ROTATORY DISPERSION AND ABSORPTION STUDIES ON DICHLORO *BIS*-PROPYLENEDIAMINE COBALT(III) CHLORIDE

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INTRODUCTION

The symmetry found in certain coordination compounds which results in their optical activity has been a subject of investigation since the early work on these complex molecules by Werner (1911:2445). Previous to that time it was thought that an asymmetric carbon atom in a molecule was necessary for optical rotation. Absolute, or total, asymmetric synthesis is now a well established fact and can be used to advantage in a number of ways.

Ordinary asymmetric synthesis involves the use of optically active reagents but without the use of any of the known methods of resolution. In this case the ligands themselves are optically active. When the ligands in coordination compounds are optically active, only certain preferred stereoisomeric modifications are found, rather than all theoretically possible forms. Stereochemists have made a study of this phenomenon and found the problem an intriguing one.

The compound, dichloro *bis*-propylenediamine cobalt (III) chloride, is one in which one of the ligands is optically active. It is analogous to

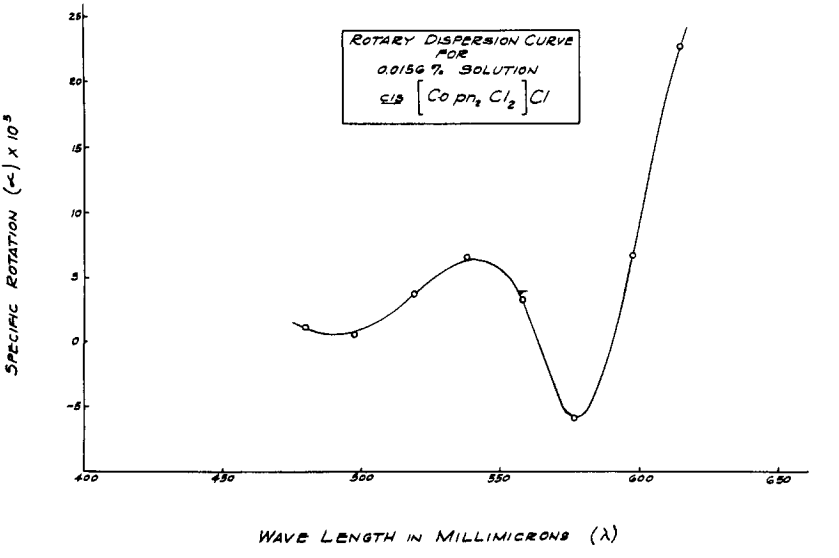

FIGURE 1.

the first coordination compound resolved by Werner, [Co $en_2(NH_3)$ Cl] Br_2, but has the ligand propylenediamine which is itself resolvable. For the first step in our study of the complex, which is presented here, *racemic* propylenediamine was used to obviate the problems which might arise from the activity of the ligand.

Experimental

Rotatory dispersion and absorption studies were carried out on *cis* (Co pn_2Cl_2)Cl which was prepared in the laboratory according to the method of Werner and Fröhlich (1907:2225) as modified by Bailar and co-workers (1939:2402) and later further modified by Martinette, *et al.* (1955:6507).

Optical activity measurements were taken across the spectrum at 25° C. using a Fric polarimeter accurate to 0.01° and a Thermionic quartz monochromator, model B, through which light from a carbon arc lamp was passed. Solutions of 0.05%, 0.025%, and 0.0156% concentrations of the complex were used. These solutions are highly colored and duplication of readings was more successful with the solution of 0.0156% concentration. Since the molecule aquates in a moderately short time it was necessary to take readings immediately upon solution of the compound. The more dilute solution permitted more rapid reading of the instrument. Figure 1 gives the rotatory dispersion curve obtained by plotting the specific rotation, $[\alpha]_{\lambda}^{25^c}$, versus the wave length, λ.

Absorption data were taken on solutions of the same compound and across the same range of the spectrum. A Coleman Universal Spectrophotometer, model 14, was used and a concentration of 0.5% appeared to give optimum results. The ex-

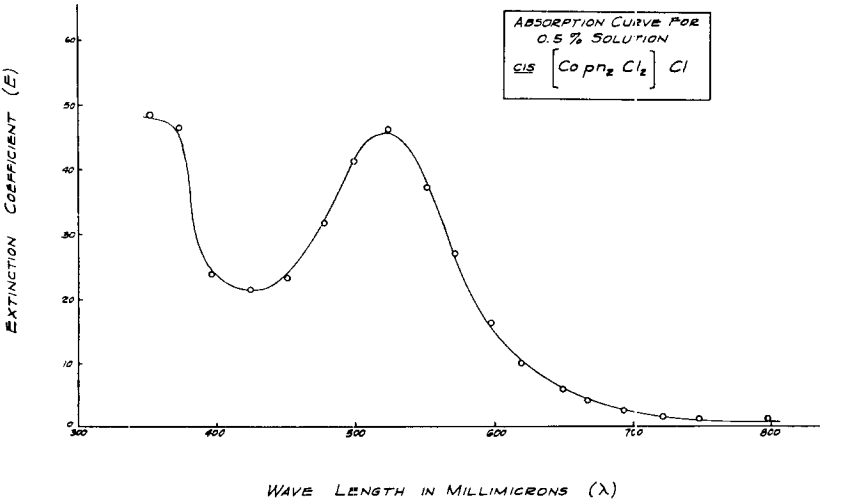

Figure 2.

tinction coefficients (E) were determined and the plot of E versus the wave length, λ, was drawn (Fig. 2).

Discussion and Summary

The rotatory dispersion of an optical isomer and a phenomenon known as circular dichroism or the "Cotton effect" are believed to be closely related. Dichloro *bis*-propylenediamine cobalt(III) chloride has the general formula $[M(AA)_2a_2]$a in which M is the metal ion, A is a bidentate ligand and a is a monodentate ligand when written within the brackets. The ion $[M(AA)_2a_2]^+$, which in this case is $(Co\ pn_2\ Cl_2)^+$, may have the two possible spatial arrangements shown in Figure 3. It is therefore postulated to have two structures which are diastereoisomers. The configurations of the ions are seen to be non-superimposable mirror images and should be, and have been found to be, optically active. A method of separation, while probably possible, has not been found as yet.

Cotton showed the rotatory power of a molecule to increase strongly as one approaches an appropriate absorption band and to change sign within the region of absorption. He showed, too, that only an "optically active band" will exhibit this anomalous dispersion of rotatory power. This light absorption within an optically active band is different for the *d*- and the *l*- components. The effect is called circular dichroism. The superimposition of the rotatory dispersion curve on the absorption curve of the compound studied here is shown in Figure 4 where the effect is immediately apparent.

The data, then, obtained in this experiment, would seem to verify the presence of two optically active forms of the compound. Throughout this work it was assumed that by using *racemic* propylenediamine in the preparation of the complex molecule, the coordination compound, no activity resulted merely from the ligand. The optical activity of the ligand may, and may not, influence the total activity. That remains to be determined.

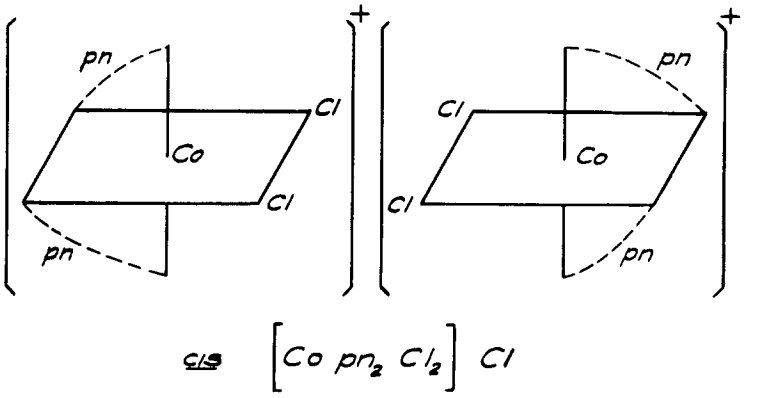

Figure 3.

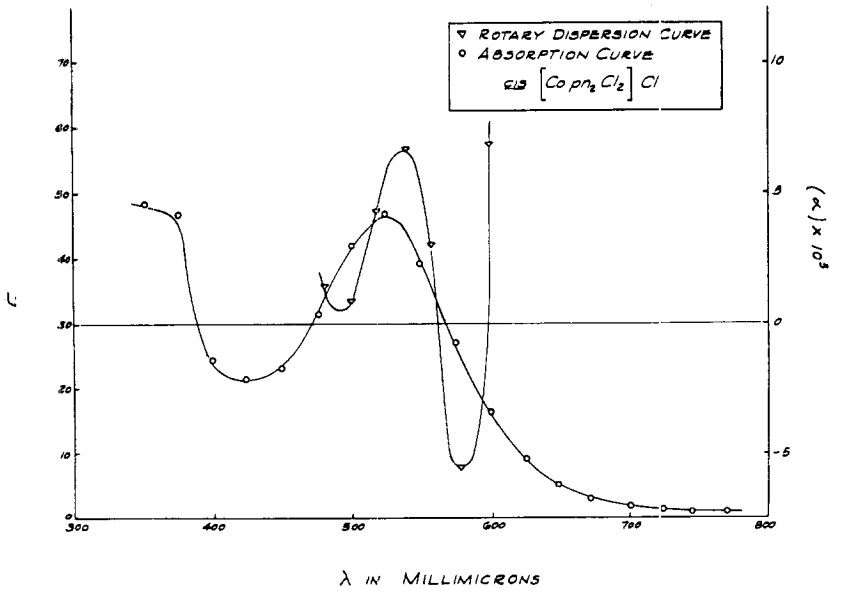

FIGURE 4.

ACKNOWLEDGMENT

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