

Discussion. Crystals of the (-)-enantiomer of phenprocoumon are essentially isostructural with the crystalline racemate. Where the racemate features hydrogen bonding along the short cell-axis between molecules of the same configuration, the enantiomer shows similar hydrogen bonding between molecules of the same conformation. Conformation 2 (Fig. 2), which differs from conformation 1 by a rotation of about 180° around the C(3)–C(11) bond, allows the H on C(11) to adopt the 'trans' arrangement with respect to the C(3)–C(4) double bond, while in conformation 1, and the racemate the arrangement is 'cis'. Least-squares planes calculated for the 13 coumarin ring atoms and the 6 phenyl ring atoms in each molecule described planarity to within 0.04 and 0.02 Å respectively. The large thermal motion observed in the racemate is dramatically enhanced in the enantiomeric structure particularly at the extremities of the coumarin and phenyl rings. It can be inferred from the direction and magnitude of the thermal motion that the structure permits a large in-lane libration of the rings that increases towards the ends of the group. The bond lengths in the two independent molecules in the enantiomer agree to within 0.04 Å, and the average agrees to within 0.02 Å of those given for the racemate. Repre-

sentative bond lengths in coumarin compounds are cited elsewhere (Valente, Trager & Jensen, 1975).

We wish to thank Dr V. Schomaker for his interest and helpful conversation during the course of this project. Programs used in the various calculations were part of the X-RAY 72 System of Stewart, Kundell & Baldwin (1970).

References

- BENEDETTI, E., PEDONE, C. & SIRIGU, A. (1973). *Acta Cryst.* **B29**, 730–733.
 BRAVIC, G., GAULTIER, J. & HAUW, C. (1971). *C. R. Acad. Sci. Paris, Sér. C*, 1112–1114.
 DI BLASIO, B., PEDONE, C. & SIRIGU, A. (1975). *Acta Cryst.* **B31**, 601–602.
 JOHNSON, C. K. (1965). *ORTEP Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory Report ORNL-3794.
 PREIS, S., WEST, B. D. & LINK, K. P. (1966). U.S. Patent 3,239,529, 8 March.
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY System, Univ. of Maryland.
 VALENTE, E., TRAGER, W. & JENSEN, L. (1975). *Acta Cryst.* **B31**, 954–960.
 WEST, B. D. & LINK, K. P. (1965). *J. Hetero. Chem.* **2**, 93–94.

Acta Cryst. (1976). **B32**, 279

Tetrakis(ethylamine)platinum(II)dibromotetrakis(ethylamine)platinum(IV) Tetrabromide Tetrahydrate

BY KEVIN L. BROWN AND DAVID HALL

Chemistry Department, University of Auckland, New Zealand

(Received 9 December 1974; accepted 13 August 1975)

Abstract. Monoclinic (pseudo-tetragonal), $a=13.495$ (2), $b=13.507$ (2), $c=11.172$ (2) Å, $\beta=92.7$ (1)°, $C_{16}H_{56}Br_6N_8Pt_2 \cdot 4H_2O$, $Z=2$, $D_m=2.08$, $D_c=2.13$ g cm⁻³. Only diffuse layer lines are observed corresponding to odd values of l ; the subcell for which $c=5.586$ Å has space group Im . The structure is interpreted in terms of chains of alternate square planar $[Pt(C_2H_5NH_2)_4]^{2+}$ and octahedral $[Pt(C_2H_5NH_2)_4Br_2]^{2+}$ ions, the disorder arising from stacking mistakes involving displacement of the chain by one half the repeat unit.

Introduction. Green needles were prepared as described by Drew & Tress (1935). Rotation photographs about c showed normal sharp reflexions on even layer lines, but the odd layer lines were diffuse and were continuous. Data for even values of l were collected on a Hilger–Watts automated diffractometer, with Mo $K\alpha$ radiation, for all reflexions $-h$ to h , 0 to k , $-l$ to l to

θ_{max} of 30°. 1907 data were observed [$I > 2\sigma(I)$], corrected for absorption and reduced to a set of 1009 on assumption of monoclinic symmetry. If these reflexions are indexed with respect to the subcell for which c is halved, systematic absences are in hkl with $h+k+l$ odd.

The subcell must contain two molecules of formula $Pt(C_2H_5NH_2)_4Br_3 \cdot 2H_2O$; on analogy with the structures reported for other compounds of this type, it was expected to show half-weight Br atoms attached to the Pt, with Pt–Br bonds parallel to the needle axis. The positions of all atoms were readily deduced from the Patterson function, except for ambiguity of sign of the z coordinates of the C atoms. It was then apparent that adoption of $I2$ or $I2/m$ as the subcell space group would imply that the disorder extends to the signs of these coordinates. Space group Im permits all atoms other than the Br atoms above, and including the bromide ions, to occupy ordered positions. If all of the C atoms have z coordinates of the same sign, then

all C...Br(ionic) and C...O(H₂O) contacts are greater than 3.5 Å. All other arrangements, ordered or disordered, require some contacts to be less than 3.2 Å, which was considered unacceptable.

Refinement in *Im* by block-diagonal least-squares calculations, assuming anisotropic thermal factors for Pt, isotropic parameters for all other atoms, and real dispersion corrections to the scattering curves for Pt and Br, converged to an *R* index of 0.072. Weights were assumed as $w = 4F/\sigma^2(F^2)$, where $\sigma^2(F^2)$ is based on counting statistics, and $\langle w(\Delta F)^2 \rangle$ was demonstrated to be invariant with $|F|$, except for the most intense reflexions which were slightly overweighted. Further refinement utilized the original set of 1907 data, applying anomalous dispersion corrections for Pt and Br, and also assuming anisotropic thermal motion for the Br atoms. The residuals were 0.0666 and 0.0570 for the two possible polarities, and the parameters corresponding to the latter were accepted as final. A final difference synthesis showed no significant region of electron density, either in the vicinity of the atoms or elsewhere.

Atom coordinates with regard to the subcell are listed in Table 1, and thermal parameters in Table 2, Br(2) and Br(3) being half-weighted. An ORTEP dia-

gram of the subcell cation is shown in Fig. 1, and a projected view of the full cell structure as assumed to exist in Fig. 2. Bond lengths and angles are listed in Table 3.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31330 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

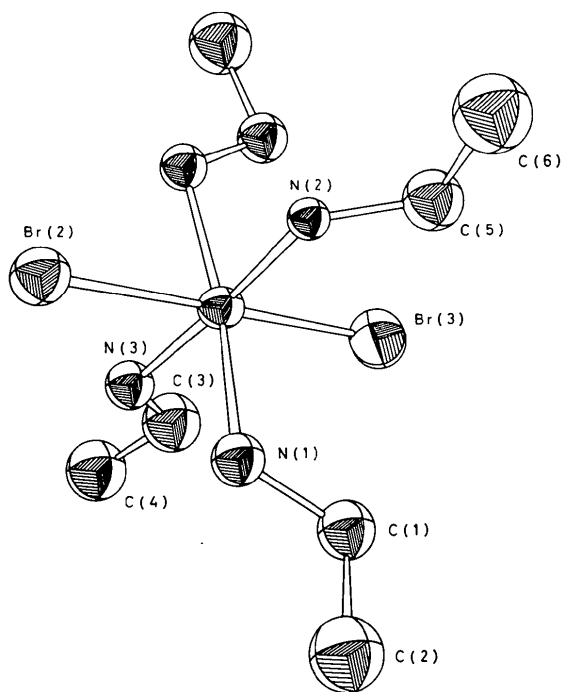


Fig. 1. The subcell complex cation, Br(2) and Br(3) being half-weighted atoms.

Table 1. Atom coordinates and standard deviations

	x	y	z
Pt	0.0000 (16)	0.0000 (0)	0.0000 (38)
Br(1)	-0.2168 (2)	0.2157 (2)	0.2685 (4)
Br(2)	0.0037 (4)	0.0000 (0)	0.4384 (8)
Br(3)	0.0016 (6)	0.0000 (0)	-0.4436 (10)
N(1)	-0.0009 (14)	0.1553 (9)	0.0307 (27)
N(2)	-0.1503 (12)	0.0000 (0)	-0.0006 (29)
N(3)	0.1537 (15)	0.0000 (0)	0.0331 (35)
C(1)	-0.0063 (15)	0.2128 (14)	-0.2099 (37)
C(2)	-0.0058 (17)	0.3267 (18)	-0.1429 (37)
C(3)	0.2104 (24)	0.0000 (0)	-0.1581 (55)
C(4)	0.3271 (26)	0.0000 (0)	-0.0894 (64)
C(5)	-0.2122 (21)	0.0000 (0)	-0.2195 (49)
C(6)	-0.3274 (24)	0.0000 (0)	-0.1580 (58)
O(1)	-0.3068 (10)	0.3056 (10)	0.7535 (24)

Table 2. Thermal parameters and standard deviations

The scattering factor for an atom is expressed as

$$f = f_0 \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

Anisotropic thermal parameters ($\times 10^4$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pt	36.8 (4)	29.7 (4)	228 (2)	0 (0)	10 (2)	0 (0)
Br(1)	83 (2)	64 (2)	379 (8)	43 (3)	-22 (6)	14 (6)
Br(2)	65 (4)	51 (4)	298 (28)	0 (0)	25 (17)	0 (0)
Br(3)	73 (4)	64 (4)	456 (40)	0 (0)	-28 (20)	0 (0)

Isotropic thermal parameters (Å^2)

N(1)	3.13 (23)	C(2)	5.88 (54)	C(5)	4.05 (55)
N(2)	2.09 (32)	C(3)	5.21 (69)	C(6)	6.16 (75)
N(3)	3.30 (41)	C(4)	6.16 (78)	O(1)	5.04 (31)
C(1)	3.80 (36)				

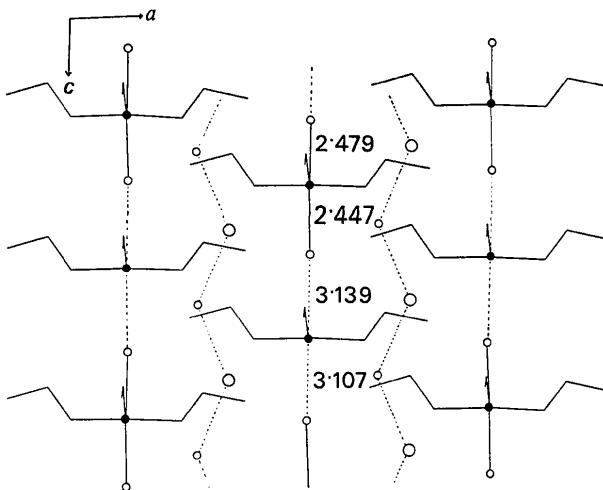


Fig. 2. The structure as interpreted, projected on (010).

Table 3. Bond lengths and bond angles with standard deviations

Pt—Br(2)	2.447 (5) Å	N(2)—C(5)	1.46 (3) Å
Pt—Br(3)	2.479 (6)	N(3)—C(3)	1.34 (3)
Pt—N(1)	2.105 (16)	C(1)—C(2)	1.58 (3)
Pt—N(2)	2.027 (14)	C(3)—C(4)	1.60 (4)
Pt—N(3)	2.075 (16)	C(5)—C(6)	1.60 (4)
N(1)—C(1)	1.55 (2)		
Br(2)—Pt—N(1)	85.3 (4) °		
Br(2)—Pt—N(2)	89.1 (4)		
Br(2)—Pt—N(3)	85.9 (5)		
Br(2)—Pt—N(1) (x, \bar{y} , z)	85.3 (4)		
Br(2)—Pt—Br(3)	179.2 (1)		
N(1)—Pt—N(2)	175.0 (6)		
N(1)—Pt—N(3)	90.1 (6)		
N(1)—Pt—N(1) (x, \bar{y} , z)	170.6 (6)		
N(1)—Pt—Br(2)	85.3 (4)		
N(2)—Pt—Br(3)	88.3 (4)		
N(2)—Pt—N(3)	175.0 (6)		
N(2)—Pt—N(1) (x, \bar{y} , z)	89.5 (6)		
N(3)—Pt—Br(3)	86.6 (5)		
N(3)—Pt—N(1) (x, \bar{y} , z)	90.1 (6)		
Br(3)—Pt—N(1) (x, \bar{y} , z)	85.3 (4)		
Pt—N(1)—C(1)	115.3 (11)		
Pt—N(2)—C(5)	123.0 (12)		
Pt—N(3)—C(3)	121.9 (15)		
N(1)—C(1)—C(2)	106.3 (15)		
N(2)—C(5)—C(6)	110.5 (18)		
N(3)—C(3)—C(4)	113.2 (21)		

Discussion. The structures of a number of similar mixed valence compounds of Pt and Pd have previously been studied (Brosset, 1948; Hall & Williams, 1958; Ryan & Rundle, 1961; Craven & Hall, 1961, 1966; Wallen, Brosset & Vannerberg, 1962), and in every case the odd layer lines about the chain axis were observed to be continuous. Invariably the subcell structure as deduced from the even-layer reflexions shows a six-coordinate complex ion in which the axial ligands are half-weight halogen atoms, other atoms usually appearing to be normal. The crystals are diamagnetic, they are highly coloured, they can commonly be formed reversibly from a mixture of the appropriate Pt(II) and Pt(IV) species, and their absorption spectra have been interpreted as indicating intervalence exchange between Pt(II) and Pt(IV) (Cohen & Davidson, 1951; Tsuchida & Yamada, 1956; Yamada & Tsuchida, 1956). The obvious structural interpretation has been in terms of chains of alternating square planar Pt(II) and octahedral Pt(IV) species, as in Fig. 2. If the dimensions of the two species are the same, other than for the axial Pt—halogen bonds, then stacking mistakes in which a chain remains internally ordered but is displaced in the chain direction by one-half the repeat unit would cause apparent disorder only of the chain halogen atoms. The only near neighbours of these atoms are within the chain, and thus little difference in packing energy would arise from such mistakes, which could then be expected to be frequent. The invariable occurrence of diffuse odd layer lines can thus be explained.

Although the analysis of the present subcell structure was somewhat more rigorous than that of previous studies, errors in the light atom parameters are still high. Within these errors the molecular dimensions are normal, as are the thermal parameters. The two Pt—Br bonds differ slightly but significantly in length, the longer bond occurring on that side to which the alkyl C atoms are directed. The Pt atom is displaced 0.11 Å from the plane of the N atoms towards the same side, the distortion of the complex ion appearing to reflect the close non-bonded approaches (3.16–3.19 Å) between Br(3) and the α -carbon atoms in the octahedral ion [Pt(C₂H₅NH₂)₄Br₂]²⁺. The intra-chain approaches between Br(2) and the α -carbon atoms of the planar [Pt(C₂H₅NH₂)₄]²⁺ ion are longer (3.49–3.54 Å) and it might be expected that this ion would show a similar but lesser distortion. Such a difference between the Pt(II) and Pt(IV) species might only result in high thermal parameters in the average subcell structure, but in fact these are not abnormally high.

The chloro analogue of the present compound, which is known as Wolfram's Red Salt, has been described (Craven & Hall, 1961) as being tetragonal, space group *I4mm*, but the structure is very similar to that described herein. At first sight photographs of the bromo compound also appeared to have tetragonal symmetry, but close investigation revealed the true symmetry to be monoclinic. Recognition of the lower symmetry obviates an anomaly that exists in the reported structure of Wolfram's Red Salt, *viz.* that the halide ions and the water molecules are randomly occupying a set of symmetry-related positions. In the present structure the bromide ions and water molecules are ordered, and form zigzag chains parallel to *c*, as in Fig. 2. The O...Br distances of 3.24, 3.31 Å and the angle Br...O...Br of 116.9° suggest hydrogen bonding within the chain. It is possible that the structure of Wolfram's Red Salt may also be only pseudo-tetragonal, and that it is isostructural with its bromo analogue.

References

- BROSSET, C. (1948). *Ark. Kem. Min. Geol.* **25A**, 1–14.
 COHEN, A. J. & DAVIDSON, N. (1951). *J. Amer. Chem. Soc.* **73**, 1955–1958.
 CRAVEN, B. M. & HALL, D. (1961). *Acta Cryst.* **14**, 475–480.
 CRAVEN, B. M. & HALL, D. (1966). *Acta Cryst.* **21**, 177–180.
 DREW, H. D. K. & TRESS, H. J. (1935). *J. Chem. Soc.* pp. 1244–1251.
 HALL, D. & WILLIAMS, P. P. (1958). *Acta Cryst.* **11**, 624–626.
 RYAN, T. D. & RUNDLE, R. E. (1961). *J. Amer. Chem. Soc.* **83**, 2814–2816.
 TSUCHIDA, R. & YAMADA, S. (1956). *Bull. Chem. Soc. Japan*, **29**, 421–425.
 WALLEN, J., BROSSET, C. & VANNERBERG, N.-G. (1962). *Ark. Kem.* **A18**, 541–551.
 YAMADA, S. & TSUCHIDA, R. (1956). *Bull. Chem. Soc. Japan*, **29**, 894–898.