (3)	5841 (8)	7138 (11)	66 (2)
N(1)	1002 (4)	−813 (11)	0	34 (3)
N(2)	437 (4)	2421 (10)	0	32 (3)
C(1)	1444 (7)	667 (18)	882 (28)	45 (5)
C(2)	1204 (7)	2224 (18)	−459 (88)	56 (15)
C(3)	2217 (6)	286 (16)	526 (46)	46 (8)

* $M = 0{\cdot}5\mathrm{Pd} + 0{\cdot}5\mathrm{Pt}$.

Table 5. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $[\mathrm{Ni}(pn)_2][\mathrm{Pt}(pn)_2\mathrm{Cl}_2](\mathrm{ClO}_4)_4$ (4)

U_{eq} according to Hamilton (1959).

	x	y	z	U_{eq}
M*	0	0	0	23·2 (3)
Cl(1)	0	0	4227 (9)	45 (2)
Cl(2)	1164 (2)	5833 (5)	5000	52 (1)
O(1)	1611 (8)	4380 (20)	5000	110 (7)
O(2)	1574 (7)	7410 (20)	5000	101 (6)
O(3)	752 (4)	5809 (12)	2828 (14)	73 (3)
N(1)	977 (5)	−823 (15)	0	42 (4)
N(2)	416 (5)	2386 (14)	0	40 (3)
C(1)	1451 (9)	689 (25)	910 (32)	43 (6)
C(2)	1197 (8)	2204 (22)	−504 (82)	54 (14)
C(3)	2195 (8)	197 (26)	497 (41)	52 (9)

*$M = 0{\cdot}5\mathrm{Ni} + 0{\cdot}5\mathrm{Pt}$.

different halides and/or mixing of metal ions (*M, M'*) might have on the geometry of the chain, on the electronic and vibrational spectra, and on the stabilities of the complexes. The important bond lengths and angles for each complex are listed in Table 6. Table 7 gives a summary of those distance parameters defining the chain geometry in all complexes of this type studied, from which the following points are worthy of note. First, the $M^{\rm II}$—$M^{\rm IV}$ distance is primarily determined by the equatorial amines, presumably on account of hydrogen bonding with the ClO_4^- ions and/or steric effects, but considerably less on either the bridging halide or *M*. Second, the $M^{\rm IV}\cdots X$ distance is virtually independent of the $M^{\rm II}\cdots M^{\rm IV}$ distance. However, substitution of Br for Cl decreases the difference between the $M^{\rm II}$—X and $M^{\rm IV}\cdots X$ distances and hence increases ρ $[r(M^{\rm IV}\text{—}X)/r(M^{\rm II}\cdots X)]$. Thus the value of ρ is principally determined by the amine and the bridging halide, and not by $M^{\rm II}$. It has been found that, for those complexes which have the same metal in both oxidation states, ρ can be directly correlated with the magnitude of the band gap (E_g) and hence with the optical and electronic properties. However, if $M^{\rm II}$ is changed, the mangitude of E_g in these anisotropic semiconductors changes and, in some cases, the optical properties as well (Clark *et al.*, 1988; Clark & Croud, 1985, 1986), even though this has little effect on ρ. For example, for the complexes $[M(\mathrm{en})_2][M'(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{ClO}_4)_4$, E_g varies from *ca* 1·5 eV [$M = M' = \mathrm{Pd}$, *via* Raman-band excitation profiles (Clark *et al.*, 1983)] to *ca* 2·2 eV [$M = M' = \mathrm{Pt}$, *via* single-crystal polarized electronic spectra (Tanino & Kobayashi, 1983)], to *ca* 2·75 eV [$M = \mathrm{Ni}$, $M' = \mathrm{Pt}$, *via* electronic spectra obtained as Nujol mulls (Clark & Croud, 1986)], to *ca* 3·0 eV [$M = \mathrm{Pd}$, $M' = \mathrm{Pt}$ *via* Raman-band excitation profiles (Clark & Croud, 1985)], yet the ρ and $M^{\rm II}\cdots M^{\rm IV}$ distances of all these complexes are almost identical with one another.

First, let us try to rationalize the effect of halide substitution in the pure palladium or platinum complexes. It is known that substituting I for Br or Br for Cl reduces the band gap and also increases ρ. Whangbo & Foshee (1981) have employed the tight-binding scheme based upon the extended Hückel method to determine the band structures of the analogous chains $[\mathrm{Pt(NH_3)_4}][\mathrm{Pt(NH_3)_4}X_2]^{4+}$, $X = \mathrm{Cl}$ or Br, and have studied the effect thereon of unit-cell distortions. The starting point is a hypothetical $[\mathrm{Pt^{III}(NH_3)_4Cl}]^{2+}$ chain which has a centrally placed bridging halide. The band formed mainly from the d_{z^2} orbital of $\mathrm{Pt^{III}}$ (d^7) and the p_z orbital of the bridging halide is half-filled (Fig. 3*a*). This symmetrically bridged structure undergoes a Peierls distortion (displacement of the halogen off-centre along the chain direction) to lower the energy of the system and thereby open up a band gap (Fig. 3*b*). This results in a filled valence band (mainly M^{II} in character) and an empty conduction band (mainly M^{IV} in character). The band gap decreases as the size of the halogen increases because it is determined in part by the extent of halide displacement from the central position in the bridge. Since the $M^{\mathrm{II}}\cdots M^{\mathrm{IV}}$ distance (*ca* 5·38 Å for en complexes, *ca* 5·53 Å for pn complexes) is largely

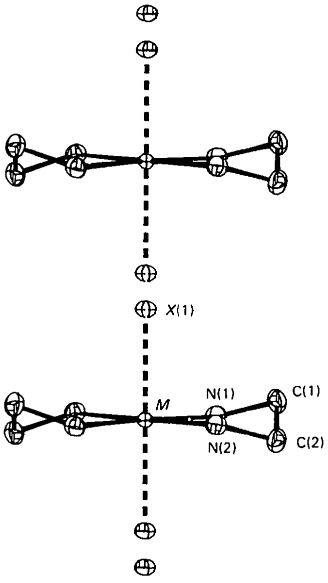

Fig. 1. A section of the linear-chain structure in $[M(\mathrm{en})_2][M'(\mathrm{en})_2X_2](\mathrm{ClO_4})_4$, complexes (1) and (2), showing labelling scheme.

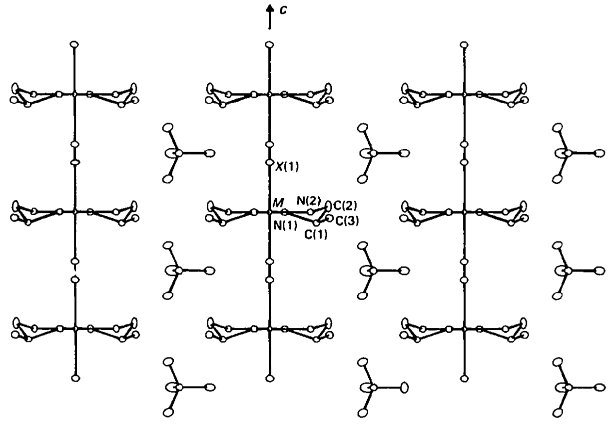

Fig. 2. A section through the unit cell (along the 110 plane) of $[M(\mathrm{pn})_2][M'(\mathrm{pn})_2X_2](\mathrm{ClO_4})_4$, complexes (3) and (4), showing the sheets of cation chains and anions, and labelling scheme.

Table 6. *Selected bond lengths* (Å) *and angles* (°) *for complexes* (1), (2), (3) *and* (4)

(1)		(2) $M = 0{\cdot}5\mathrm{Ni} + 0{\cdot}5\mathrm{Pt}$	
Pd–Br(1)	2·475 (4)	*M*–Cl(1)	2·314 (5)
Pd–N(1)	2·06 (2)	*M*–N(1)	1·97 (1)
Pd–N(2)	2·04 (2)	*M*–N(2)	1·97 (1)
N(1)–C(1)	1·53 (3)	N(1)–C(1)	1·54 (2)
N(2)–C(2)	1·45 (3)	N(2)–C(2)	1·46 (2)
C(1)–C(2)	1·52 (2)	C(1)–C(2)	1·50 (1)
Pd···Br(1$^{\mathrm{i}}$)	2·912 (5)	*M*···Cl(1$^{\mathrm{i}}$)	3·058 (6)
Br(2)–Pd–Br(1)	180·0	Cl(2)–*M*–Cl(1)	180·0
N(1)–Pd–Br(1)	88·2 (4)	N(1)–*M*–Cl(1)	90·4 (5)
N(1)–Pd–Br(2)	91·8 (4)	N(1)–*M*–Cl(2)	89·6 (5)
N(2)–Pd–Br(1)	86·4 (5)	N(2)–*M*–Cl(1)	88·9 (5)
N(2)–Pd–Br(2)	93·6 (5)	N(2)–*M*–Cl(2)	91·1 (5)
N(2)–Pd–N(1)	83·0 (4)	N(2)–*M*–N(1)	84·2 (4)
N(2$^{\mathrm{ii}}$)–Pd–N(1)	96·8 (4)	N(2$^{\mathrm{ii}}$)–*M*–N(1)	95·9 (4)
C(1)–N(1)–Pd	102 (1)	C(1)–N(1)–*M*	105·6 (7)
C(2)–N(2)–Pd	115 (1)	C(2)–N(2)–*M*	114·2 (8)
C(2)–C(1)–N(1)	118 (2)	C(2)–C(1)–N(1)	112 (1)
C(1)–C(2)–N(2)	96 (2)	C(1)–C(2)–N(2)	100 (1)

(3) $M = 0{\cdot}5\mathrm{Pd} + 0{\cdot}5\mathrm{Pt}$		(4) $M = 0{\cdot}5\mathrm{Ni} + 0{\cdot}5\mathrm{Pt}$	
M–Cl(1)	2·317 (6)	*M*–Cl(1)	2·310 (7)
M–N(1)	2·04 (1)	*M*–N(1)	2·00 (1)
M–N(2)	2·06 (1)	*M*–N(2)	2·02 (1)
N(1)–C(1)	1·51 (2)	N(1)–C(1)	1·57 (2)
N(2)–C(2)	1·52 (2)	N(2)–C(2)	1·54 (2)
C(1)–C(2)	1·49 (3)	C(1)–C(2)	1·49 (3)
C(1)–C(3)	1·54 (2)	C(1)–C(3)	1·51 (3)
M···Cl(1$^{\mathrm{iii}}$)	3·179 (7)	*M*···Cl(1$^{\mathrm{iii}}$)	3·155 (8)
Cl(1)–*M*–Cl(1$^{\mathrm{iii}}$)	180·0	Cl(1)–*M*–Cl(1$^{\mathrm{iii}}$)	180·0
N(1)–*M*–Cl(1)	90·0	N(1)–*M*–Cl(1)	90·0
N(2)–*M*–Cl(1)	90·0	N(2)–*M*–Cl(1)	90·0
N(2)–*M*–N(1)	83·7 (4)	N(2)–*M*–N(1)	85·2 (5)
N(1)–*M*–N(2$^{\mathrm{ii}}$)	96·3 (4)	N(1)–*M*–N(2$^{\mathrm{ii}}$)	94·9 (5)
C(1)–N(1)–*M*	107·8 (8)	C(1)–N(1)–*M*	108 (1)
C(2)–N(2)–*M*	108·2 (8)	C(2)–N(2)–*M*	108 (1)
C(2)–C(1)–N(1)	106 (1)	C(2)–C(1)–N(1)	103 (2)
C(3)–C(1)–N(1)	112 (1)	C(3)–C(1)–N(1)	109 (2)
C(3)–C(1)–C(2)	113 (2)	C(3)–C(1)–C(2)	116 (2)
C(1)–C(2)–N(2)	108 (2)	C(1)–C(2)–N(2)	108 (2)

Symmetry operations: (i) $-x, y, -0{\cdot}5 + z$; (ii) $-x, -y, z$; (iii) $x, y, 1{\cdot}0 - z$.

Table 7. *Structural data on linear-chain complexes* $[M(LL)_2][M'(LL)_2X_2](\mathrm{ClO_4})_4$

Complex				Bond length (Å)				
M	*M′*	*X*	*LL*	M^{IV}–*X*	$M^{\mathrm{II}}\cdots X$	*M*–N	ρ*	Ref.
Pd	Pd	Cl	en	2·324 (3)	3·033 (3)	2·042 (5)	0·77	(*a*)
Ni	Pt	Cl	en	2·314 (5)	3·058 (6)	1·97 (2)	0·76	(*b*)
Pt	Pt	Cl	en	2·318 (7)	3·087 (7)	2·07 (2)	0·75	(*c*)
Ni	Pt	Cl	pn	2·310 (7)	3·155 (8)	2·01 (2)	0·73	(*b*)
Pd	Pt	Cl	pn	2·317 (6)	3·179 (7)	2·05 (2)	0·73	(*b*)
Pt	Pt	Cl	pn	2·31 (2)	3·20 (2)	2·11 (2)	0·72	(*c*)
Pd	Pd	Br	en	2·475 (4)	2·912 (5)	2·05 (2)	0·85	(*b*)
Pt	Pt	Br	pn	2·476 (5)	3·094 (5)	2·08 (2)	0·80	(*d*)

References: (*a*) Beauchamp *et al.* (1982); (*b*) this work; (*c*) Matsumoto *et al.* (1978); (*d*) Cannas *et al.* (1983).

* $\rho = r(M^{\mathrm{IV}}\text{–X})/r(M^{\mathrm{II}}\cdots X)$.

independent of the halide (being determined by hydrogen-bonding and/or steric/packing effects) the ρ value is effectively determined by the $M^{IV}-X$ distance, which is, in these complexes, only slightly different from that for isolated $[MX_6]^{2-}$ ions. Thus, since M^{IV}—Cl < M^{IV}—Br < M^{IV}—I (greater orbital size in this order), then the ρ value must increase in the order Cl < Br < I, an effect which is known to lead to an increase in chain conductivity (Clark, 1984).

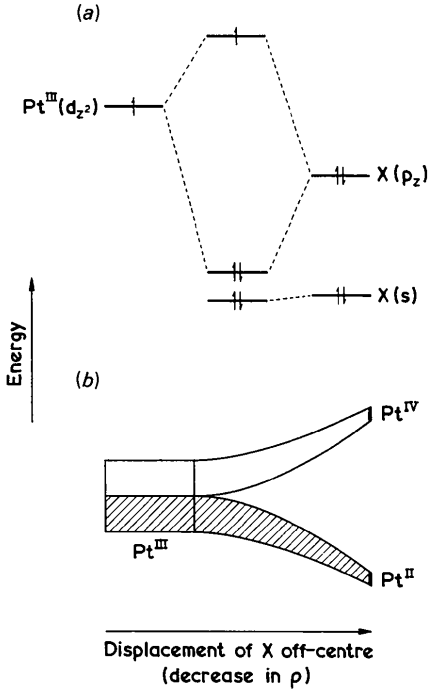

Fig. 3. (*a*) Band formed between $Pt^{III}(d_{z^2})$ and $X(p_z)$ orbitals of the chain complexes under study. (*b*) The effect of a Peierls distortion along this chain such that the halide moves off-centre by varying amounts.

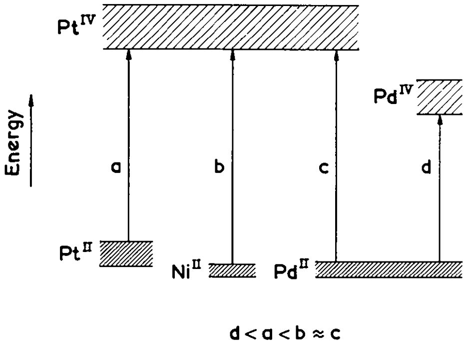

Fig. 4. Schematic representation of the relative band energies of analogous $Pt^{II}\rightarrow Pt^{IV}$, $Ni^{II}\rightarrow Pt^{IV}$, $Pd^{II}\rightarrow Pt^{IV}$ and $Pd^{II}\rightarrow Pd^{IV}$ transitions in linear-chain complexes.

Although changing M^{II} from Pt to Pd or Ni has a negligible effect on either the $M^{II}\cdots M^{IV}$ distance or ρ, it does lead to a substantial increase in E_g. This can be understood on the basis that the M^{II} bands for Ni^{II} or Pd^{II} are narrower than for Pt^{II}, being constructed from d_{z^2} orbitals of a lower quantum number. Moreover, they are of slightly the lower energy (Fig. 4). For the mixed-metal complexes, the nature of the $\cdots M^{III}-X-M^{III\prime}-X\cdots$ excited state is not well defined and will require more extensive theoretical work for clarification.

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