from both mechanistic and thermodynamic considerations. 11,12

Enzymic degradation of the polymer is being investigated by Dr. Elwyn T. Reese at the U. S. Army Natick Laboratories.

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The Circular Dichroism of the [PtCl₄]²⁻ Ion

Sir:

The weak-to-moderate intensity $d \rightarrow d$ transitions of dissymmetric metal complexes show strong circular dichroism when the transition is magnetic dipole allowed in the donor group microsymmetry of the complex. This selection rule has been employed in the assignment and the interpretation of these spectra, but, except for one reported example, the use of this criterion has been restricted to complexes which are dissymmetric. We wish here to draw attention to the possibility of extending this method to complexes which are formally optically inactive and, in the present example, to determining the polarization direction of the transition.

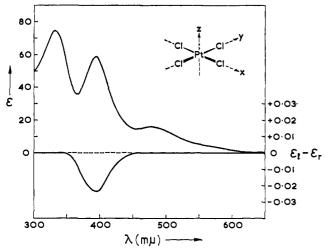


Figure 1. The visible absorption spectrum and circular dichroism of the $[PtCl_4]^{2-}$ ion in D(-)-2,3-butanediol. Shown in the inset is the coordinate frame of the ion referred to in the text.

When the complex $Na_2[PtCl_4]$ is dissolved in D(-)-2,3-butanediol, the unpolarized electronic absorption spectrum of a fresh solution of the ion is hardly altered in position and intensity from that found in the solid and in aqueous solution, but circular dichroism is observed at one of the $d \rightarrow d$ transitions (Figure 1).

The square-planar d8 diamagnetic ion [PtCl₄]²⁻ has

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three spin-allowed d \rightarrow d transitions, ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$, ${}^{1}A_{2g}$, ${}^{1}E_{g}$, which have been assigned with some certainty. 4,5 The ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transition has been shown by a vibronic analysis of the polarized crystal spectrum to occur at about 390 m μ , and from the magnetic circular dichroism of the ion the ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ transition has been shown to occur at about 335 m μ (Figure 1). It can be shown that the ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transition is magnetic dipole allowed in z-axis polarization while the ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ transition should be allowed in the x,y plane of the axis system shown in Figure 1. The ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition (at 480 m μ) is forbidden in magnetic dipole radiation fields, and we would expect that if this band shows any circular dichroism it should be very much weaker than that exhibited by the other two.

Experiment shows that only the ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ (zpolarized) band has any detectable circular dichroism, suggesting that the dissymmetric influences of the solvent are concentrated and directed at the tetragonal (+z and -z) positions of the ion. Although this may indicate weak coordination of the solvent in these positions, the extent of covalent participation must be extremely small since the spectrum of the ion is not appreciably altered by this effect. Alternatively, it seems unlikely that the appearance of circular dichroism is due to dissymmetric distortion of the molecular framework of the ion by the solvent, because under these circumstances we would expect to see the appearance of circular dichroism in both the z- and x,y-polarized transitions and not only in the unique polarization which is observed.

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A New Reaction of Diborane with Carbon Monoxide Catalyzed by Sodium Borohydride. A Convenient Synthesis of Trimethylboroxine

Sir:

In 1937 it was reported by Schlesinger and Burg that diborane reacts with carbon monoxide at 100° in a sealed tube under 20 atm pressure to form a simple addition compound, borane carbonyl. The product is a gas, stable at low temperatures, but largely dissociated into its components at ordinary temperatures and pressures (eq 1). This reaction and its product

$$B_2H_6 + 2CO \Longrightarrow 2H_3B:CO$$
 (1)

have since been the subject of numerous investigations.² We have examined the reaction of carbon monoxide with diborane in tetrahydrofuran solution, following the rate of absorption by adapting the automatic hydrogenator previously described.³ In the absence of sodium borohydride only a small quantity of carbon monoxide

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