Until recently all of the reported single-crystal CD spectra were with k parallel to the optic axis of a uniaxial crystal where all of the linear terms vanish so that eq 8 becomes

$$R_a \sim -\gamma b_2/[1 + (\gamma^2/2)b_2^2] \sim -\gamma b_2 \tag{9}$$

when $\gamma b_2 \ll 1$.

Equation 8 is also considerably simplified if $a_1 = b_1 = 0$. Thus if we observe the crystal structure and orientation restrictions discussed for linear polarization, eq 8 becomes

$$R_a \sim -\gamma b_2/[1 + (\gamma^2/2)(b_3^2 + b_2^2) - J_0(\delta)\gamma b_3] \tag{10}$$

Thus if γb_3 is measured independently or if $\gamma b_3 \ll 1$, γb_2 is in principle obtainable.[13] We have encountered difficulty in applying eq 10, because we find that the Pockels cell in our instrument is not a perfect polarization modulator and in practice it introduces an ac component into the intensity of the incident beam.[14] If this effect is included by writing $s_0 = 1 + D \sin \omega t$ for the incident beam, eq 10 becomes (to first order in D)

$$R_a \sim (-\gamma b_2 - K\gamma b_3)/[1 + (\gamma^2/2)(b_2^2 + b_3^2) - J_0(\delta)\gamma b_3] + \text{baseline shift} \tag{11}$$

where $K = DJ_0(\delta)/W$

$W = \int_0^\pi \sin(\delta \sin \omega t)\, d\omega t$

The baseline shift does not interfere, but we find that frequently $\gamma b_2 \ll K\gamma b_3$ making CD values difficult to obtain.

We have attacked this difficulty in the following way. If the crystal structure is such that it is possible to choose the x and y axes such that $a_1 = b_1 = 0$, then in a crystal fixed coordinate system the Stokes vector of the incident beam becomes

$$\mathbf{S}_i = \begin{bmatrix} 1 + D \sin \omega t \\ s_0 \cos(\delta \sin \omega t) \sin 2\phi \\ s_0 \sin(\delta \sin \omega t) \\ s_0 \cos(\delta \sin \omega t) \cos 2\phi \end{bmatrix}$$

where ϕ is the angle between the plane polarized light in instrument and the x crystal axis. Equation 11 now becomes

$$R_a \sim \frac{-\gamma b_2^2 + K[S \sin 2\phi - \gamma b_3 \cos 2\phi]}{1 + (\gamma^2/2)(b_2^2 + b_3^2) + J_0(\delta)[S \sin 2\phi - \gamma b_3 \cos 2\phi]} \tag{12}$$

where $S = (\gamma^2/2)(a_2 b_3 - a_3 b_2)$. Thus, if γb_3 is known from linear polarization measurements, the only remaining unknown terms in eq 12 that depend on the wavelength of the light beam are γb_2 and S. Then if readings of R_a are taken at a number of different values of ϕ, γb_2 can be extracted for a given wavelength by a computer least-squares fit to eq 12.

The results of an application of eq 12 will be reported elsewhere.[15]

Another possibility, which does not seem to have been considered, is to increase δ from its usual value of 113.4° (which maximizes W) to 137.8° where $J_0(\delta) = 0$. Since K also becomes zero under these conditions, eq 11 and 12 reduce to

$$R_a \sim -\gamma b_2/[1 + (\gamma^2/2)(b_3^2 + b_2^2)] \tag{13}$$

for a uniaxial crystal in any orientation and for a biaxial crystal when x and the two optic axes lie in the same plane. The only other effect would be a slight reduction in the ac amplification factor.

References and Notes

(1) One of the more recent reasonably complete reviews of this field is: N. S. Hush and R. J. M. Hobbs, *Prog. Inorg. Chem.*, **10**, 259 (1968). This review contains 460 references, and work in this area has increased since that time.
(2) (a) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965); (b) R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970); (c) R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, **49**, 433 (1976); (d) H. P. Jensen, *Acta Chem. Scand., Ser. A*, **30**, 137 (1976); (e) H. P. Jensen and F. Galsbøl, *Inorg. Chem.*, **16**, 1294 (1977).
(3) J. Ferguson, "Electronic States of Inorganic Compounds; New Experimental Techniques", P. Day, Ed., D. Reidel, Boston, Mass., 1975, pp 59–95.
(4) Y. Saito, *Coord. Chem. Rev.*, **13**, 305 (1974); ref 2c.
(5) H. P. Jensen[2d] gives a brief apparently incomplete derivation for CD spectra using a phase modulation spectrophotometer. We do not question the results presented in ref 2d and 2e, but our analysis indicates some limitations inherent in their technique.
(6) This formulation, which is well known in the field of optics, does not seem to be familiar to many chemists so it will be outlined briefly here. One of the purposes of this letter is to point out that such an analysis is possible and that it can be applied to a wider variety of problems than the previous literature would imply.
(7) W. A. Shurcliff, "Polarized Light", Harvard University Press, Cambridge, Mass., 1966, Chapter 2.
(8) This order of the components is the "natural order" suggested by R. W. Schmieder, *J. Opt. Soc. Am.*, **59**, 297 (1969).
(9) N. Gō, *J. Phys. Soc. Jpn.*, **23**, 88 (1967).
(10) T. C. Troxell and H. A. Scheraga, *Macromolecules*, **4**, 519 (1971).
(11) The possibility of circular activity is related to the point group symmetry of the crystal. The 11 centrosymmetric and the six acentric groups, $3m$, $4mm$, $6mm$, $\bar{6}$, $\bar{6}m\bar{2}$, and $\bar{4}3m$ must be circularly inactive. The remaining 15 acentric point groups permit circular activity: G. N. Ramachandran and S. Ramaseshan, "Handbuch der Physik", S. Flügge, Ed., Vol. 25/1, Springer, Berlin, 1961, pp 82–85.
(12) M. Grosjean and M. Legrand, *C. R. Hebd. Seances Acad. Sci.*, **251**, 2150 (1960).
(13) Equation 10 is given in essentially this form by Jensen.[5] However, he seems to have arrived at it by ignoring the a_1 and b_1 terms in eq 8.
(14) Our instrument is a JASCO ORD/UV-5 with CD attachment. It is not obvious whether or not this will be a problem with all instruments.
(15) N. C. Moucharafieh, P. G. Eller, J. A. Bertrand, and D. J. Royer, *Inorg. Chem.*, in press.

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Errata

In the December 1977 issue of *Inorganic Chemistry* entries did not appear in the Author Index and Keyword Index to Volume 16, 1977, for the following papers:

Adegboye Adeyemo and M. Krishnamurthy*: A Novel Metal Ion–Porphyrin Equilibrium (page 3355).

H. R. Allcock,* C. H. Kolich, and W. C. Kossa: Pyrolysis of Aminophosphazenes (page 3362).