

the adjacent bridging O—C—O moieties deviate from the ideal angle, 90°, by 4–13° for the complexes listed in Table 3. This distortion may arise from intramolecular steric repulsions between the bulky R_3 groups. The average Si—C(carboxyl) bond length is longer by 0.05 (1)–0.07 (2) Å than the average Si—C(Ph) or Si—C(Me) bond length in (I) and (V), while the average C—C(carboxyl) bond length is almost the same as the average C—C(Ph) or C—C(Me) bond length in (II) and (III). The same trend is also observed for the Ge—C bond length in (IV). Long Si—C(carbonyl) and Ge—C(carbonyl) bonds of a similar length have been reported in the related acylsilanes and -germanes (Chieh & Trotter, 1969; Harrison & Trotter, 1968). The Si—C(Ph) and Ge—C(Ph) bond lengths are similar to those reported for Ph_4Si [1.872 (7) Å; Glidewell & Sheldrick, 1971] and Ph_4Ge [1.957 (4) Å; Karipides & Haller, 1972], respectively.

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Structure of *trans*-Dichlorobis(ethylenediamine)platinum(IV) Perchlorate, *trans*-[PtCl₂(NH₂CH₂CH₂NH₂)₂](ClO₄)₂

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Abstract. [PtCl₂(C₂H₈N₂)₂](ClO₄)₂, $M_r = 585.1$, orthorhombic, *Ccmb*, $a = 9.604$ (1), $b = 18.746$ (2), $c = 8.604$ (1) Å, $V = 1549.1$ (3) Å³, $Z = 4$, $D_x = 2.51$ Mg m⁻³, $\text{Mo } K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 9.89$ mm⁻¹, $F(000) = 1112$, $T = 300$ K. $R = 0.018$ for 1360 unique observed reflections. The Pt atom is coordinated octahedrally by two Cl atoms in *trans* positions and four amino N atoms. The complex

cation has a center of symmetry; the five-membered chelate rings adopt the *meso* form with the ligands in symmetric *gauche* (synclinal) conformations. The geometry of the perchlorate ion is very close to a regular tetrahedron. Two-dimensional networks of the cations and anions are formed *via* N—H...O hydrogen bonds. There is no linear stacking chain such as ...Cl—Pt—Cl...Cl—Pt—Cl... in the crystal.

Introduction. Recently there has been much interest in one-dimensional halogen-bridged mixed-valence complexes analogous to Wolfram's red salt $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{PtCl}_2(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$. The alternating valence of the Pt ions can be regarded as a charge density wave with a commensurability index of 2, which means that they have a doubly degenerate linear chain structure. These complexes have attracted attention to the characteristic structure in the studies of nonlinear excitations like solitons, polarons *etc.* (Onodera, 1987; Baeriswyl & Bishop, 1987; Kuroda, Sakai, Nishina, Tanaka & Kurita, 1987). In fact, the defect state induced by light excitation in $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ ($\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) is well explained in terms of a polaron model (Kurita, Haruki & Miyagawa, 1988; Donohoe, Ekberg, Tait & Swanson, 1989; Kurita & Haruki, 1989). A similar defect is produced by halogen doping on the $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ (Haruki & Kurita, 1989). To study the effect of doped halogen on the nonlinear excited state, we have synthesized $[\text{Pt}(\text{en})_2]_{1-x}[\text{PtCl}_2(\text{en})_2]_{1+x}(\text{ClO}_4)_4$ where x is a measure of the amount of excess halogen. The title compound as an end member with $x = 1$ was obtained in the course of sample preparation. The compound in the crystalline state easily changes from colourless to red under pressure, showing the appearance of an absorption band like that of $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ in the visible region. The crystal structure of this compound, therefore, arouses intense interest especially in relation to that of the undoped crystal with $x = 0$.

Experimental. Crystals grown by slow evaporation of an aqueous solution of $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ containing saturated chlorine are transparent, plate like and easily cleave along the (010) plane. A crystal kept in the mother liquid was shaped to a sphere with diameter of about 0.4 mm with wet filter paper under a stereoscopic microscope. A Rigaku AFC-3 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, $2\theta_{\text{max}} = 70^\circ$, ω scan, scan width 2.0 ($2\theta < 60$) and 2.2° ($2\theta \geq 60^\circ$), scan speed 2° min^{-1} ; 1748 hkl reflections measured ($h \rightarrow 15$, $k \rightarrow 30$, $l \rightarrow 13$), 1360 observed with $|F_o| > 3\sigma(|F_o|)$, 388 unobserved. Five standard reflections (600, 0,12,0, 006, 068 and 864) monitored every fifty reflections gradually decreased by about 3% in their $|F|$ values at the end of the intensity measurement. Cell dimensions from a least-squares calculation on the basis of θ values of 35 reflections ($22.5 < \theta < 25.0^\circ$). Corrections applied: Lp, stability, absorption ($\mu r = 2.0$, transmission factor 0.07–0.11) and extinction.

Two space groups $Cc2a$ (C_{2v}^{17} , noncentrosymmetric) and $Ccmb$ (D_{2h}^{18} , centrosymmetric) were possible for the systematic absences observed [$h + k = 2n + 1$ for

hkl , $l = 2n + 1$ for $0kl$ and h (and $k) = 2n + 1$ for $hk0$]. We started the structure analysis assuming space group $Cc2a$. The reflections with all-even or all-odd indices were strong. These characteristics suggested that the Pt atoms were located in a face-centered lattice. Such a location of the Pt atoms was confirmed by a Patterson synthesis. The structure was solved by the heavy-atom method, and refined by full-matrix least squares; function minimized $\sum w(F_o - F_c)^2$, $w = [\sigma^2(|F_o|) + (0.015|F_o|)^2]^{-1}$. The positions of the H atoms were deduced from difference Fourier maps and included in the refinement. The thermal parameters were anisotropic for the non-H atoms and isotropic for the H atoms. At a later stage of the refinement, the structure became almost centrosymmetric so space group $Ccmb$ was adopted in the final refinement. Final $R = 0.018$, $wR = 0.023$ and $S = 1.2^*$ (a trial refinement of the noncentrosymmetric structure, as a confirmation, converged to almost the same R value as above); 69 parameters, $(\Delta/\sigma)_{\text{max}} = 0.1$. Isotropic extinction parameter $0.84(7) \times 10^{-5}$. Peaks of residual electron density: $+3.0$ and $-1.3 \text{ e } \text{Å}^{-3}$ near the Pt atom, $+1.0 \text{ e } \text{Å}^{-3}$ at the midpoint of C—C bond, and $-0.6 < \Delta\rho < +0.4 \text{ e } \text{Å}^{-3}$ in the rest of the map.

Atomic form factors including anomalous-scattering corrections taken from *International Tables for X-ray Crystallography* (1974). The calculations performed on a FACOM M-380R computer at ISSP, the University of Tokyo. Computational programs used were *UNICSII* (Sakurai, 1987), *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979), *ORTEPII* (Johnson, 1971) and local programs prepared at ISSP.

Discussion. The atomic numbering and the H-bond formation around the cation are shown in Fig. 1. The Pt and perchlorate Cl atoms are located on the twofold axis of rotation along \mathbf{b} so that two anions which are mirror images to each other are arranged between the cations. A projection of the structure along \mathbf{b} is drawn in Fig. 2. The final atomic parameters are listed in Table 1. Bond lengths, intermolecular short contacts, angles and torsion angles in the en ring are tabulated in Table 2. The central Pt atom is coordinated octahedrally by two *trans* Cl atoms and four N atoms. The coordination octahedron is elongated along the Pt—Cl bonds. The cation has a center of symmetry, a twofold axis of rotation through the en rings, and a mirror plane perpendicular to the twofold axis and through the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52933 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Pt—Cl bonds. The coordination of the five-membered chelate rings is *meso* with symmetrical *gauche* conformations: thus one is δ and the other λ . The C atoms are oppositely shifted about 0.3 Å from the PtNN plane. The basal PtN₄ coordination plane is strictly planar, but deformed from square to rectangular because of the acute NPtN angle of the chelate ring. The Pt—Cl bond is almost perpendicular to the basal plane but slightly inclined, about 1° from the normal of the plane. The bond lengths and angles are all normal. The residual peak at the midpoint of the C—C bond, as mentioned above, is thought to be an accumulation of the bonding electrons. The positive and negative residual peaks around the Pt atom may indicate excess and deficient density of the *d* electrons, respectively.

The perchlorate ion shows the fairly large thermal motions commonly reported for this ion in many crystals. The geometry of the anion, however, is very close to a regular tetrahedron with normal Cl—O bonds, and has a twofold axis of rotation. The Cl(2)O(2)O(2') plane [(i): $-x, y, -z$] is almost parallel to the PtN₄ plane of the cation as is shown in

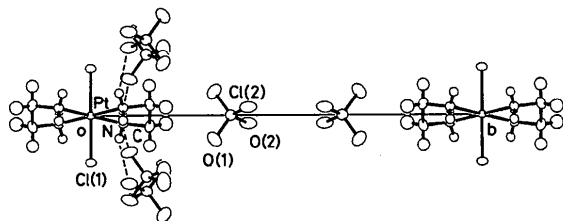


Fig. 1. The arrangement of the complex cations and anions on the *b* axis viewed along [101] together with the numbering scheme of the atoms. Anions around the en ring are also drawn. Broken lines indicate hydrogen bonds. Thermal ellipsoids are drawn at the 50% probability level.

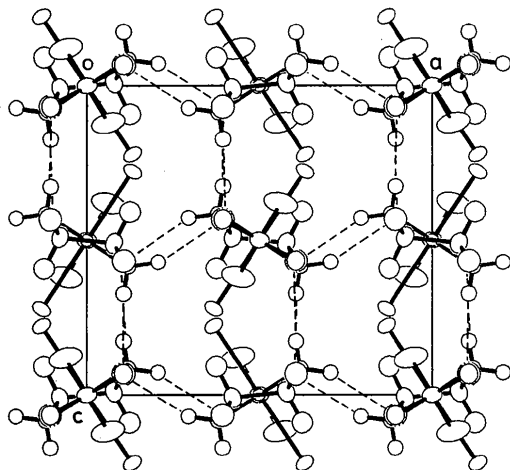


Fig. 2. A projection of the structure along the *b* axis. Broken lines indicate the hydrogen bonds.

Table 1. *Positional and thermal parameters with standard deviations in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Pt	0.0	0.0	0.0	0.01492 (7)
Cl(1)	0.13175 (8)	0.0	0.22226 (8)	0.0260 (3)
N	0.1192 (2)	0.0824 (1)	-0.0847 (2)	0.0214 (7)
C	0.0778 (3)	0.1507 (1)	-0.0094 (3)	0.028 (1)
Cl(2)	0.0	0.35734 (6)	0.0	0.0293 (4)
O(1)	0.0616 (4)	0.3146 (1)	0.1193 (3)	0.061 (2)
O(2)	0.1058 (2)	0.4020 (1)	-0.0668 (2)	0.045 (1)

Table 2. *Bond lengths (Å), relevant short intermolecular contacts (Å), angles (°) and torsion angles (°)*

Pt—Cl(1)	2.293 (1)	C—C ⁱ	1.503 (6)
Pt—N	2.056 (2)	Cl(2)—O(1)	1.430 (3)
N—C	1.489 (3)	Cl(2)—O(2)	1.437 (2)
N...O(2 ⁱⁱ)	2.960 (3)*	N...O(2 ⁱⁱⁱ)	3.015 (2)*
N...Cl(1 ⁱ)	3.098 (2)	N...Cl(1 ^{iv})	3.062 (2)
C...O(1)	3.270 (3)	C...O(2 ⁱⁱ)	3.262 (3)
Cl(1)—Pt—N	89.33 (6)	O(1)—Cl(2)—O(1 ⁱ)	111.9 (2)
Cl(1)—Pt—N ⁱ	90.67 (6)	O(1)—Cl(2)—O(2)	108.7 (1)
N—Pt—N ⁱ	82.60 (7)	O(1)—Cl(2)—O(2 ⁱ)	109.4 (1)
Pt—N—C	110.1 (1)	O(2)—Cl(2)—O(2 ⁱ)	108.7 (1)
N—C—C ⁱ	108.2 (2)		

Torsion angles

N ⁱ —Pt—N—C	-13.8	Pt—N—C—C ⁱ	38.5
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Symmetry operations: (i) $-x, y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x, \frac{1}{2} - y, -\frac{1}{2} - z$; (iv) $x, -y, z$.

* Denotes H bond.

Fig. 2; the inclination is about 3°. The position of the ligand Cl atom is near the line connecting adjacent Pt atoms which are about 6.4 Å apart in the (010) plane. Four anions in $\pm a$ and $\pm c$ directions are bonded to an en ligand of the complex cation through N—H...O hydrogen bonds; thus the cations and anions are linked to form two-dimensional networks along the (010) plane. Only a linear stack, cation, anion, anion *etc.*, is formed along *b*: there is no strong bond in this direction. The (010) cleavage plane may be due to this two-dimensionality of the bonding in the crystal.

Besides the intensity decrease in the course of data collection, the crystal became pale yellow at the end of the intensity measurement. Furthermore, the crystal easily changes its colour to red under slight pressure (even when held softly with tweezers). These facts suggest that the crystal is not very stable. The irradiation by X-rays or the stress might cause some structural change, possibly in the cation, such as, for example, partial removal of the ligand Cl atoms, or a change in the ring conformation accompanied by reorientations of the H bonds due to the flexibility of the ring conformation. The former inevitably results in a change of the valence state of the Pt ion. The colour of the stressed crystal is similar to that of a

mixed-valence compound $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ (Kida, 1965). In this case, the Cl atom is expected to be loosely bonded to the Pt atom; the Pt—Cl bond as well as the thermal parameter of the Cl atom, however, is quite normal, and shows no such indication. The compound $[\text{Pt}(\text{en})_2]\text{Cl}_2$ which takes the *meso* form for the ring conformation is colourless (Sato, Haruki & Kurita, 1990). In the compound $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$, the conformation is not *meso* but $\delta\delta$ [Matsumoto, Yamashita, Ueda & Kida (1978); the absolute configuration has not been determined]. The structure of the present compound differs greatly from that of the undoped crystal. Further investigations are necessary to clarify the changes that arise in the structure.

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Two Dimolybdenum Tetracarboxylato Compounds from Heteroaromatic Acids, 2-Thiophenecarboxylate and Nicotinic Acid

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Abstract. Bis(tetrahydrofuran)tetra- μ -2-thiophenecarboxylato-(*O,O'*)-dimolybdenum(II) (1), $[\text{Mo}_2(\text{C}_5\text{H}_3\text{O}_2\text{S})_4(\text{C}_4\text{H}_8\text{O})_2]$, $M_r = 816.44$, monoclinic, $P2_1/n$, $a = 10.274$ (1), $b = 9.990$ (1), $c = 15.904$ (3) Å, $\beta = 90.60$ (2)°, $V = 1632$ (1) Å³, $Z = 2$, $D_x = 1.66$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 5.87$ cm⁻¹, $F(000) = 404$, $T = 293$ K, $R = 0.0336$ for 1310 observed reflections. The centrosymmetric molecule has Mo—Mo = 2.102 (1), mean Mo—O(carbox) = 2.107 (3), and Mo—O(THF) = 2.593 (5) Å. Dichlorotetra- μ -nicotinato-(*O,O'*)-dimolybdate(II) dichloride hexahydrate (2), $[\text{Mo}_2(\text{Cl})_2(\text{C}_6\text{H}_4\text{NO}_2)_4]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $M_r = 934.23$, monoclinic, $P2_1/c$, $a = 10.154$ (1), $b = 17.681$ (4), $c = 9.825$ (2) Å, $\beta = 91.42$ (2)°, $V = 1763$ (1) Å³, $Z = 2$, $D_x = 1.759$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 5.55$ cm⁻¹, $F(000) = 454$, $T = 293$ K, $R = 0.0245$ for 2604 observed reflections. The centrosymmetric molecule has Mo—Mo = 2.122 (1), mean Mo—O(carbox) =

2.113 (4) and Mo—Cl = 2.835 (1) Å. All pyridyl N atoms are protonated and there is an extensive series of hydrogen bonds.

Introduction. Many $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds have been structurally characterized, but nearly all have contained non-aromatic *R* groups; the only exceptions are $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ and its diglyme adduct (Cotton & Walton, 1982). Questions concerning the chemistry and spectroscopy of $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds generated interest in the structures and other properties of those with heteroaromatic *R* groups. The structures of two such compounds have been determined and are reported here.

Experimental. To prepare (1), $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (0.10 g) was added to a solution of 2-thiophenecarboxylic acid (0.149 g) in 25 ml of THF under argon with stirring. The slurry, initially yellow, became bright orange over 5 min. The orange solid was collected by filtration, washed with THF and

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