Discussion. Fig. 1 gives a projection along the b axis of the atomic arrangement.

The Cd atoms, located on the mirror plane, have their most usual environment: six neighbouring O atoms form an almost regular octahedron with Cd—O distances varying from 2·176 to 2·265 Å (Table 2). The Ta atoms, in general positions, have their usual octahedral coordination with Ta—O distances in the range 1·920–1·970 Å (Table 2). The P_2O_7 groups present two different conformations. The first has mirror symmetry with five atoms of the group [P(3), P(4), O(E41), O(L34) and O(E32)] in the mirror plane. This rare configuration has already been observed in $Nb_2CaO(P_2O_7)(P_4O_{13})$ (Averbuch-Pouchot, 1987). The mean P—O distance is 1·523 Å for this anion. The second type of P_2O_7 group has no internal symmetry and a mean P—O distance (1·519 Å) that is practically identical. This atomic arrangement is related to that of $Nb_2Co(P_2O_7)_3$ (Averbuch-Pouchot & Durif, 1987). This last compound is monoclinic ($P2_1/m$) with a unit cell ($a = 15·320$, $b = 7·890$, $c = 6·490$ Å, $\beta = 90·76°$) quite comparable with that of the title compound after a doubling of c. The analogy is not limited to the crystal metrics but extends to the atomic arrangements as can be seen by comparing Figs. 1 and 2. The atomic framework of $Ta_2Cd(P_2O_7)_3$ can be deduced from that of $Nb_2Co(P_2O_7)_3$ by a doubling of its unit cell and a translation of about 0·15 along the y axis.
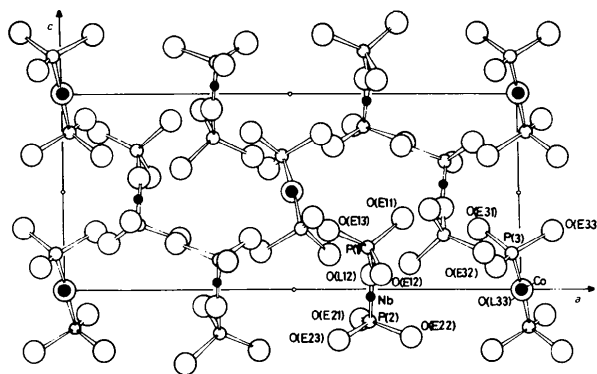

Fig. 2. Projection along the b axis of the atomic arrangement of $Nb_2Co(P_2O_7)_3$.

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Structure Based on a Twinned Crystal of Wolffram's Red Salt, [Pt(C₂H₅NH₂)₄Cl₂][Pt(C₂H₅NH₂)₄]Cl₄.4H₂O

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Abstract. Dichlorotetrakis(ethylamine)platinum(IV) tetrakis(ethylamine)platinum(II) tetrachloride tetrahydrate, $[Pt(C_2H_7N)_4Cl_2][Pt(C_2H_7N)_4]Cl_4.4H_2O$, $M_r = 1035·6$, monoclinic, Im, $a = 13·302$ (3), $b = 13·337$ (5), $c = 5·391$ (1) Å, $\beta = 90·98$ (3)°, $V = 956·3$ (4) Å³, $Z = 1$, $D_x = 1·80$ Mg m⁻³, λ(Mo $K\alpha$, graphite monochromated) = 0·7107 Å, $\mu = 7·84$ mm⁻¹, $F(000) = 506$, $T = 298$ K, final $R = 0·036$ for 1218 unique significant reflections. The crystals show a twinning with c as the twin axis of $\pi/2$ rotations; the twin individuals have a structure similar to that of the bromo analog, Reihlen's green. The structure is pseudo-tetragonal except for the anions and water molecules. The Pt^{IV} coordination octahedron is slightly deformed through non-bonded repulsion of the axial Cl atom and the methylene groups. A three-dimensional network of hydrogen bonds is formed involving anions and water molecules.

Introduction. Dichlorotetrakis(ethylamine)platinum(IV) tetrakis(ethylamine)platinum(II) tetrachloride tetrahydrate, known as Wolffram's red salt, has been extensively studied by means of many

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experimental and theoretical techniques as a typical example of halogen-bridged one-dimensional mixed-valence complexes. The structure is characterized by chains of alternate octahedral $[Pt(C_2H_5NH_2)_4Cl_2]^{2+}$ and square-planar $[Pt(C_2H_5NH_2)_4]^{2+}$ ions; mis-stacks, however, occur within the chains as indicated by very weak odd-layer diffuse streaks (Craven & Hall, 1961; Iida, Iwazumi & Terauchi, 1983); the arrangement of the chains is also disordered. Therefore, the structure could be thought to consist of averaged octahedral complexes with half-weighted Cl atoms and to have a half-period chain axis. The subcell structure deduced from the even-layer reflections was initially determined by Craven & Hall (1961) as pseudo-tetragonal with the most probable space group $I4mm$, the chain axis being parallel to c. In this paper we report a twinning of the crystal of Wolffram's red salt and the structure of the subcell.

Experimental. Crystals prepared by the method of Reihlen & Flohr (1934): dark yellow and of needle-like shape elongated along c.

A preliminary measurement showed a twinning on all crystals examined; all pseudo-tetragonal reflections except $hk0_{tet}$ systematically split into four as illustrated in Fig. 1; the $00l_{tet}$ reflections split with an inclination of about 1° from the pseudo-tetragonal c^*. This splitting is also observed clearly on Weissenberg photographs around c. Some $hk0_{tet}$ reflections examined using Cu $K\alpha$ radiation at $2\theta \simeq 100°$ showed no clear splitting other than those of $K\alpha_1$ and $K\alpha_2$. This means that the c axis is common to the individuals. The crystal is essentially monoclinic and twinned with c as the twin axis of $\pi/2$ rotations [the ratio b^*/a^*, of the monoclinic cell, is nearly the same as $\lambda(K\alpha_1)/\lambda(K\alpha_2)$].

Intensity measurements made for reflections from the largest individual. Rigaku automated four-circle diffrac-

Fig. 1. Schematic drawing of the splitting of the reflections from the twinned crystal of Wolffram's red in reciprocal space. The tetragonal lattice is indicated by the lines along with the indices.

tometer. Graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan, scan width $\Delta\omega = (1\cdot3 + 0\cdot5 \tan\theta)°$, scan speed 2° min^{-1} in ω. Crystal dimensions $0\cdot23 \times 0\cdot23 \times 0\cdot28$ mm. $2\theta < 70°$, $[(\sin\theta)/\lambda]_{max} = 0\cdot807$ Å^{-1}. The aperture of the receiving slit minimized in order to avoid overlap of extra reflections from other individuals; the resolution, however, partly insufficient as mentioned below. Four standard reflections monitored every fifty reflections: no significant variations. In total, 3650 $\pm h$ $\pm k$ $+l$ ($l > 0$) reflections with $|F_o| > 3\sigma(|F_o|)$ obtained (3845 possible); additionally 126 $hk0$ reflections ($2\theta < 55°$) measured. Lorentz and polarization correction. Absorption correction made by the numerical integration method (Busing & Levy, 1957), transmission factor $0\cdot19$–$0\cdot26$. Intensities of the split peaks of the pseudo-tetragonal reflections did not differ much even for very thin crystals. Examination of small crystals under a polarizing microscope showed no distinct mosaic areas; the pattern was only monotonic. These observations suggest that the twin individuals are quite small in size and can be assumed to be homogeneously distributed in the crystal; therefore, the absorption correction described above should be regarded as an approximation. Cell dimensions determined by a least-squares calculation on the basis of 28 computer-centered reflections ($17\cdot5 < \theta < 20\cdot0°$).

Positions of all non-H atoms were deduced clearly from the Patterson maps except for the sign of the coordinates of the C atoms. In the calculation of the Patterson maps, the $hk0$ reflections were included with a suitable scale; this was a reasonable approximation in view of the pseudo-tetragonality of the structure; from this inclusion, peaks corresponding to the interatomic vectors between the Pt and the ligand Cl atoms appeared along c. The structure refinement started with all non-H atoms except C by assuming the space group Im (C_s^3, extinction rule: $h + k + l = 2n$), the Pt atom being fixed at the origin. Space groups $I2$ or $I2/m$ are also possible for the systematic absences observed. These two, however, were not accepted because of (i) higher R values in preliminary calculations adopting these space groups and (ii) unusual short contacts as well as disordered disposition of many atoms besides the ligand Cl atoms as reported by Brown & Hall (1976) for Reihlen's green. In the refinement, $hk0$ reflections were not used. The C atoms were located by subsequent Fourier syntheses. The peaks of the C atoms appeared nearly centrosymmetrically on both sides of the (001) plane in the Fourier maps, because the phases of the structure factors were predominantly determined by the Pt atoms which occupy the origin and its equivalent; the positive sense of the z coordinates was accepted, since the peak heights were 10–20% greater than those at the alternative positions. The structure was refined by the block-diagonal least-squares method introducing anisotropic temperature factors.
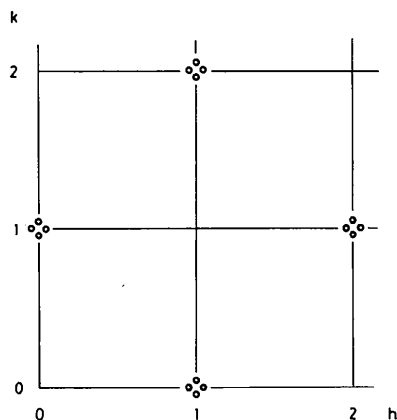
At a later stage of the refinement ($R \simeq 0\cdot11$), some reflections concentrated in several regions of reciprocal space showed $|F_o| > |F_c|$ systematically and a few diagonal terms of the temperature factors (U_{ii}) of the ligand atoms became slightly negative. Unreasonable deformation was also observed in the geometry of the complex ion. These were thought to be caused by insufficient separation of the reflections between the individuals of the twinned crystal. After careful examination of the reflection data, the $|F_o|$ values of the equivalent reflections were simply averaged if $||F_o(hkl)| - |F_o(h\bar{k}l)||<\sigma\{|F_o(hkl)|\}+\sigma\{|F_o(h\bar{k}l)|\}$;if not, the smaller ones were accepted; $hk1$ and $hk2$ reflections were totally excluded, because nearly all of them showed overestimation of $|F_o|$ values; a few reflections which had reciprocal-lattice vectors nearly perpendicular to b^* were also ruled out. Finally, 1218 independent reflections ($I \geq 3$, 1271 possible) were used in subsequent refinements. The positions of the amino and methylene H atoms were deduced from difference-Fourier maps; these H atoms were included in the calculation with an isotropic temperature factor, but not refined. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(|F_o|) + (0\cdot025|F_o|)^2]^{-1}$. $R =0\cdot036$ and $wR=0\cdot043$; $S=1\cdot2$.† $\Delta/\sigma<0\cdot1$, $\Delta\rho_{max}$ $0\cdot9$ e Å^{-3} around the Pt atom, $0\cdot3$ e Å^{-3} for the rest.

The alternative structure with reversed signs of x and z coordinates [strictly analogous to that of Reihlen's green reported by Brown & Hall (1976)] was separately refined; it converged to nearly the same but a slightly greater R value, but not significant for the determination of the absolute structure. The atomic scattering factors and the anomalous-scattering-correction terms were taken from *International Tables for X-ray Crystallography* (1974); for H those of Stewart, Davidson & Simpson (1965) were used. All the calculations were performed on a FACOM M-360 computer at this institute with a local version of the *UNICS*II program system (Sakurai, 1967).

Discussion. The final atomic parameters are listed in Table 1; Fig. 2 shows a projection of the structure together with the numbering scheme of the atoms. The structure is really pseudo-tetragonal except for the arrangement of the anions and the water molecules. The bond lengths and angles (simply averaged) within the complex ion are: Pt—N $2\cdot07$ (1), N—C $1\cdot48$ (2), C—C $1\cdot49$ (3) Å; N—Pt—N $89\cdot9$ (5) and $175\cdot7$ (5), Pt—N—C $120\cdot9$ (9), N—C—C $112\cdot4$ (12)°. The geometry of the coordination octahedron shows a slight deformation

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44055 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters with their e.s.d.'s in parentheses*

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

|	x	y	z	U_{eq}(Å^2)
Pt	0·0	0·0	0·0	0·0309 (1)
N(1)	0·1574 (8)	0·0	−0·0013 (19)	0·034 (4)
N(2)	−0·1530 (15)	0·0	−0·0286 (26)	0·052 (8)
N(3)	0·0010 (11)	0·1558 (7)	−0·0137 (16)	0·041 (3)
C(1)	0·2132 (17)	0·0	0·2294 (30)	0·057 (10)
C(2)	0·3271 (19)	0·0	0·1788 (58)	0·076 (17)
C(3)	−0·2187 (15)	0·0	0·1991 (33)	0·054 (9)
C(4)	−0·3307 (28)	0·0	0·1490 (50)	0·069 (14)
C(5)	0·0002 (14)	0·2160 (11)	0·2152 (19)	0·053 (6)
C(6)	0·0027 (27)	0·3233 (13)	0·1636 (46)	0·092 (9)
Cl(1)	−0·0055 (8)	0·0	0·4334 (9)	0·061 (4)
Cl(2)	−0·0082 (9)	0·0	−0·4314 (13)	0·101 (7)
Cl(3)	0·2150 (3)	0·2146 (3)	0·7425 (4)	0·056 (1)
O(w)	0·3005 (11)	0·3024 (11)	0·2564 (13)	0·072 (6)
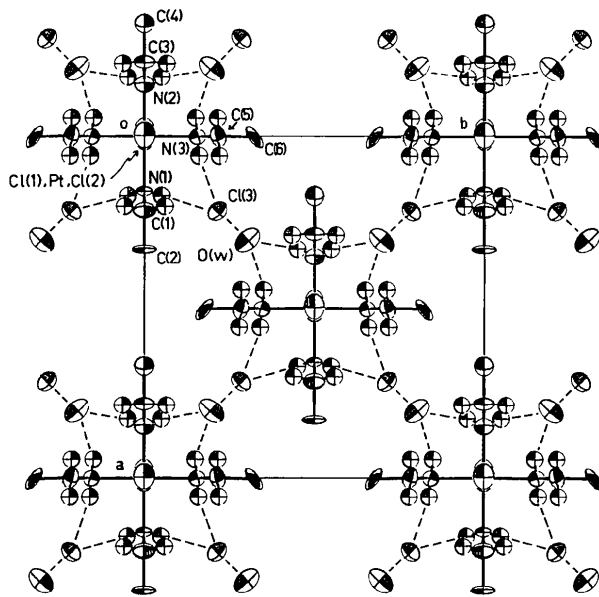
Fig. 2. A projection of the crystal structure along **c**. The vibrational ellipsoids and spheres are drawn at 50% probabilities (Johnson, 1965). Proposed hydrogen bonds are indicated by broken lines.

from the symmetrical disposition probably caused by non-bonded repulsion between the axial Cl(1) atom and the methylene groups: (i) the Pt—Cl(1) bond is a little longer than the Pt—Cl(2) bond [$2\cdot339$ (5) compared with $2\cdot326$ (7) Å]; (ii) the Pt atom is shifted $0\cdot08$ Å towards the Cl(1) atom from the equatorial plane made by the four N atoms. Either an anion or a water molecule is situated between the nearest-neighbor complex ions, and linked to the complex ion through N$\cdots$Cl or N$\cdots$O H bonds. The anions and the water molecules are arranged nearly on the (110) and its equivalent planes and are bonded alternately by O$\cdots$Cl H bonds to form zigzag chains along **c**. Thus, a three-dimensional network of H bonds is formed. All these structural features are similar to that of Reihlen's green (Brown & Hall, 1976).

Relatively high e.s.d.'s for the parameters as well as unusually large or small values for a few thermal parameters were obtained. These unsatisfactory results are due to some inevitable difficulties: insufficient accuracies of the $|F_o|$ values owing to the overlap of the reflections from the other individuals of the twinned crystal; the neglect of the geometrical difference between the octahedral Pt^{IV} and planar Pt^{II} complexes; the exclusion of many low-angle reflections owing to the restrictive use of the reflection data (the light atoms contribute mainly to the low-angle reflections).

The positional symmetry of the anions and the water O atoms, as a whole, is closely related to that of 8(c) sites of the space group $I4mm$. The formation of the twinned crystal consisting of four individuals is probably caused by misfits in the arrangement of the anions and the water molecules accompanied by a slight shift between the chains of the complex ions: i.e. exchanging the positions of the anions and the water molecules and a $\pi/2$ rotation of the mirror plane around c. Twinning occurs in the present complex, but not in Reihlen's green. This appears to depend on whether the deviation of the cell parameter β from 90° is small or large: the deviation is 0·98° in Wolffram's red, whereas it is 2·7° in Reihlen's green.

A rough estimation of the cell parameters at 100 K based on the θ values of six reflections ($15 < \theta < 18°$) is: $a = 13·22$ (7), $b = 13·24$ (3), $c = 5·37$ (1) Å, $\beta = 91·4$ (3)°. No anomalous expansion of the cell dimensions as reported for tetraammineplatinum(II) tetraamminedibromoplatinum(IV) hydrogensulfate (Tanaka, Tsujikawa, Toriumi & Ito, 1982) was observed.

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Aqua[1,9-di(2-pyridyl)-2,5,8-triazanonane]cobalt(III) Nitrate Diperchlorate

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Abstract. $[Co(C_{16}H_{23}N_5)(H_2O)](ClO_4)_2(NO_3)$, $M_r = 623·2$, monoclinic, $P2_1/a$, $a = 16·587$ (3), $b = 10·791$ (2), $c = 13·538$ (2) Å, $\beta = 94·1$ (1)°, $U = 2416·9$ (7) Å^3, $Z = 4$, $D_x = 1·71$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0·71069$ Å, $\mu = 93·3$ mm^{-1}, $F(000) = 1280$, $T = 295$ K, $R = 0·064$ ($wR = 0·066$) for 2324 unique observed reflections. The coordination geometry of the complex cation $[Co(picdien)(H_2O)]^{3+}$ is nearly regular octahedral with the pentadentate picdien ligand in α, β configuration.

Introduction. The great sensitivity of complexes of the type syn- and anti-$\alpha,\beta[Co(picdien)X]^{2+}$ ($X = Cl$, Br, NO_2, NCS) to base-catalysed hydrolysis which is observed as an inverse-first-order acid-dependent rate law even in moderately acid solution has led us to examine the reverse process which also has an inverse acid dependence (Humanes, 1984). This allows a

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