[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part II.[1] Some of the Optical Isomers of Tris-(propylenediamine)-platinum(IV) Ion

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The reaction between hydrogen hexachloroplatinate(IV) and *dextro*-propylenediamine in alcoholic solution resulted in the formation of two optical isomers of tris-(*d*-propylenediamine)-platinum(IV) chloride and, as well, substantial amounts of bis-(*d*-propylenediamine)-platinum(II) chloride. Separation of the tris-complexes was effected through the sparingly soluble oxalates from which the isomers designated L-*ddd* and D-*ddd* have been isolated. The oxalates had $[\alpha]_{\mathrm{D}}$ −168° and +13°, respectively, in 0.015 *N* sodium hydroxide. Similar results were obtained by the use of *l*-propylenediamine. The predominant isomers L-*ddd* and D-*lll* accounted for approximately 85% of the tris-complexes formed in the reaction.

Introduction

The most convincing evidence for the stereospecific limitation of the number of optical isomers in octahedral complexes with three optically active ligands comes from the work of Smirnoff[3] who isolated only one isomer in the synthesis of tris-(propylenediamine)-platinum(IV) chloride from either *d* or *l*-propylenediamine (rotations of the bases used not quoted) or by the resolution of the substance prepared from the racemic base. The bromides prepared from the *d*- and *l*-forms of the base had $[\alpha]_{\mathrm{D}} \mp 140^\circ$ and this value was unchanged following transformation to the *d*- and *l*-tartrates, respectively, recrystallization of the diastereoisomers and regeneration of the bromide. The bromides prepared from $\mathrm{DL}[\mathrm{Pt}(dl\text{-pn})_3]\mathrm{Cl}_4$ by resolution through the *d*- and *l*-tartrates had $[\alpha]_{\mathrm{D}} \mp 137.4^\circ$, respectively. The isomers were designated[4] L-*ddd* and D-*lll* and the base recovered from the latter had $[\alpha]_{\mathrm{D}}$ −26.71°. Though this rotation is low compared with the best values for the "anhydrous" base[5] ($[\alpha]_{\mathrm{D}}$ − 29.78°) this may be due either to the presence of water or optical impurity.

In this investigation the complexes with Pt(IV) have been prepared with 99% pure *d*-and *l*-propylenediamine and subjected to systematic fractional crystallization through the chloride, oxalate and tetraiodocadmiate(II). Though the chloride ultimately proved unsuitable because of its high solubility in water, the initial fractionation experiments demonstrated that the complex prepared from either optical form of the base was not a single entity but a mixture of at least three substances. The crude chloride prepared from the dextro base and hydrogen hexachloroplatinate(IV) had $[\alpha]_{\mathrm{D}}$ − 116°, a much lower value than that recorded by Smirnoff, ($[\alpha]_{\mathrm{D}}$ − 172°). This was split into seven fractions by crystallization from water. The least soluble fraction had $[\alpha]_{\mathrm{D}}$ − 202°, falling to −12° for the second fraction, rising again to −142° for the fourth and falling to −68° for the most soluble portion. The first fraction, which was much less soluble than would appear from Smirnoff's description, could be purified easily to give a substance with $[\alpha]_{\mathrm{D}}$ −212°, $[\alpha]_{5461}$ −252°, values much higher than Smirnoff's pure chloride[3] ($[\alpha]_{\mathrm{D}}$ − 178°).

The best method of separation of the mixture was found to be through the oxalates. The crude chloride in aqueous solution was treated with potassium oxalate and fractions removed while the volume was evaporated to about one fifth of the original amount. The excess oxalate was then removed as calcium oxalate and the remaining platinum compound in the solution precipitated as tetraiodocadmiate(II). This proved to be the bis-complex, $[\mathrm{Pt(pn)_2}][\mathrm{CdI_4}]\cdot\mathrm{H_2O}$. From the oxalate fractions two isomeric tris-complexes were obtained which after transformation to the chlorides gave $[\alpha]_{\mathrm{D}}$ −213° and +1.3°. The corresponding oxalates gave $[\alpha]_{\mathrm{D}}$ − 168° and +13° in 0.015 *N* sodium hydroxide. These have been designated L-*ddd* and D-*ddd*, respectively. Repeated fractionation gave no evidence for the isolation of the *cis/trans* forms of these isomers, and it is concluded that, like the Co(III) complexes,[1] the solubility differences are unfavorable for the separation. The relative amounts of the thermodynamically stable (L-*ddd*) and unstable (D-*ddd*) isomers were also of the same order as with the Co(III) complexes[1] (85 and 15%, respectively.)

Because of the high positive charge, the tris-(propylenediamine)-platinum(IV) ion, like the hexammine and tris-(ethylenediamine)–platinum (IV) ions, behaved as a weak acid[6] by the loss of a proton from an $-\mathrm{NH_2}$ group. A decrease in rotation accompanied the formation of a yellow color in alkaline solution, but no loss in rotation ensued after boiling for 15 minutes in 2.5 *N* sodium hydroxide.

High concentrations of extraneous ions, especially iodide and oxalate, caused considerable rotational changes due presumably to association with the cation. A 0.5% aqueous solution of the chloride of the L-*ddd* isomer gave $[\alpha]_{\mathrm{D}}$ −213°; $[\alpha]_{5461}$ −252°, and in 10% sodium iodide $[\alpha]_{\mathrm{D}}$ −182°, $[\alpha]_{5461}$ −217°. A 1.5% aqueous solution of the chloride of the D-*ddd* isomer gave $[\alpha]_{\mathrm{D}}$ + 1.3° and in concentrated potassium oxalate solution $[\alpha]_{\mathrm{D}}$ + 13°. In the same way the chloride of the D-*ddd* isomer had $[\alpha]_{\mathrm{D}}$ + 1.3° while the oxalate had $[\alpha]_{\mathrm{D}}$ + 15° in water.

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[1] Part I, F. P. Dwyer, F. L. Garvan and A. Shulman, THIS JOURNAL, **81**, 290 (1959).

[2] General Motors–Holden's Limited Post Graduate Research Fellow.

[3] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[4] Some confusion has arisen because in the introduction to his paper, Smirnoff quoted the isomer containing *l*-propylenediamine as having a negative rotation, but in the experimental section with a positive rotation.

[5] L. Tschugaeff and W. Sokoloff, *Ber.*, **42**, 55 (1909).

[6] "Gmelin's Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim Bergstrasse, 1957, 68D, pp. 28, 30.

The separation of the platinum complex into two optical isomers present in unequal amounts and with unequal and opposite rotations suggests strongly that the recent conclusions of O'Brien and Toole[7] on partial induced asymmetry may be in error. The platinum compound is one of the colorless complexes containing optically active ligands for which the constant dispersion ratio $\alpha_{4705}/\alpha_{5880} = 1.74$ was observed.[7] But for the fact that bis-(*d*-propylenediamine)-platinum(II) chloride, in which the complex cation itself is not dissymmetric, has the same ratio one might conclude very reasonably that the constant dispersion ratio means simply that the isomeric composition of all of the substances quoted is similar. The lability of the zinc and cadmium complexes quoted does not affect the equilibrium composition but only its rate of attainment. However the dispersion ratio does not appear to be a reliable guide. In Table I, the dispersion ratio $\alpha_{5461}/\alpha_{5893}$ (a smaller wave length range), has been listed for a number of complexes. It will be observed, for instance, that the ratio 1.19–1.20 applies for the $[\mathrm{Pt}(d\text{-pn})_2]^{2+}$ ion where the activity resides in the ligand alone and the D-$[\mathrm{Pt}(l\text{-pn})_3]^{4+}$ ion where the whole complex also contributes. Similarly, from the arguments adduced[7] one should conclude that the source of optical activity is different in the D-$[\mathrm{Rh(en)_3}]^{3+}$ and D-$[\mathrm{Rh}(m\text{-ptn})_3]^{3+}$ ions in which the ligands are inactive and the whole of the activity arises from the complex.

TABLE I

Compound[8]	$\alpha_{5461}/\alpha_{5893}$	Ref.
$[\mathrm{Pt}(d\text{-pn})_2]^{2+}$	1.20	This work
D-$[\mathrm{Pt}(l\text{-pn})_3]^{4+}$	1.19	This work
D-$[\mathrm{Pt(en)_3}]^{4+}$	1.19	Mathieu[9]
D-$[\mathrm{Rh(en)_3}]^{3+}$	1.21	Jaeger[10]
$[\mathrm{Rh}(d\text{-ptn})_3]^{3+}$	1.21	Dippel and Jaeger[11]
D-$[\mathrm{Rh}(m\text{-ptn})_3]^{3+}$	1.26	Dippel and Jaeger[11]

The bis-complex $[\mathrm{Pt(pn)_2}]^{2+}$ which accounted for about 40% of the material which was obtained in the synthesis can be prepared in quantitative yield by heating the tris compound with aqueous propylenediamine at 80 to 90°. No search has been made for the *cis* and *trans* isomers of this substance. It seems probable that a 7- or 8-covalent platinum(IV) intermediate is formed with the loss of the stabilizing inert gas configuration, by the utilization of higher d or f orbitals, and rapid reduction and dismutation then ensues. Recently it has been shown that bis-(α-aminoethylamido)-ethylenediamine-osmium(IV) bromide, (a tris-(ethylenediamine)-osmium(IV) complex from which two protons detach), reacts with a further molecule of ethylenediamine to yield an 8-covalent osmium-(IV) complex.[12] Similar reactions that occur when Co(III) complexes are heated with various coordinating molecules will be discussed in Part III.

Experimental

All rotations were measured at 20° in a 2-dm. tube.

Fractional Crystallization of Tris-(*d*-propylenediamine)-platinum (IV) Chloride.—The substance was prepared as described by Smirnoff[3] by the reaction between alcoholic hydrogen hexachloroplatinate(IV) (from platinum, 13.3 g.) and *d*-propylenediamine (39.6 g. of 73.5% w./w., $[\alpha]_D$ in benzene +34.0°). The crude product (24.1 g., $[\alpha]_D$ −116°) in water (80 ml.) at 90° was evaporated to 50 ml. on a steam-bath with a current of air and cooled to yield fraction A_1. Successive fractions A_2 to A_6 were obtained by evaporation and cooling. The final fraction A_7 was obtained by evaporation to dryness. The observed specific rotations at the D-line of sodium were: A_1, −202°; A_2, −12°; A_3, −88°; A_4, −142°; A_5, −78°; A_6, −72°; A_7, −68°. Repeated recrystallization of fraction A_1 gave a pure substance having $[\alpha]_D$ −212° and $[\alpha]_{5461}$ −252°. Systematic fraction of the material in such a way as to concentrate the least soluble material in the head fractions demonstrated that the dextrorotatory isomer was next in solubility to the strongly levorotatory material, $[\alpha]_D$ −212°, though the fractions always had a small negative rotation.

L-Tris-(*d*-propylenediamine)-platinum(IV) Oxalate 1-Hydrate, L-*ddd* Isomer.—The crude chloride (24.1 g.) in water (300 ml.) at 90° was treated with potassium oxalate 2-hydrate (15.4 g. in water, 150 ml.) at 90°. Fine white needles of the oxalate separated and the mixture was cooled and allowed to stand in ice for 1 hr. The precipitate, sucked as dry as possible, was suspended in ice-water (100 ml.), stirred well and refiltered. The washings were added to the original filtrate. Finally the solid was washed with ethanol and acetone and air-dried (yield 13.21 g.). The material was suspended in water (300 ml.), heated with stirring to 90° and then allowed to cool and remain in an ice-bath overnight. Most of the substance (13.1 g.) was recovered, showing its insolubility, while the mother liquor had a very small levo rotation. Purification was effected by dissolution of a portion (2.2 g.) in water (250 ml.) containing potassium acetate (4 g.) by heating to 80°. The pale yellow filtered solution was treated with glacial acetic acid (0.8 ml.) and potassium oxalate (4 g.) and allowed to crystallize for 24 hr. at 20°. The fine white needles of the complex were collected and the purification repeated as before. A 0.5% solution of the pure material in 0.05 *N* hydrochloric acid gave $[\alpha]_D$ −188°; $[\alpha]_{5461}$ −224°, and in 0.015 *N* sodium hydroxide $[\alpha]_D$ −168°; $[\alpha]_{5461}$ −194°.

Anal. Calcd. for $[\mathrm{Pt(C_3H_{10}N_2)_3}](\mathrm{C_2O_4})_2\cdot\mathrm{H_2O}$: C, 25.52; H, 5.27; N, 13.74. Found: C, 25.66; H, 5.3; N, 13.50.

L-Tris-(*d*-propylenediamine)-platinum(IV) Chloride 1-Hydrate, L-*ddd* Isomer.—This was prepared from the oxalate by heating an aqueous suspension with calcium chloride 6-hydrate and adjusting to *p*H 8 by the addition of lithium hydroxide 1-hydrate. After removal of the calcium oxalate precipitate the filtrate was made acid with hydrochloric acid and evaporated to dryness. The lithium chloride was washed out with ethanol and the white residue recrystallized from a little hot water. The substance gave $[\alpha]_D$ −213°, $[\alpha]_{5461}$ −252°, and was identical with the chloride above.

Anal. Calcd. for $[\mathrm{Pt(C_3H_{10}N_2)_3}]\mathrm{Cl_4\cdot H_2O}$: C, 18.72; H, 5.59; N, 14.56. Found: C, 18.77; H, 5.37; N, 14.38.

D-Tris-(*d*-propylenediamine)-platinum(IV) Oxalate 5-Hydrate, D-*ddd* Isomer.—The filtrate and washings remaining from the separation of the least soluble oxalate above were evaporated on the steam-bath with a current of air to a volume of 130 ml. and allowed to stand for crystallization for 14 days. By this time the volume had decreased to 70 ml. The white crystalline material (4.58 g.) after washing with ice-water, was dissolved in water (500 ml.) at 85°, cooled and kept in ice for 5 hr. The small amount of material (0.34 g., $[\alpha]_D$ −134°) that crystallized out was mostly the L-*ddd* isomer. The filtrate remaining was dextrorotatory and was fractionally crystallized by gradual evaporation. All of the fractions (total weight of material, 3.86 g.) had positive specific rotations in the range +4 to +8°. This material was transformed back to the chloride by the addition of calcium chloride 6-hydrate (2.8 g.) to a hot aqueous solution (300 ml.) and adjustment to *p*H 8 by the addition of small amounts of lithium hydroxide 1-hydrate. After cooling and filtering the solution was made acid with hydrochloric acid and evaporated in such a way as to yield four fractions. The three least soluble fractions (total

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[7] T. D. O'Brien and R. C. Toole, THIS JOURNAL, **77**, 1368 (1955).

[8] ptn = 2,4-*n*-pentanediamine; *m* = meso.

[9] J. P. Mathieu, *Bull. soc. chim.*, **6**, 1258 (1939).

[10] F. M. Jaeger, *Rec. trav. chim.*, **38**, 171 (1919).

[11] C. J. Dippel and F. M. Jaeger, *ibid.*, **50**, 547 (1931).

[12] F. P. Dwyer and J. W. Hogarth, THIS JOURNAL, **77**, 6152 (1955).

wt., 2.83 g.) had positive specific rotations of the order of +1°. The last fraction gave $[\alpha]_D$ −34° (0.5 g.) and was impure [Pt(*d*-pn$_2$]Cl$_2$. The dextrorotatory material (2.6 g.) in cold water (150 ml.) was shaken with silver oxalate, and after filtration to remove silver chloride the solution was evaporated to 40 ml. Addition of methanol (10 ml.) caused the separation of a white amorphous material that crystallized out as needles on standing overnight. A 0.5% aqueous solution gave $[\alpha]_D$ +10°, and in 0.05 *N* hydrochloric acid gave $[\alpha]_D$ +1°. By repeated recrystallization from water by the addition of ethanol the pure oxalate (0.5 g.) was obtained, $[\alpha]_D$ + 15°; $[\alpha]_{5461}$ +18° in water and $[\alpha]_D$ +13°; $[\alpha]_{5461}$ + 16° in 0.015 *N* sodium hydroxide.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_3](C_2O_4)_2\cdot 5H_2O$: C, 22.83; H, 5.90; N, 12.29. Found: C, 22.96; H, 5.88; N, 12.25. Calcd. for $[Pt(C_3H_{10}N_2)_3]Cl_4\cdot H_2O$: C, 18.72; H, 5.59; N, 14.56. Found: C, 18.97; H, 5.43; N, 14.47.

A 1.5% aqueous solution gave α_D +0.04°, whence $[\alpha]_D$ +1.3°. From a total amount of tris-complex isolated (17.2 g.) an estimated quantity of 2.5 g. of pure D-*ddd* isomer was obtained, *i.e.*, approximately 15%.

Bis-(*d*-propylenediamine)-platinum(II) Tetra-iodocadmiate(II) 1-Hydrate.—The filtrate remaining after the separation of the isomers of the tris-complex as oxalate was strongly levorotatory. Oxalate ion was removed as before by precipitation as calcium oxalate at *p*H 8. The filtered solution was acidified and on the addition of cadmium(II) acetate 2-hydrate and sodium iodide gave a white crystalline precipitate. The tetra-iodocadmiate(II) was repeatedly recrystallized from hot water by the addition of a little sodium iodide and gave $[\alpha]_D$ −20°; $[\alpha]_{5461}$ −24° in acetone.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2][CdI_4]\cdot H_2O$: C, 7.34; H, 2.26; Cd, 11.45; I, 51.7. Found: C, 7.30; H, 2.22; Cd, 11.53; I, 52.07.

The chloride was prepared by the elimination of cadmium ion as the carbonate by the addition of a slight excess of lithium carbonate and then of the iodide ion by shaking with excess of freshly precipitated silver chloride. The aqueous filtrate then was made acid with hydrochloric acid, evaporated to dryness and the lithium chloride extracted with a little ethanol. The salt was recrystallized from water by the addition of acetone and ether. A 0.5% aqueous solution gave $[\alpha]_D$ −44°; $[\alpha]_{5461}$ −53° (for the monohydrate), which compares well with the previous value $[\alpha]_D$ −46° (for the anhydrous material) recorded by Tschugaeff and Sokoloff.[4]

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2]Cl_2\cdot H_2O$: C, 16.66; H, 5.13; N, 12.96. Found: C, 16.48; H, 5.03; N, 12.82.

D-Tris-(*l*-propylenediamine)-platinum(IV) Oxalate 1-Hydrate and Chloride 1-Hydrate, D-*lll* Isomer.—This isomer was prepared from *l*-propylenediamine, ($[\alpha]_D$ in benzene −34.1°) and purified through the oxalate as described above. A 0.5% solution in 0.05 *N* hydrochloric acid gave $[\alpha]_D$ +188°, $[\alpha]_{5461}$ +244°.

Anal. Found: C, 25.54; H, 5.3; N, 13.4.

The chloride gave $[\alpha]_D$ +212°, $[\alpha]_{5461}$ +252° in 0.5% aqueous solution.

Anal. Found: C, 19.08; H, 5.55; N, 14.58.

L-Tris-(*l*-propylenediamine)-platinum(IV) Oxalate 5-Hydrate, L-*lll* Isomer.—This isomer was separated from the D-*lll* isomer as described previously and gave $[\alpha]_D$ −10°, $[\alpha]_{5461}$ −12° in aqueous solution. A 1.11% solution in 0.03 *N* hydrochloric acid gave α_D −0.04°, α_{5461} −0.05° whence $[\alpha]_D$ −1.8°, $[\alpha]_{5461}$ −2.25°.

Anal. Found: C, 23.2; H, 5.6; N, 12.56.

Bis-(*l*-propylenediamine)-platinum(II) Tetra-iodocadmiate(II) 1-Hydrate.—This was obtained from the mother liquor after the removal of the D-*lll* and L-*lll* isomers as the oxalates. A 1.0% solution in acetone gave $[\alpha]_D$ +20° and $[\alpha]_{5461}$ +24°.

Anal. Found: C, 7.53; H, 2.26; Cd, 11.62; I, 51.9.

Bis-(*l*-propylenediamine)-platinum(II) Chloride 1-Hydrate.—The chloride was isolated from the tetra-iodocadmiate(II) as described above. A 0.5% aqueous solution gave $[\alpha]_D$ +45° and $[\alpha]_{5461}$ +54°.

Anal. Found: C, 16.30; H, 5.36; N, 12.84.

Bis-(*l*-propylenediamine)-platinum(II) Iodide.—The iodide was prepared from the tetra-iodocadmiate(II) after removal of the cadmium as cadmium(II) carbonate. A 0.5% aqueous solution gave $[\alpha]_D$ +31° and $[\alpha]_{5461}$ +37°.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_2]I_2$: C, 12.06; H, 3.38; N, 9.38. Found: C, 12.28; H, 3.39; N, 9.27.

Reaction of D-Tris-(*l*-propylenediamine)-platinum(IV) Chloride with *l*-Propylenediamine.—The tris complex (0.5 g.) in water (15 ml.) was heated on the steam-bath with *l*-propylenediamine (1 ml., 67% w./w.) at 80–90° for 2 hr. and finally allowed to become dry. The orange yellow residue was dissolved in water and the solution adjusted to *p*H 5 with acetic acid. Addition of potassium oxalate gave no precipitate of [Pt(*l*-pn)$_3$](C$_2$O$_4$)$_2$. The solution was then made strongly acid by the addition of hydrochloric acid when the color darkened to brown. Addition of cadmium acetate 2-hydrate and sodium iodide gave a yellowish crystalline precipitate of bis-(*l*-propylenediamine)-platinum-(II) tetra-iodocadmiate(II) 1-hydrate. After recrystallization from hot water this gave $[\alpha]_D$ +20.0°; $[\alpha]_{5461}$ +24.0° in acetone. These values agree exactly with the rotations reported above.

CANBERRA, AUSTRALIA

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

The Molecular Structure of Perfluorocarbon Polymers. Infrared Studies on Polytetrafluoroethylene[1]

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The infrared absorption spectrum of polytetrafluoroethylene was studied in the 5000–270 cm.$^{-1}$ region. The variations in the spectrum with crystallinity were investigated to make possible an extrapolation to the crystalline spectrum. Several absorption bands were shown to be associated with vibrations of the amorphous configurations. The bands in the crystalline spectrum have been assigned on the basis of selection rules derived from the symmetry of the crystalline chain configuration. A crystalline density of 2.30 g./cc. was determined by an extrapolation based on an amorphous band intensity. The first-order transition at 19° was found to be accompanied by spectral changes.

Introduction

While the application of group theoretical methods to the analysis of high polymer spectra might seem to be a profitless undertaking, the tremendous length of a polymer molecule actually results in simplification rather than complexity. The treatment of a polymer molecule as a one-dimensional crystal was discussed by Tobin.[2] Polytetrafluoroethylene is an interesting subject for such a study because of its high symmetry, high crystallinity and its helical structure.

Several spectra of polytetrafluoroethylene have been published, but in general the regions of strong

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[1] Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[2] M. C. Tobin, *J. Chem. Phys.*, **23**, 891 (1956).