Optical Isomers of the *cis*-Dichlorobisethylenediamineplatinum(IV) and its Stereospecific Reaction with Ethylenediamine

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SINCE the geometry of the platinum(IV) ion is well known and its complexes are hydrolytically stable, they serve as excellent material for mechanism studies and for the study of stereospecific reactions. Comprehensive studies on the stereospecific reactions of cobalt(III) complexes have been extended to platinum(IV) compounds.[1] However, up to this time optical isomers of *cis*-[Pt en_2 Cl_2]Cl_2 have not been available for such studies. Preparation of the *cis*-dichlorobis(ethylenediamine)platinum(IV) ion was reported by Bailar and Heneghan.[2] Attempted resolution of the optical isomers with ammonium (+)-α-bromocamphor-π-sulphonate did not yield the isomers in their free form. Instead, these investigators studied the rotation *versus* boiling time of a solution of one of their isomers in the presence of the resolving agent and concluded that racemization of the complex ion occurred. Basolo, Morris, and Pearson[3] found that the rate of chloride exchange of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ is approximately 2000 times faster than that for the *cis*-isomer, but observed little difference in the rate between *cis*- and *trans*-[Pt en_2 Cl_2]$^{2+}$. Consequently it is doubtful that the *cis*-ion was obtained in these two investigations. Here we report the resolution of *cis*-[Pt en_2 Cl_2]Cl_2 into its optical isomers.

The infrared spectra (Nujol mulls) of *cis*-* and *trans*-[Pt en_2 Cl_2]Cl_2 are given in Figure 1. The *trans*-compound, prepared according to the method of Basolo, Bailar, and Tarr,[4] was analysed as the monohydrate. Due to the higher symmetry of the *trans*-compound, its infrared spectrum is slightly less complex than that of the *cis*-compound: though similar to the *cis*-[Co en_2 Cl_2]Cl, the maximum in the 1550—1600 cm.$^{-1}$ region assigned to the (N–H) bending frequency appears at a higher frequency in the *trans*-isomer than in the *cis*-isomer.[5]

Resolution of *cis*-[Pt en_2 Cl_2]Cl_2 was carried out by adding potassium antimonyl (+)-tartrate to the complex in a 1 : 1 ratio. The salt $(+)_{450}$-[Pt en_2-Cl_2][(+)-$SbO(C_4H_4O_6)]_2$ was precipitated, and the resolving agent removed by dissolving the solids in dilute HCl, filtering off the SbOCl which formed, evaporating the filtrate to crystallization, and adding alcohol. The resolved complex is white in colour. [Found: C, 10·6; H, 3·6; N, 12·2; Cl, 31·2; Pt, 42·7. Calc. for $Pt(C_2H_8N_2)_2Cl_4$: C, 10·5; H, 3·5; N, 12·3; Cl, 31·0; Pt, 42·7%.] The opposite enantiomer was obtained by using potassium antimonyl (−)-tartrate as resolving agent. The optical rotatory dispersion curves of the two optical isomers are shown in Figure 2.

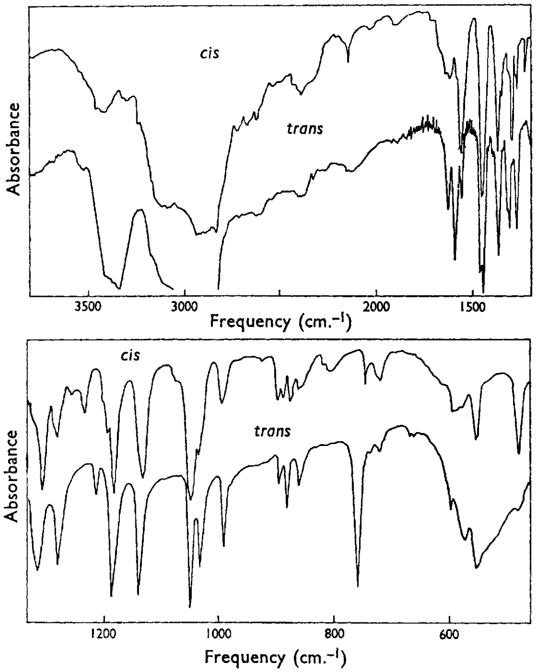

FIGURE 1. *Infrared spectra of* -cis- *and* -trans-[Pt en_2 Cl_2]Cl_2.

The n.m.r. spectra of the *cis*- and *trans*-isomers in deuterium oxide were obtained at 100 and 60 Mc./sec. using $Me_3Si(CH_2)_3{\cdot}SO_3Na$ as internal standard. The *trans*-compound exhibits methylene resonance, consisting of a central peak at 3·04 p.p.m. and a doublet arising from the splitting of the methylene protons by ^{195}Pt (J_{Pt-H} = 26

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* The *cis*-isomer used in this investigation was prepared by a new method which is being published elsewhere.

c./sec.). The doublet has approximately 34% of the total area of the three peaks which is in agreement with the natural abundance of ^{195}Pt. The spectrum of *trans*-[Pt en_2 Cl_2]Cl_2 at 100 Mc. is identical with that at 60 Mc. The spectrum of the *cis*-complex at 60 Mc. is similar to that of the *trans*-compound. However, in the 100 Mc. spectrum the peaks are further split, indicating there is more than one chemical shift involved. This is expected for the *cis*-isomer since there are two types of methylene groups, those on the nitrogen *cis* to two chlorine atoms and those on the nitrogen *cis* and *trans* to a chlorine atom. In deuterium oxide one sees no NH protons as the exchange of deuterium for hydrogen is rapid. The *cis*-compound in 50% H_2SO_4 exhibits two broad NH peaks at 4·83 and 6·83 p.p.m. indicating there are two different NH protons. *cis*-[Co en_2 Cl_2]$^+$ also shows two peaks for amine groups[6] which are further separated than in the platinum complex.

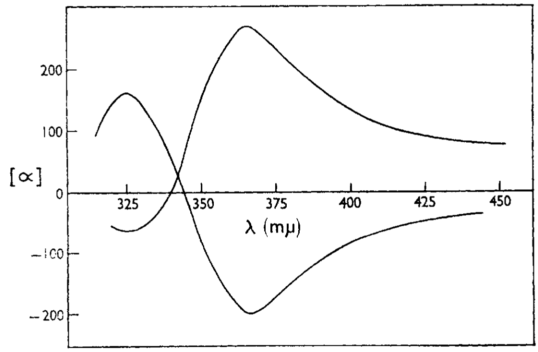

FIGURE 2. *The optical rotatory dispersion of* (+)- *and* (−)-[Pt en_2 Cl_2]Cl_2

Reaction of $(+)_{450}$-[Pt en_2 Cl_2]Cl_2 with a stoicheiometric amount of ethylenediamine in aqueous solution at room temperature yielded optically pure D-[Pt en_3]Cl_4. {Found: C, 13·9; H, 4·7; N, 16·2; Pt, 37·6. Calc. for [Pt($C_2H_8N_2$)$_3$]Cl_4: C, 13·9; H, 4·7; N, 16·3; Pt, 37·7.} The [Pt en_3]Cl_4 obtained gave $[\alpha]_D = +89°$; $[\alpha]_{405} = +215°$; $[\alpha]_{365} = +282°$. The literature[7] reports $[\alpha]_D = +88°$; $[\alpha]_{405} = +217°$; $[\alpha]_{365} = +275°$.

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