

The Crystal Structure of *trans*-Dichlorobis[(—)-1(*R*),2(*R*)-cyclohexanediamine]platinum(IV)-bis[(—)-1(*R*),2(*R*)-cyclohexanediamine]platinum(II) Tetrachloride. A Note on the Corresponding Bromide Compound

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The title compound is orthorhombic, *I*222 with $a = 24.268(4)$ Å, $b = 6.820(1)$ Å, $c = 5.158(1)$ Å, and $Z = 1$. The structure has been solved by conventional X-ray methods and refined by the method of least-squares to an *R*-value of 0.025 based on 1528 independent counter reflections. The structure consists of a stacking of chains parallel to the *c*-axis along which quadratic $[\text{Pt}(-\text{chxn})_2]^{2+}$ and tetragonal $[\text{Pt}(-\text{chxn})_2\text{Cl}_2]^{2+}$ alternate. The Pt—Cl and Pt—N distances are 2.324(2) Å and 2.056(4) Å, respectively. The cyclohexane ring has the chair conformation with the nitrogen atoms in equatorial positions.

Platinum(III) complexes containing amines and halogens as ligands are now generally believed not to exist. X-Ray investigations ¹⁻⁷ have shown that these compounds more adequately are described as mixed-valence complexes of quadratically coordinated Pt(II) and octahedrally coordinated Pt(IV) linked together by unsymmetrical halide bridges. The compounds subjected to X-ray investigations until now, have all shown a certain degree of disorder revealed as continuous streaks in reciprocal space and interpreted as due to stacking faults. The initial X-ray examination of the present compound by film methods showed no sign of partial disorder. A complete three-dimensional X-ray analysis has therefore been undertaken in an attempt to clarify the structure of these mixed-valence Pt complexes. The analogous bromide $[\text{Pt}(-\text{chxn})_2\text{Br}_2][\text{Pt}(-\text{chxn})_2]\text{Br}_4$

with cell parameters $a = 23.80(2)$ Å, $b = 7.009(6)$ Å and $c = 5.373(4)$ Å is isostructural with the chloride.

EXPERIMENTAL

Preparations

Bis[(—)-1,2-cyclohexanediamine]platinum(II) chloride. To a boiling solution of 4.2 g potassium tetrachloroplatinate(II) (10 mmol) in 30 ml of water containing a few drops of ethanol was slowly added 2.51 g pure (—)-1,2-cyclohexanediamine (22 mmol). The precipitate which immediately separated was gradually dissolved during vigorous mechanical stirring and heating for 1 h. The reaction mixture was filtered and 2 ml conc. hydrochloric acid was added. After cooling in ice for 1 h the product was collected on a filter and washed with ethanol and dried in air. Yield: 4.3 g (87 %).

trans-Dichloro-bis[(—)-1,2-cyclohexanediamine]platinum(IV) chloride. 2 g of $[\text{Pt}(-\text{chxn})_2]\text{Cl}_2$ (4.05 mmol) was dissolved in 40 ml of water and chlorine gas was slowly bubbled through the solution until its colour began to change from light yellow to orange. Air was bubbled through the solution to remove the excess chlorine gas. The solution was filtered and evaporated in vacuum to approximately 5 ml and after addition of 1.0 ml conc. hydrochloric acid the mixture was cooled in ice for $\frac{1}{2}$ h. The crystalline product was collected on a filter and washed with ethanol. Yield: 1.7 g (74.3 %).

trans-Dichlorobis[(—)-1,2-cyclohexanediamine]platinum(IV) - bis[(—)-1,2-cyclohexanediamine]platinum(II) chloride. A 50 °C hot solution of 0.56 g *trans* $[\text{Pt}(-\text{chxn})_2\text{Cl}_2]\text{Cl}_2$ (1.0 mmol) in 12 ml water was added to a 50 °C hot

solution of 0.5 g [Pt(-chxn)₂]Cl₂ (1.0 mmol) in 6 ml of water. 10 ml of a saturated solution of lithium chloride in methanol was slowly added. The solution turned black and soon crystals with a metallic sheen commenced to separate. The mixture was cooled in ice and filtered after 1 h. The product was washed with ethanol and dried in air. Yield 0.8 g (75.5 %).

The black crystals of the compound dissolved in a minimum of hot water give an almost colourless solution, from which black crystals separate out on cooling. (Found: C 27.92; H 5.33; N 10.58; Cl 20.08; Pt 36.3. Calc. for [Pt(C₆H₁₄N₂)₂Cl₂][Pt(C₆H₁₄N₂)₂]Cl₄: C 27.22; H 5.66; N 10.82 Cl 19.92; Pt 36.8).

trans-Dibromobis[(-)-1,2-cyclohexanediamine]platinum(IV)-bis[(-)-1,2-cyclohexanediamine]platinum(II) bromide. To a solution of 0.5 g [Pt(-chxn)₂]Cl₂ (1.0 mmol) in 10 ml of water was added 2.2 ml of a saturated aqueous bromine solution (0.5 mmol). After 15 min 1 ml of a saturated ammonium bromide solution was added dropwise. Black crystals with a golden sheen separated. The mixture was cooled in ice and filtered after ½ h. The product was washed with ethanol and dried in air. Yield 0.55 g (83 %). Anal. [Pt(C₆H₁₄N₂)₂Br₂][Pt(C₆H₁₄N₂)₂]Br₂: C, H, N, Br, Pt.

X-Ray technique. Space groups were determined from Weissenberg and precession photographs using Cu and Mo radiation ($\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$, $\lambda(\text{MoK}\alpha) = 0.7107 \text{ \AA}$). Lattice parameters for the chlorine compound were obtained from a least-squares refinement of setting angles for 26 reflections with $18.9^\circ \leq 2\theta < 37.6^\circ$. Three-dimensional intensity data were collected with an automatic Picker four-circle instrument using graphite monochromatized MoK α radiation. The background-peak-background technique was used in a $\omega/2\theta$ scan, $t_{\text{background}} = 20 \text{ s.}$, scan rate = $2^\circ/\text{min}$. The crystal which had the linear dimensions $0.03 \times 0.35 \times 0.46 \text{ mm}^3$ bounded by {100}, {010} and {001} and was mounted in an arbitrary orientation. Data were collected out to $\sin \theta/\lambda \approx 0.9 \text{ \AA}^{-1}$ giving 3665 reflections which were reduced to 1529 independent reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Data processing included absorption correction. A $4 \times 10 \times 12$ grid was used and the transmission factor varied between 0.0853 and 0.7578. Lattice parameters for the bromine compound were determined by film technique.

CRYSTAL DATA

[Pt(C₆H₁₄N₂)₂Cl₂][Pt(C₆H₁₄N₂)₂]Cl₄; M = 1059.6, orthorhombic. Unit cell: $a = 24.268(4) \text{ \AA}$, $b = 6.820(1) \text{ \AA}$, $c = 5.158(1) \text{ \AA}$, $V = 853.7 \text{ \AA}^3$, $D_m = 2.058 \text{ g cm}^{-3}$, $D_c = 2.061 \text{ g cm}^{-3}$, $Z = 1$. $\mu_{\text{MoK}\alpha} = 91.0 \text{ cm}^{-1}$. Systematic absences: hkl : $h + k + l = 2n + 1$. Space group: $I222$ (D_2^2 , No. 23); from structure analysis. [Pt(C₆H₁₄N₂)₂Br₂]-

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[Pt(C₆H₁₄N₂)₂]Br₂; M = 1326.4. Crystal system: orthorhombic. Unit cell: $a = 23.80(2) \text{ \AA}$, $b = 7.009(6) \text{ \AA}$, $c = 5.373(4) \text{ \AA}$.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by the Patterson heavy atom method. The systematic absences indicated four possible space groups: $I222$, $I2_12_12_1$, $Imm2$ and $Immm$ of which the last two were impossible due to the lack of mirror planes in the *chxn* molecule. As $I2_12_12_1$ has only eightfold and fourfold point positions $I222$ was left as the most probable space group requiring the overall formula to be [Pt(-*chxn*)₂Cl]₂Cl₂ with $Z = 2$. This was confirmed by the three-dimensional Patterson map from which all non-hydrogen atoms could be found and which clearly showed the appearance of two half-weight chlorine atoms (point position 4(i)). Least-squares refinement of atomic coordinates, scale factor and isotropic temperature factors gave $R = 0.081$. Hydrogen atoms were inserted in fixed calculated positions with constant B -values of 3.0 \AA^2 , weighting was introduced and the (200) reflection removed because of probable extinction effects. Finally the z -coordinates of N and C₃ were allowed only to move half the calculated distance in the least-squares refinement as these parameters oscillated severely; this may be due to their closeness to $z = 0.0$. With anisotropic temperature factor parameters for non-hydrogen atoms final R and R_w values of 0.025 and 0.031, respectively, were obtained and a difference Fourier map showed no further atoms, the largest peak being less than 0.5 electron/ \AA^3 . Atomic coordinates are given in Table 1, temperature factor parameters in Table 2. A list of observed and calculated structure factors is available on request.

Data processing was performed with the programs DATAPP and DSORTH. Least-squares refinement was carried out with the full matrix program LINEX, the quantity minimized was

$$R_w = \sum w ||F_o| - k|F_c|| / \sum |F_o|, \text{ where}$$

$$w = 1/(\mu(F))^2$$

$$\mu(F) = [\sigma(F_o^2)_{\text{count}} + 1.02F_o^2]^{\frac{1}{2}} - |F_o|$$

Table 1. Atomic coordinates with standard deviations $\times 10^4$ in parentheses. Calculated hydrogen positions under the assumption of sp^3 hybridized atoms and distances N-H = 0.95 Å, C-H = 1.00 Å. The atom Cl₁ is disordered.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0	0	0	H ₁	0.056	0.299	0.138
Cl ₁	0	0	0.4505(4)	H ₂	0.067	0.263	-0.154
Cl ₂	0.5834(1)	0	0	H ₃	0.116	0.070	0.267
N	0.0634(2)	0.2019(5)	0.0115(79)	H ₄	0.167	0.345	0.094
C ₁	0.1150(2)	0.0954(7)	0.0763(10)	H ₅	0.167	0.240	-0.189
C ₂	0.1670(2)	0.2162(7)	0.0057(75)	H ₆	0.216	0.062	0.268
C ₃	0.2181(2)	0.0947(9)	0.0801(13)	H ₇	0.252	0.171	0.045

Table 2. Mean square vibration amplitudes u_{ij} with estimated standard deviations (both $\times 10^4$). The u_{ij} are defined by: $\exp[-2\pi^2(u_{11}a^{*2}h^2 + \dots + 2u_{12}a^*b^*hk + \dots)]$.

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Pt	210(1)	130(1)	117(1)	0	0	0
Cl ₁	352(13)	297(11)	147(10)	-147(31)	0	0
Cl ₂	564(10)	269(6)	278(7)	0	0	33(46)
N	298(14)	170(10)	221(7)	-11(10)	54(29)	5(24)
C ₁	268(19)	205(15)	213(16)	-18(15)	-30(16)	-17(14)
C ₂	295(19)	256(17)	637(38)	-4(16)	96(134)	103(89)
C ₃	256(21)	400(27)	381(28)	-73(21)	-23(20)	26(24)

The atomic scattering factors used were those given by Cromer and Mann⁸ for Pt, Cl, N, and C. For hydrogen the scattering curve given by Stewart, Davidson and Simpson⁹ was used. No correction was made for anomalous dispersion. Interatomic distances and angles were calculated with the program ORFFE including variance-covariance matrix and cell parameter errors; drawings were made using ORTEP. Detailed references to the programs are given in Ref. 10.

RESULTS AND DISCUSSION

The title compound is to our knowledge the first described analogue to Wolfram's red salt¹¹ and Reihlen's green salt¹² Pt *etn*₄x₃.2H₂O (*etn* = ethylamine, x = Cl and Br).

Wolfram obtained his salt from [Pt *etn*₄]Cl₂.2H₂O by the action of hydrogen peroxide in hydrochloric acid. The same procedure with [Pt(-*chxn*)₂]Cl₂ (-*chxn* = (-)-1,2-cyclohexanediamine) yields the colourless sparingly soluble hydroxo-complex: [Pt(-*chxn*)₂OH]Cl₂.H₂O. Reihlen and Flohr¹² found that Wolfram's salt

Table 3. Interatomic distances and angles with standard deviations in parentheses.

Distance	Å	Angle	Degrees
Pt-Cl ₁	2.324(2)	N-Pt-Cl ₁	88.4(1.1)
Pt-Cl ₁ ⁱ	2.834(2)	N-Pt-N ⁱⁱ	83.7(0.2)
Pt-N	2.056(4)	Pt-N-C ₁	108.0(0.4)
N-C ₁	1.485(11)	N-C ₁ -C ₂	111.9(0.6)
C ₁ -C ₁ ⁱⁱ	1.521(9)	N-C ₁ -C ₁ ⁱⁱ	107.6(1.0)
C ₁ -C ₂	1.550(10)	C ₁ ⁱⁱ -C ₁ -C ₂	109.5(1.0)
C ₂ -C ₃	1.541(12)	C ₁ -C ₂ -C ₃	108.2(0.9)
C ₂ -C ₃ ⁱⁱ	1.534(14)	C ₂ -C ₃ -C ₃ ⁱⁱ	108.6(1.1)
Cl ₁ -Cl ₂	3.974(1)		
Cl ₂ -Cl ₂ ⁱⁱⁱ	4.050(4)		
Hydrogen bonds			
N...Cl ₂	3.274(31)		
N...Cl ₂ ^{iv}	3.366(31)		
H ₁ -Cl ₂	2.41		
H ₂ -Cl ₂ ^{iv}	2.44		
Dihedral angles			
(N-Pt-N ⁱⁱ)-(N ^v -Pt-N ^{vi})			11.5(3.7)
(N-Pt-N ⁱⁱ)-(C ₁ -C ₁ ⁱⁱ -C ₃ ⁱⁱ)			25.5(1.9)
(C ₁ -C ₁ ⁱⁱ -C ₃ ⁱⁱ)-(C ₁ -C ₂ -C ₃)			58.7(2.1)
Symmetry operations			
(i) <i>x, y, 1-z</i> ; (ii) <i>x, \bar{y}, \bar{z}</i> ; (iii) \bar{x}, y, z			
(iv) <i>x, y, \bar{z}</i> ; (v) \bar{x}, \bar{y}, z ; (vi) \bar{x}, y, \bar{z}			

could be prepared directly by mixing aqueous solutions of [Pt(*etn*)₂]Cl₂ and *trans*[Pt(*etn*)₂]Cl₂. The same method is used by preparation of [Pt(-*chxn*)₂]Cl₂ and [Pt(-*chxn*)₂]Br₂.

It seems to be obvious that Wolfram's salt and the present salts contain platinum in the oxidation states +2 and +4, and not +3. As is the case for Wolfram's salt¹⁸ [Pt(-*chxn*)₂]Cl₂ is diamagnetic. The black-green crystals of the compound dissolved in a minimum of hot water give a colourless solution from which the black-green crystals of the original compound separate out on cooling. The crystals show a striking dichroism. They are black with polarized light having the electric vector along the *c*-axis and almost colourless with polarized light having its electric vector normal to the *c*-axis.

Description of the structure. The structure is interpreted in terms of chains of Pt(-*chxn*)₂ groups connected by chloride ions with the

Pt-Cl bonds parallel to the *c*-axis (Figs. 1 and 2). Film data showed no sign of disorder in the structure. But the appearance of two half-weight chloride ions attached to each platinum indicate stacking faults. A chain remains internally ordered but is displaced in the chain direction by one-half the repeat unit. Thus there is no crystallographic distinction between Pt(II) and Pt(IV). Each chlorine atom in the chain may be regarded as forming a covalent bond to a Pt(IV) with length 2.324 Å. This is significantly longer than the Pt(IV)-Cl distance in Wolfram's salt (2.26 Å).⁵ On the other hand the distance to the Pt(II) 2.834 Å compared with 3.13 Å for Wolfram's salt suggests a much stronger interaction between the two units in the (-)-1,2-cyclohexanediamine complex salt. It is interesting that [Pt(-*chxn*)₂]Cl₂ is nearly black (absorbs at all wavelengths in the visible region) whereas Wolfram's salt only absorbs at wavelengths less

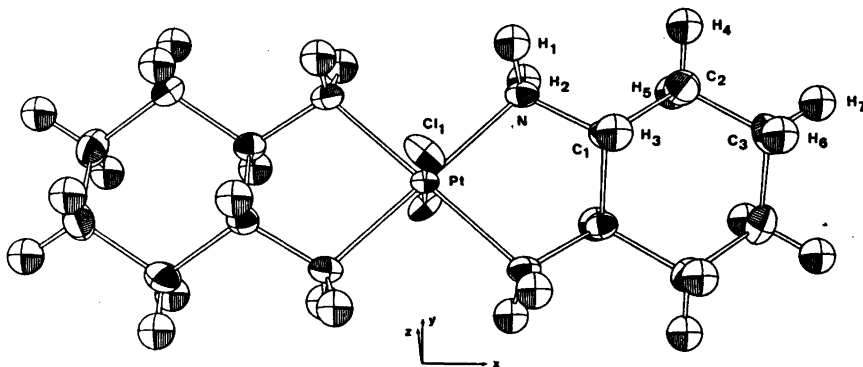


Fig. 1. Perspective drawing of *trans*-[Pt(-*chxn*)₂Cl₂]⁺² in *trans*-[Pt(-*chxn*)₂Cl₂][Pt(-*chxn*)₂]Cl₄. Thermal ellipsoids enclose 50 % probability (ORTEP II).

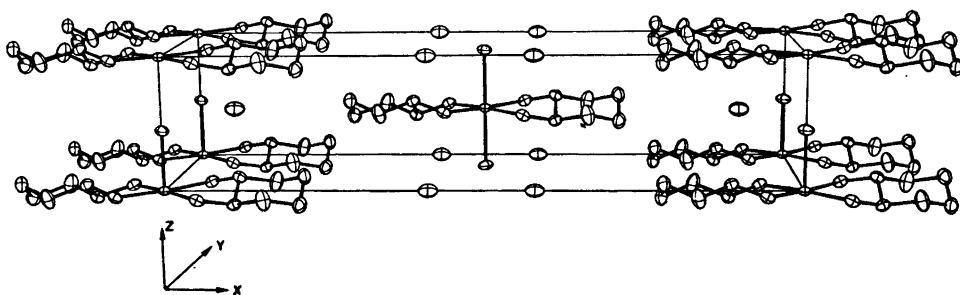


Fig. 2. Perspective drawing of *trans*-[Pt(-*chxn*)₂]Cl₂. Hydrogen atoms have been omitted for clarity.

than about 600 nm. Thus the charge transfer from Pt(II) to Pt(IV) along the chains appears at lower energy when the two oxidation states are in more similar environment.

As no correction was made for anomalous dispersion, the small differences in interatomic distances and angles between this structure and similar structures should not be regarded as significant.

The geometrical data for the coordinated (-)-1,2-cyclohexanediamine may also be affected by the disorder along the *c*-axis. The Pt-N distance which is a mean value between Pt(II)-N and Pt(IV)-N distances is close to other reported Pt-N distances.^{3,7} Angles and distances in (-)-1,2-cyclohexanediamine are within two standard deviations of those found in $AlCl_3[Co(+chxn)_2]Cl_3 \cdot 5H_2O$.¹⁴ However, the N-Pt-N angle in the five-membered chelate ring is significantly smaller than the analogous angle in the Co(III) complex.¹⁴

The absolute configuration of (-)-1,2-cyclohexanediamine is 1(*R*), 2(*R*).¹⁴ Thus in the Pt(-*chxn*)₂ unit the chelate rings have the conformations $\lambda\lambda$.

The fact that the Pt(-*chxn*)₂ unit is unable to perform any changes of conformation and is rather flat is probably the reason why a packing with such a short Pt-Cl-Pt distance can be achieved. Hydrogen bonds between the ionic chloride and the amino groups may also be of importance in this respect. In contrast to Wolfram's salt the present salt does not contain water of crystallization. This is quite remarkable as Wolfram's salt changes colour to pale yellow on dehydration.

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