JOURNAL OF THE

AMERICAN CHEMICAL SOCIETY

PHYSICAL AND INORGANIC CHEMISTRY

Rotatory Dispersion Studies of Coördination Compounds. II. Analysis of Rotatory Dispersion Curves[1]

BY J. G. BRUSHMILLER, E. L. AMMA AND BODIE E. DOUGLAS

Circular dichroism data published by Mathieu have been used for the calculation of the individual components of the rotatory dispersion curves in the region of the first absorption band for 16 complexes of the type $(+)_D\text{-}[Co(en)_2(AA)]^{n+}$. The complexes with essentially octahedral symmetry, where (AA) = en, $(NH_3)_2$, CO_3^-, and $C_2O_4^-$, have a single anomalous dispersion in this region. For complexes with tetragonal symmetry, where (AA) = NH_3 with H_2O, Cl^-, or Br^-; NO_2^- with NH_3, NO_2^-, H_2O, Cl^-, Br^-, or SCN^-; and Cl^- with Cl^-, Br^-, or SCN^-, this band is split and gives two anomalous dispersions. In each case the individual anomalous dispersion curves were added to give a composite curve in good agreement with the measured curve. All the complexes exhibit a positive Cotton effect for one of the long wave length inversion centers. The slight discrepancy between the measured curves and the calculated curves can be attributed to a contribution from a negative inversion center located in the ultraviolet region.

Introduction

In recent years, interest in the study of rotatory dispersion curves, *i.e.*, molecular rotation *vs.* wave length, of complex inorganic compounds as a tool for investigating structural and stereochemical problems has undergone a major revival.[2-5] During this period very important advances in the theoretical understanding of the phenomenon of optical rotatory power were made.[6-10] While the exact mechanism of the rotation remains unknown, continued investigation of the problem should bring a solution in the near future.

For the purpose of this and succeeding papers, the analysis of rotatory dispersion curves of coördination compounds requires the use of some

(1) This work was supported by a grant (A-2219) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

(2) T. D. O'Brien, J. P. McReynolds and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **70**, 749 (1948).

(3) J. Hidaka, S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 921 (1958).

(4) Y. Shimura, *ibid.*, **31**, 315 (1958).

(5) J. Hidaka, Y. Shimura and R. Tsuchida, *ibid.*, **33**, 847 (1960).

(6) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

(7) W. Moffitt and A. Moscowitz, *ibid.*, **30**, 648 (1959).

(8) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phy. Chem.*, **7**, 107 (1956).

(9) A. Moscowitz, in C. Djerassi, "Optical Rotatory Dispersion," McGraw–Hill Book Co., Inc., New York, N. Y., 1960. pp. 150–177.

(10) A. Liehr in "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961. p. 422.

spectroscopic terminology and some terminology used for rotatory dispersion studies of organic compounds which absorb light primarily in the ultraviolet region. A few modifications of the latter seem to be worthwhile for this discussion. Some other terms need to be defined here since they have not been commonly used and some have been used loosely at times.

At some distance from an optically active absorption band an optically active substance exhibits "normal" dispersion, *i.e.*, the optical rotation changes monotonically with wave length. As one approaches the spectral region of an isolated optically active absorption band, the optical rotation increases in magnitude to a maximum, then decreases abruptly to zero near the center of the absorption band, increases (with a change in sign) to a maximum, and finally decreases gradually, once again exhibiting "normal" dispersion. In the vicinity of the optically active absorption band the dispersion has been called "anomalous." Anomalous dispersion is only one of the manifestations of what is referred to as the *Cotton effect*. The Cotton effect arises due to differences in the interaction of d and l circularly polarized light with the optically active substance in the vicinity of the absorption band (plane polarized light can be considered to be made up of a beam of d and l circularly polarized light). Thus the difference be-

tween the indices of refraction ($n_1 - n_d$) changes sign within the absorption band. The substance is said to exhibit *circular dichroism* because of a difference in the absorption of d and l circularly polarized light.

In the region of normal dispersion the plane of polarization is rotated when plane polarized light passes through an optically active substance because of the difference in velocity of d and l circularly polarized light. Within the absorption band the unequal absorption of d and l circularly polarized light causes the plane polarized light to become elliptically polarized. Since the difference in the absorption coefficients ($k_1 - k_d$) is quite small, the deviation from plane polarization usually is not great (the ellipse is very much elongated). The circular dichroism can be expressed in terms of the *ellipticity* of the resulting wave. The ellipticity (θ) is defined as the ratio of the minor to the major axis of the ellipse. For an elongated ellipse this ratio is the tangent of an angle (β) which is small enough that the angle can be equated to its tangent

$$\theta = \frac{\text{minor axis}}{\text{major axis}} = \tan \beta = \beta \qquad (1)$$

Circular dichroism or ellipticity per unit length can also be expressed in terms of the difference between the absorption coefficients

$$\theta = \frac{1}{4}(k_1 - k_d) \qquad (2)$$

The molar ellipticity ($[\theta]$) is given by

$$[\theta] = \theta \frac{18 \, M}{\pi \, C} \qquad (3)$$

where M is the molecular weight and C is the concentration in grams per cm.[3]. We will use the term circular dichroism when the effect is measured in terms of k_1 and k_d and the term ellipticity when it is measured in degrees or radians.

The circular dichroism is very small except within an optically active absorption band. If the circular dichroism is plotted against wave length it is Gaussian in shape with its maximum at the wave length of the center of the corresponding anomalous dispersion curve. The Cotton effect is said to be positive if the circular dichroism ($k_1 - k_d$) is positive, indicating that absorption of l circularly polarized light is greater than that of d circularly polarized light. The ellipticity gives the sign of the Cotton effect. The corresponding (positive) anomalous dispersion curve[11,12] has its peak at a longer wave length than its trough.

Optical absorption bands obtained for solutions of complexes are usually very broad so that it is often difficult to resolve the band into its individual components. An anomalous dispersion curve changes rapidly in the region of the absorption band, but the rotation decreases gradually further from the band center. Consequently at any wave

length the experimental molecular rotation, [M], contains significant contributions, in the form of partial molecular rotations, [M_K] (resulting from the Kth electronic transition), from other optically active electronic transitions which the molecule undergoes, even if they are far removed from the wave length selected. Thus, it is usually not possible to isolate experimentally the individual

$$[M] = \Sigma_K[M_K] \qquad (4)$$

partial molecular rotations [M_K]. On the other hand, ellipticity curves are gaussian curves which drop off more sharply than the optical absorption curves so that the contribution from neighboring transitions is slight unless the transitions are very close together. The ellipticity associated with the Kth transition is much more easily isolated from an experimental curve than corresponding anomalous dispersions or optical absorption bands. In practice the molecular ellipticity [θ] does not require the summation of all (K) inverse transitions, but only those in the immediate neighborhood.

Kuhn[13] and Moscowitz[9] have shown that the anomalous dispersion curve can be calculated using the ellipticity measured through the absorption band. Partial molar rotations can be calculated for

TABLE I

ELLIPTICITY DATA FOR $[\text{Co(en)}_2(\text{AA})]^{n+}$ SYSTEMS[a]

Complexes with essentially octahedral crystal field		Ellipticity maximum		Half-width of ellipticity band
		Wave length λ_K^0 (mμ)	Peak height $[\theta]_K^0$ degrees	Δ_K^0 (mμ)
[Co(en)$_3$]Br$_3$		496	5800	32
cis-[Co(en)$_2$(NH$_3$)$_2$]Cl$_3$		496	1747	33
[Co(en)$_2$CO$_3$]Cl		530	5810	37
[Co(en)$_2$C$_2$O$_4$]Cl		529	6125	35
Complexes with essentially tetragonal crystal field				
cis-[Co(en)$_2$(NH$_3$)(H$_2$O)](NO$_3$)$_3$	E[b]	520	1172	43
	A	455	560	40
cis-[Co(en)$_2$(NH$_3$)(Cl)]Cl$_2$	E	554	1048	33
	A	478	558	33
cis-[Co(en)$_2$(NH$_3$)(Br)]Cl$_2$	E	561	1143	45
	A	482	750	33
cis-[Co(en)$_2$(NH$_3$)(NO$_2$)](NO$_3$)$_2$	E	No data available		
	A	485	1674	19
cis-[Co(en)$_2$(NO$_2$)(H$_2$O)]Cl$_2$	E	504	1750	49
	A	No data available		
cis-[Co(en)$_2$(NO$_2$)(Cl)]Cl	E	545	1140	35
	A	445	675	32
cis-[Co(en)$_2$(NO$_2$)(Br)]Br	E	548	1000	42
	A	440	485	28
cis-[Co(en)$_2$(NO$_2$)(NCS)]Cl	E	500	1115	48
	A	No data available		
cis-[Co(en)$_2$(NO$_2$)$_2$]Cl	E	464	3654	24
	A	No data available		
cis-[Co(en)$_2$(Cl)$_2$]Cl	E	534	2000	41
	A	608	−1230	40
cis-[Co(en)$_2$(Br)(Cl)]Cl	E	550	1928	41
	A	628	−1400	41
cis-[Co(en)$_2$(Cl)(NCS)]Cl	E	505	1370	45
	A	578	−1424	35

[a] All complexes included exhibit positive rotations at the D line. [b] E Represents the assignment $^1A_{1g} \rightarrow {}^1E_g$ and A represents the assignment $^1A_{1g} \rightarrow {}^1A_{2g}$.

(11) All rotatory dispersion curves are either single anomalous dispersion curves or composites of such curves. A "plain curve" as defined by Djerassi[12] is merely the tail of an anomalous dispersion curve. A sign should be associated only with the anomalous dispersion responsible for the tail. It seems undesirable to refer to the right tail of a positive anomalous dispersion curve as a positive plain curve and the left tail as a negative plain curve.

(12) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 12.

(13) W. Kuhn and H. L. Lehmann, Z. Elektrochem., 37, 549 (1931); Z. Phys. Chem., 18, 32 (1932).

TABLE II

COMPARISON OF THE CALCULATED AND OBSERVED ROTATORY DISPERSION CURVES FOR COMPLEXES NOT REPRESENTED IN FIGURES 1-8

Complex		Peak λ (mμ)	Peak [M]	Zero λ (mμ)	Trough λ (mμ)	Trough [M]
cis-[Co(en)₂(NO₂)₂]Cl	Obsd.	488	+1420	470	430	−4120
	Calcd.	484	+2190	464		
cis-[Co(en)₂(NO₂)NH₃](NO₃)₂	Obsd.	512	+590	485		
	Calcd.	502	+990	485	464	−1040
cis-[Co(en)₂(NH₃)H₂O](NO₃)₃	Obsd.	557	+535	527		
	Calcd.	556	+750	512	420	−700
cis-[Co(en)₂(NH₃)Br]Cl₂	Obsd.	595	+480	563	541	−410
	Calcd.	600	+730	554	528	−325
cis-[Co(en)₂(NO₂)H₂O]Cl₂	Obsd.	550	+690	523	463	−1800
	Calcd.	548	+1030	506	460	−1120
cis-[Co(en)₂(NO₂)Br]Br	Obsd.	590	+350	560	516	−960
	Calcd.	588	+660	545	510	−500
cis-[Co(en)₂(NO₂)NCS]Cl	Obsd.	538	+720	510		
	Calcd.	545	+650	500	455	−710
cis-[Co(en)₂Cl(NCS)]Cl	Obsd.	536	+1950	595, 492		
	Calcd.	546	+1740	590, 494		

all the transitions for which circular dichroism data are available to give a composite dispersion curve. This approach has not been generally applied because rotatory dispersion studies have not been accompanied by circular dichroism studies, although the value of such information has been recognized.[9,13,14] The only extensive concurrent investigation of rotatory dispersion and circular dichroism of coördination compounds was carried out by Mathieu[15,16] in the 1930's. His work has not received its just recognition. This paper reports the results of calculations of rotatory dispersion curves from Mathieu's circular dichroism data in the region of the first absorption band (i.e., the longest wave length visible band) for a number of complexes of the type [Co(en)₂(AA)]ⁿ⁺ where (AA) = en, C₂O₄⁻, CO₃⁻, (NH₃)₂, (Cl)₂, etc.

Experimental

The rotatory dispersion and ellipticity data were taken from graphs published by Mathieu.[15] Table I contains a list of the complexes with the circular dichroism data used for the calculations.

We obtained the rotatory dispersion curves of (+)ᴅ-[Co(en)₃]Br₃, (+)ᴅ-[Co(en)₂(C₂O₄)]Cl and (+)ᴅ-cis-[Co-(en)₂(NO₂)₂]Cl in this Laboratory and find our results agree with those of Mathieu to within 2%. Except for (+)ᴅ-[Co(en)₂(C₂O₄)]Cl[17] these complexes were prepared and resolved by standard methods described in "Inorganic Syntheses." Tsuchida and Shimura[3,4] have checked the rotatory dispersion curves of (+)ᴅ-cis-[Co(en)₂(NH₃)Cl]Br₂, (+)ᴅ-cis-[Co(en)₂Cl₂]Cl and (+)ᴅ-cis-[Co(en)₂(NO₂)Cl]Cl and have found their results agree quite well with those of Mathieu.

Using the ellipticity data published by Mathieu[15] and equation (5) [Mₖ] was calculated for 16 coördination complexes in the wave length region of their first absorption bands (split into two bands for tetragonal complexes). Values for the integral $\int e^{x^2}dx$ were obtained from tables published by Terrill and Sweeny.[18] Values of e^{-x^2} were obtained from Dwight.[19] The [Mₖ] was calculated in incre-

(14) C. Djerassi, Record Chem. Progress, 20, 103 (1959).

(15) J. P. Mathieu, Bull. soc. chim., (5) 3, 476 (1936); J. chim. phys., 83, 78 (1936).

(16) J. P. Mathieu, Bull. soc. chim., (5) 6, 873 (1939).

(17) F. P. Dwyer, I. K. Reid and F. L. Garvan, J. Am. Chem. Soc., 83, 1285 (1961).

(18) H. M. Terrill and L. Sweeny, J. Franklin Institute, 237, 495 (1944); 238, 221 (1944).

(19) H. B. Dwight, "Mathematical Tables of Elementary and Some Higher Mathematical Functions," 2nd Ed., Dover Pub. Inc., New York, N. Y., 1956.

ments of 5 mμ for 100 mμ on each side of λₖ⁰. The calculated and experimental curves for eight of these complexes are given in Figs. 1 through 8. Only typical curves for each type of complex are included because of space limitations. Table II contains the necessary data to compare the results for the remainder of the complexes.
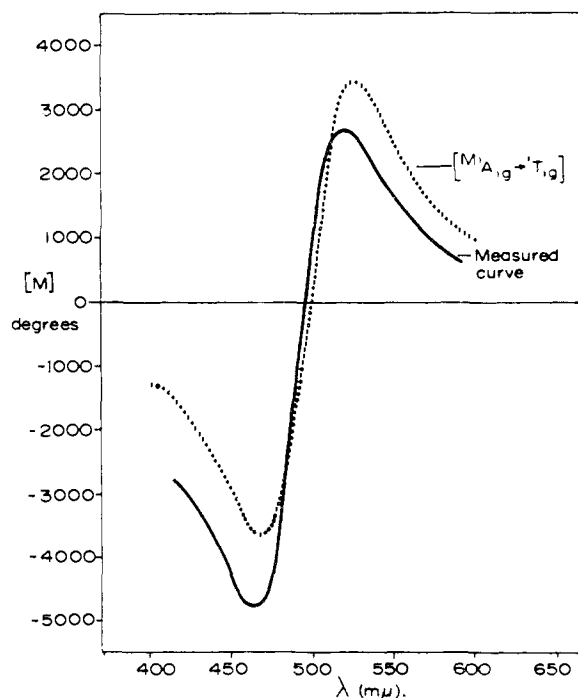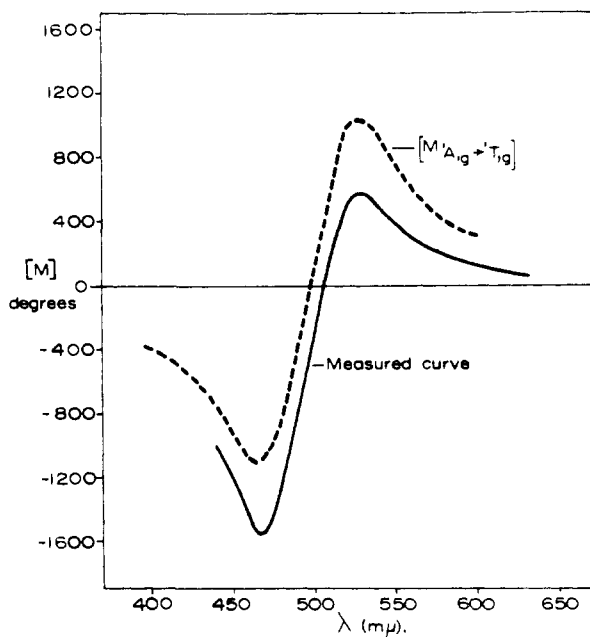

Fig. 1.—Single anomalous dispersion for [Co(en)₃]Br₃.

Results

The complexes represented in Figs. 1 through 4 have essentially octahedral crystal fields, as shown by the optical absorption and ellipticity data, and show a single optically active transition in the region of their first visible absorption band (¹A₁g → ¹T₁g). The complexes in Figs. 5 and 6 have essentially tetragonal symmetry, as shown by the optical absorption and ellipticity data, and their first visible absorption band is split into two components. The shorter wave length band is assigned to the ¹A₁g →

Fig. 2.—Single anomalous dispersion for cis-[Co(en)₂(NH₃)₂]Cl₃.
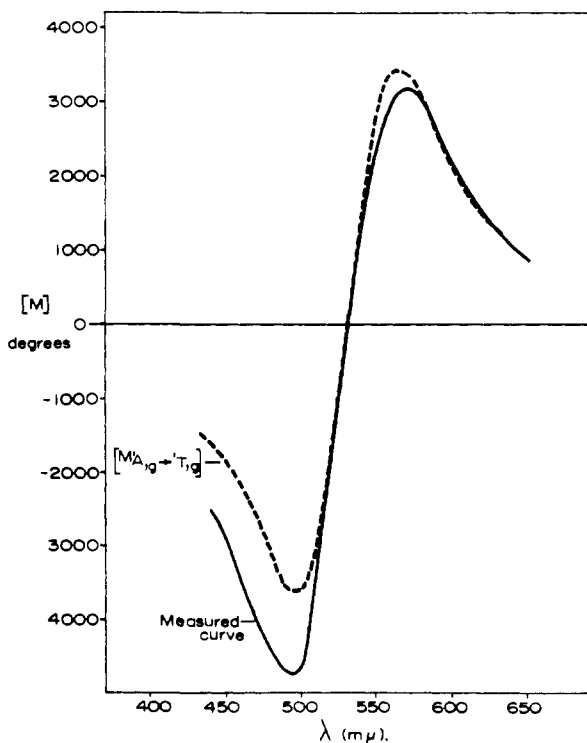
Fig. 3.—Single anomalous dispersion for [Co(en)₃CO₃]Cl.

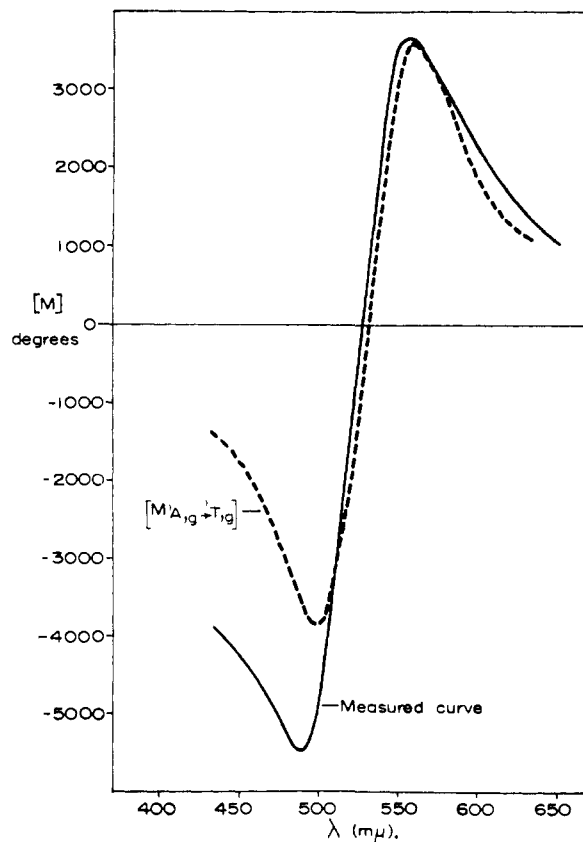Fig. 4.—Single anomalous dispersion for [Co(en)₂C₂O₄]Cl.
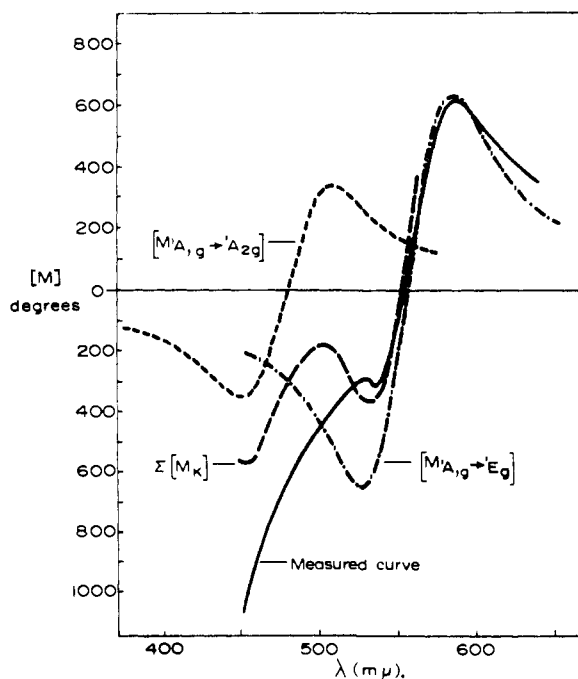
Fig. 5.—Two anomalous dispersions of the same sign for cis-[Co(en)₂(NH₃)Cl]Cl₂.

$^1A_{2g}$ inverse transition and the longer wave length band is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ inverse transition.[20] Both optically active transitions are positive. The complexes in Figs. 7 and 8 (tetragonal) differ from those in Figs. 5 and 6 in one important aspect, the assignment of the two transitions are interchanged, i.e., $^1A_{1g} \rightarrow {}^1A_{2g}$ is assigned to the

(20) C. J. Ballhausen and C. K. Jorgensen, K. danske vidensk. Selsk., Mat. fys. medd., 29, (14) (1955).

longer wave length transition. The inverse transitions in Figs. 7 and 8 have opposite signs for the Cotton effect. The curves labelled Σ[M_K] in Figs. 5 through 8 were obtained by summing the partial dispersion curves in the overlap region.
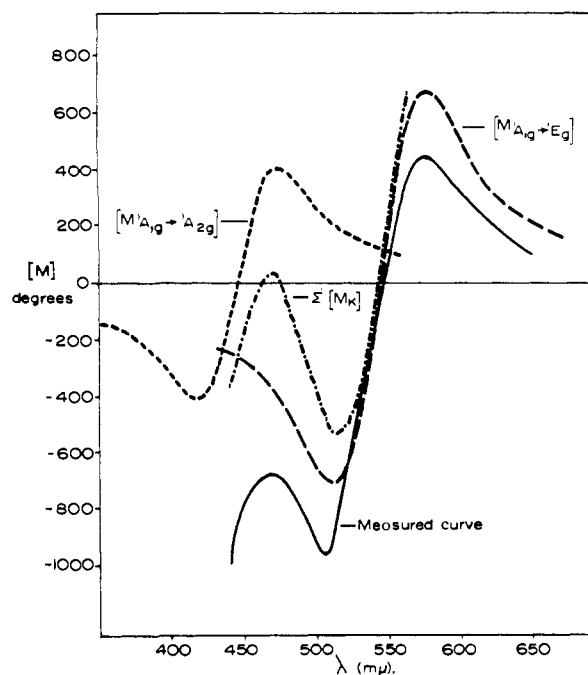
Fig. 6.—Two anomalous dispersions of the same sign for cis-[Co(en)₂(NO₂)Cl]Cl.

Fig. 7.—Two anomalous dispersions of opposite sign for cis-[Co(en)₂Cl₂]Cl.

Discussion

The fact that both the absorption spectrum and the optical rotation are related to certain electronic transitions within the molecule suggests that some correlation exists between these two properties, although they are not brought about by the same mechanism.[21,22] The optical activity of solutions of complex ions is assessed by the molecular rotation [M]. The partial molecular rotation associated with any particular transition falls off comparatively slowly in regions away from the band center, according to the Drude–Rosenfeld equation, i.e., as $1/(\lambda^2 - (\lambda_K{}^0)^2)$. Since we are concerned with the calculation of the partial molecular rotation in the region of the optically active absorption band, the Drude equation is of little value for the resolution of the curve.

Attempts have been made at resolving the experimental rotatory dispersion curve into its component partial rotations using the method of trial and error.[3] It was assumed that the observed curve was the super-position of partial rotations in the visible region and the tail of a large partial rotation which had its inversion center in the far ultraviolet region. Several partial rotations and an ultraviolet tail were then fitted by trial and error to the observed curve. The assumption that there was a large contribution from an ultraviolet tail has been substantiated by recent rotatory dispersion curves of inorganic complexes in the 220–350 mμ region[23] which have rotations with values two to four times greater than that observed in the visible. Although this method gives good resolution in certain cases, it is empirical and lacks precise

(21) S. Sugano, J. Chem. Phys., 33, 1883 (1960).
(22) J. G. Brushmiller, E. L. Amma and B. E. Douglas, J. Am. Chem. Soc., 84, 111 (1962).
(23) M. Billardon, Compt. rend., 251, 2320 (1960).

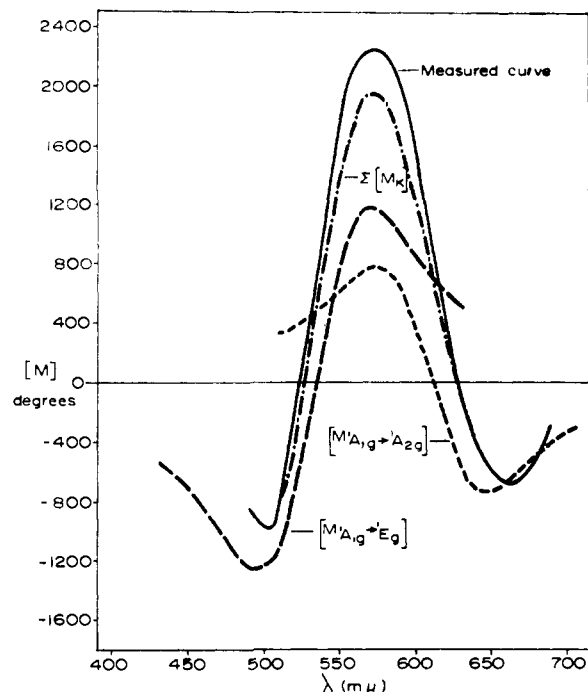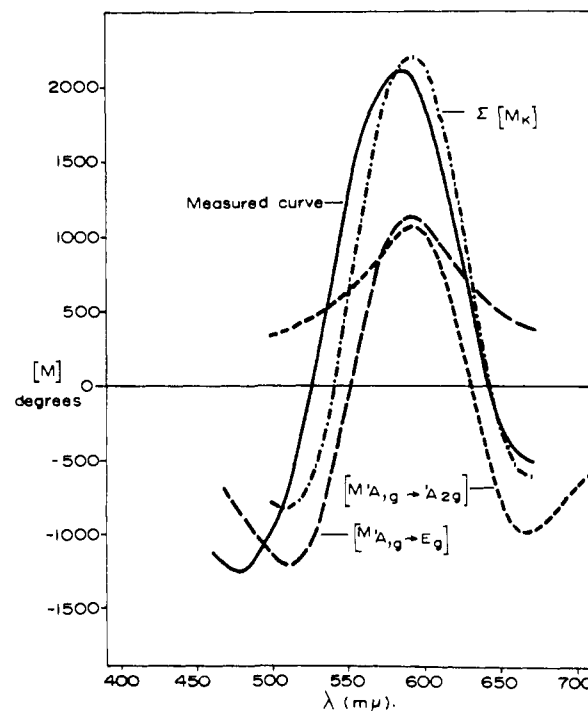Fig. 8.—Two anomalous dispersions of opposite sign for cis-[Co(en)₂(Br)Cl]Cl.

parameters which may be applied to further theoretical development and stereochemical study.

The use of circular dichroism data to obtain an unambiguous resolution of the measured rotatory dispersion curve was recognized by Werner Kuhn in the early 1930's. Kuhn derived an equa-

tion using the coupled oscillator approach to relate the molecular rotatory power to the circular dichroism.[24] However, the physical interpretation of Kuhn's classical theory was not widely accepted and his equation never came into widespread use. Kar[25] used Kuhn's equation to calculate the rotatory dispersion curve for potassium vanadyl tartrate from ellipticity data for two inversion centers in the visible region of the spectrum but made no interpretation of the results.

Using a Kronig–Kramers type of relationship, Moscowitz[3] showed that it was possible to calculate the shape of the partial molecular rotation [M_K] from a knowledge of the partial molar ellipticity for the Kth transition. Moscowitz's quantum mechanical result, equation 5, is essentially identical with Kuhn's equation.

$$[M_{K(\lambda)}] = \frac{2[\theta_K^0]}{\sqrt{\pi}} \left[e^{-(\lambda - \lambda_K^0)^2/(\Delta_K^0)^2} \int_0^{\lambda - \lambda_K^0/\Delta_K^0} e^{x^2}dx - \frac{\Delta_K^0}{2(\lambda + \lambda_K^0)} \right]$$

(5)

The symbols are defined in Table I. Because of the absence of dichroism data for organic systems, no direct calculations of anomalous dispersion curves were carried out by Moscowitz. Instead Moscowitz has concentrated, with great success, on calculation of the rotatory dispersion curves for molecules which contain "inherent dissymmetry." For these molecules, whose optically active absorption bands have electric dipole and magnetic dipole transition moments which must be co-linear, it is possible to construct the rotatory dispersion curve solely from a knowledge of absorption curve.[26-28] Equation 5 was also used, in conjunction with an abbreviated two term Drude equation, for curve fitting with the aid of a computer.[9] Good agreement over a wide range of wave lengths was obtained for a number of organic compounds.

For the octahedral complexes in Table I the measured curve is displaced to the negative side of the zero rotation line. This indicates that a tail from at least one other partial molecular rotation, probably centered in the ultraviolet region, makes an appreciable negative contribution to [M] in the vicinity of 500 mμ. The diminution of the negative tail with increasing wave length indicates that all the octahedral complexes in Table I possess an ultraviolet inversion center which has a negative sign for the Cotton effect.

The tetragonal complexes in Table I also have measured rotatory dispersion curves which are displaced to the negative side of the zero line, indicating that they likewise possess an ultraviolet inversion center with a negative sign for the Cotton effect. In the region above 550 mμ there is good agreement between the calculated and measured curve indicating that the ultraviolet inversion tail contributes little at the longer wave lengths.

It should be pointed out that it is fortuitous that all of these complexes have negative inversion

centers in the ultraviolet and are all dextrorotatory at the D line. At some other wave length all the complexes would not be likely to have the same sign of rotation. The use of these data for the establishment of absolute configurations will be discussed later.[29]

Mathieu's data indicate a second ellipticity maximum for [Co(en)₃]Br₃ at 442 mμ. The assignment of this band is uncertain. A reasonable assignment for this weak band may be the $^1A_2$ component of the $^1T_{1g}$ band, the splitting being caused by the trigonal distortion. Since it occurs at shorter wave length than the main band, an assignment to a $^1A_{1g} \rightarrow {}^3T_{1g}$ transition, which should be a lower energy transition, can be ruled out. The anomalous dispersion curve corresponding to the small negative ellipticity band was calculated. Its contribution to the composite rotatory dispersion curve was negligible so that it was not included in Fig. 1. Remeasurement of the ellipticity data provides the only means for ascertaining the presence of a transition in the vicinity of the small ellipticity band reported by Mathieu. The presence of this transition cannot be established from solution spectra or from the rotatory dispersion curve.

The complexes with essentially tetragonal crystal field symmetry of the type cis-[Co(en)₂XX'] can be seen to have two ellipticity maxima of opposite sign within the long wave length absorption band when the two groups are identical or have nearly the same crystal field strength (see the last 4 compounds in Table I). The other tetragonal complexes, with X and X' differing appreciably in crystal field strength, have two ellipticity maxima of the same sign within the long wave length absorption band.

The splitting of the first absorption band for [Co(en)₂(NH₃)NO₂](NO₃)₂ is appreciable from the spectrum. The ellipticity maximum measured by Mathieu comes under the shoulder of the main absorption band so that the presence of another ellipticity maximum at shorter wave length can be inferred. It can be predicted that the two ellipticity maxima should have the same sign. Unfortunately Mathieu's data did not extend far enough to show the presence of the second ellipticity maximum.

Basolo, et al.,[30] treated cis-[Co(en)₂(NO₂)₂]Cl as essentially octahedral with no splitting of the long wave length absorption band. Mathieu's rotatory dispersion data do not extend to short enough wave lengths to detect any splitting of this band or to show the presence of a second ellipticity maximum. Hidaka, et al.,[5] reported rotatory dispersion data down to 335 mμ, indicating the presence of a second inverse dispersion (negative) near 330 mμ. The splitting of the absorption band is obscured by the strong absorption band extending from the ultraviolet region. The non-Gaussian character of Mathieu's ellipticity curve strongly suggests the presence of a negative ellipticity maximum at shorter wave length as predicted above.

(24) W. Kuhn and E. Braum, Z. physik. Chem. (Leipzig), B8, 445 (1930); W. Kuhn, Ann. Rev. Phys. Chem., 9, 417 (1958).

(25) B. C. Kar, J. Indian Chem. Soc., 24, 117 (1947).

(26) K. Mislow, M. A. W. Glass, A. Moscowitz and C. Djerassi. J. Am. Chem. Soc., 83, 2771 (1961).

(27) A. Moscowitz, Tetrahedron, 13, 48 (1961).

(28) A. Moscowitz, F. Charney, U. Weiss and H. Ziffer, J. Am. Chem. Soc., 83, 4661 (1961).

(29) J. G. Brushmiller, E. L. Amma and B. E. Douglas, in preparation.

(30) F. Basolo, C. J. Ballhausen and J. Bjerrum, Acta Chem. Scand., 9, 810 (1955).

These results not only confirm the general reliability of Mathieu's data and the validity of equation 5 but show that ellipticity data can provide the necessary information for the resolution of rotatory dispersion curves into their individual components. If the curves can be resolved, it is then possible to correlate the rotatory dispersion data with spectral data and assign the transitions. The ellipticity curves permit one to detect small or very large splittings and make assignments in cases where no splitting is evident from absorption spectra.

The agreement between the calculated and the measured curves is very good. The addition of the expected contribution from the ultraviolet inversion center should make the calculated and measured curves coincide. It is indeed remarkable that Mathieu's extensive, but little recognized, work of thirty years ago gives such good agreement with

modern theory. It should be kept in mind that the ellipticity data used here were read from graphs published by Mathieu. An improvement in the data might be expected to produce even better agreement between the calculated and the measured curve. When circular dichroism data are available in the region of the second visible absorption band (weak as it must be[6]) and the ultraviolet absorption bands, this approach should lead to an unambiguous resolution of the observed rotatory dispersion curves.

Work is planned to measure ellipticities and extend the calculations over a wider wave length range. The use of ellipticity parameters and rotational strengths in dealing with structural and stereochemical problems as well as the theoretical implications of these results to the mechanism of rotation and the nature of vibrations that bring about the optical absorption will be the subject of later papers.[29]

Nucleophilic Substitution Reactions in Octahedral Complexes

BY RALPH G. PEARSON, DAVID N. EDGINGTON AND FRED BASOLO

The dissociation of octahedral tris-(acetylacetonato)-silicon(IV) cation is subject to catalysis by a variety of nucleophilic reagents. The relative rates form a series which is entirely reasonable if the mechanism of the slow step is an S_N2 displacement process in which the nucleophile pushes off one end of an acetylacetonate ligand. This seems to be the first clear-cut example of an S_N2 mechanism in an octahedral complex. Basicity, rather than polarizability, of the nucleophile is the dominant factor in determining its reactivity with this particular substrate.

Octahedral complexes, particularly of the transition metal ions, appear to have a strong preference for dissociation (S_N1) mechanisms in their substitution reactions.[1] At the present time there is no well substantiated case of a displacement (S_N2) mechanism in an octahedral system. A number of possible examples have appeared in the literature.[2] These all suffer from being fairly complex systems where alternative explanations are possible. Furthermore, generality has not been demonstrated in these cases. In a well behaved system it is expected that a variety of nucleophilic reagents (ligands) will be found to be effective and that their respective second order rate constants will bear some clear relationship to recognized nucleophilic properties.

The reaction of cis-[Co(en)₂Cl₂]⁺ with a variety of reagents in methanol has been reported.[3] The apparently convincing result that some reagents (basic anions) react by an S_N2 mechanism is in-

validated by recent observations. One is that the major influence of these basic ions is due to the methoxide ion which they generate by reaction with the solvent.[4] The small residual effect is almost certainly due to ion-pair formation in which the ion-pair is more reactive than the original complex cation. This is best shown by a recent study of the effect of basic anions on the rate of aquation of [Cr(NH₃)₅Cl]²⁺ in water.[5] The rate constants for various basic anions correlate perfectly with the ion-pair association constants of the same anions with [Co(NH₃)₆]³⁺. Also the product of reaction continues to be [Cr(NH₃)₅-H₂O]³⁺ instead of the expected product if the anion functioned as a nucleophile.

There are two possible reasons why displacement mechanisms are uncommon for octahedral complexes. One is that an expanded coördination number is a requirement for such a process. It may be sterically difficult to arrange seven groups around a central metal ion if the ion is small. Even for larger ions, six ligands may be much more stable than seven if the ligands are polyatomic. Hence, van der Waals and electrostatic ligand repulsions may hinder an S_N2 mechanism. The second barrier to S_N2 mechanisms is specific for the transition metal ions. Partly filled d-orbitals produce a crystal field stabilization in the ground state which usually resists the change from octahedral coördination to seven-

(1) For discussions see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. 3; F. Basolo and R. G. Pearson, "Substitution Reactions of Metal Complexes," Advances in Inorganic and Radiochemistry, Vol. III, H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, Inc., New York, N. Y., 1961; R. G. Pearson, J. Chem. Ed., 38, 164 (1961); D. R. Stranks, "Modern Coördination Chemistry," R. G. Wilkins and J. Lewis, Editors, Interscience, New York, N. Y., 1960.

(2) A. J. Poë and M. S. Vaidya, J. Chem. Soc., 2981 (1961); A. L. Hope and J. E. Prue, ibid., 2782 (1960); D. W. Cooke, G. A. Im and D. H. Busch, Inorg. Chem., 1, 13 (1962); D. W. Margerum and L. P. Morgenthaler, "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 481.

(3) D. D. Brown and C. K. Ingold, J. Chem. Soc., 2674 (1953).

(4) R. G. Pearson, P. M. Henry and F. Basolo, J. Am. Chem. Soc., 79, 5379, 5382 (1957).

(5) T. P. Jones, W. E. Harris and W. J. Wallace, Can. J. Chem., 39, 2371 (1961).