wavelength than does the analogous transition in the spectra of $Re_2X_8^{2-}$, where X = Cl or Br.[19-21] A similar trend is observed between the spectra of I, IV, V, and VI (Table I and Figure 1) and their chloride analogues.[10,12,13] In these instances, the lowest energy transition in the spectra of the isothiocyanato complexes exhibits a red shift of 100–135 nm relative to $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(L–L)_2$, where L–L = dppm, bpy, and phen. The 830-nm absorption of complex III (Table I) is at a lower energy than the corresponding band in the spectra of either α-Mo_2Cl_4(dppe)$_2$ or β-Mo_2Cl_4(dppe)$_2$ (at 675 and 780 nm, respectively).[13] These two molybdenum complexes possess different structures:[13] the α isomer contains chelating dppe molecules, a cis disposition of Mo–Cl bonds, and an eclipsed ligand configuration, while β-Mo_2Cl_4(dppe)$_2$ is believed to have a staggered noncentrosymmetric structure wherein the dppe ligands bridge the molybdenum atoms within the dimer. At the present time we have no definitive evidence as to which (if either) structure is appropriate for $Mo_2(NCS)_4$(dppe)$_2$. However, in view of the significant shift observed between the lowest energy electronic absorption band of the other isothiocyanato complexes listed in Table I and their chloride analogues (i.e., >100 nm), III may structurally resemble α-Mo_2Cl_4(dppe)$_2$ since here the red shift is 155 nm.

In summary, it is clear that, in contrast to the failure of $Re_2(NCS)_8^{2-}$ to yield derivatives of the type $Re_2(NCS)_6L_2$ via ligand substitution reactions, little difficulty was experienced in isolating the molybdenum complexes $Mo_2(NCS)_4L_4$ and $Mo_2(NCS)_4(L–L)_2$. Accordingly, substitution of thiocyanate for halide in species derived from dimers of the type $M_2X_8^{n-}$ does not necessarily lead to cleavage of the metal–metal bond, the actual reaction course being dependent upon the nature of M. In view of our successful isolation of the salt $(Bu_4N)_2Mo_2(NCS)_6(PEt_3)_2$ and the existence of $(Bu_4N)_2Re_2(NCS)_8$,[1,2] it is possible that salts of the octaisothiocyanatodimolybdate(II) anion can be isolated upon choice of a suitable cation.

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Registry No. I, 64784-48-1; II, 64784-50-5; III, 64784-51-6; IV, 64784-41-4; V, 64784-42-5; VI, 64784-43-6; $Mo_2Cl_4(PEt)_4$, 59780-36-8.

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Correspondence

Polarized Absorption Spectroscopy of Anisotropic Single Crystals

Sir:

Polarized absorption spectra of single crystals have been used extensively in recent years in the study of the electronic structure of transition metal complexes. Both linearly polarized and circularly polarized spectra of anisotropic crystals are frequently of interest. A large number of linearly polarized spectra[1] and a significant number of circularly polarized spectra[2] have appeared in the literature.

It is well known that both of these types of spectra are subject to the effects of birefringence and that the circularly polarized spectra are affected by the linear dichroism of the crystal.[3,4] On the other hand, it does not seem to be generally recognized that linearly polarized spectra can be affected by circular dichroism in the crystal.

Unfortunately, there seems to be no readily available general analysis of these possible interferences,[5] and thus the information in such spectra and their limitations have probably not been as clear as they should be. Such a general analysis is fairly simple, when the problem is formulated in terms of the Mueller matrix calculus,[6] and is presented here.

The usual experimental procedure is to place a reasonably thin slice of crystalline material with parallel faces in the appropriate instrument with the crystal faces perpendicular to the propagation vector, k_i, of the incident light beam. Under these conditions, the effect of an anisotropic crystal upon the light beam may be analyzed in a straightforward way in terms of the Stokes vector of the light beam and the Mueller matrix of the crystal.[7]

The Stokes vector is the four-dimensional vector

$$\mathbf{S} = \begin{bmatrix} s_0 \\ s_1 \\ s_2 \\ s_3 \end{bmatrix} \tag{1}$$

where s_0 is the intensity and the remaining s_i describe the degree and type of polarization. If we consider a "nearly" monochromatic beam in a right-handed coordinate system with the propagation vector, k, in the positive z direction, the Stokes vector becomes[8]

$$\mathbf{S} = \begin{bmatrix} s_0 \\ s_1 \\ s_2 \\ s_3 \end{bmatrix} = \begin{bmatrix} \langle a_x^2 + a_y^2 \rangle \\ \langle 2a_x a_y \cos\delta \rangle \\ \langle 2a_x a_y \sin\delta \rangle \\ \langle a_x^2 - a_y^2 \rangle \end{bmatrix} \tag{2}$$

where δ is the phase angle between the instantaneous amplitudes of the electric field in the x and y directions, a_x and a_y. δ is defined so that when $\pi > \delta > 0$, circular polarization of the beam is right handed.

The effect of any optical device can be expressed as a 4 × 4 matrix, the Mueller matrix, **F**, which transforms the Stokes

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vector of the input beam, $\mathbf{S}_i$, into the Stokes vector of the ouput beam, $\mathbf{S}_o$

$$\mathbf{S}_o = \mathbf{F} \times \mathbf{S}_i \tag{3}$$

Gō[9] has shown that in the case where the input and output propagation vectors are collinear there are at most seven independent matrix elements in the Mueller matrix. Under these conditions $\mathbf{F}$ may be written in terms of ordinary optical parameters to second-order accuracy[9,10] as

$$\mathbf{F}(l) = e^{-(\ln 10)A} \left\{ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} - \gamma \begin{bmatrix} 0 & b_1 & b_2 & b_3 \\ b_1 & 0 & a_3 & -a_2 \\ b_2 & -a_3 & 0 & a_1 \\ b_3 & a_2 & a_1 & 0 \end{bmatrix} + \gamma^2/2 \times \begin{bmatrix} (b_1{}^2 + b_2{}^2 + b_3{}^2) & (a_2 b_3 - a_3 b_2) & (a_3 b_1 - a_1 b_3) & (a_1 b_2 - a_2 b_1) \\ (a_3 b_2 - a_2 b_3) & (b_1{}^2 - a_3{}^2 - a_2{}^2) & (b_1 b_2 + a_1 a_2) & (b_1 b_3 + a_1 a_3) \\ (a_1 b_3 - a_3 b_1) & (b_1 b_2 + a_1 a_2) & (b_2{}^2 - a_3{}^2 - a_1{}^2) & (b_2 b_3 + a_2 a_3) \\ (a_2 b_1 - a_1 b_2) & (b_1 b_3 + a_1 a_3) & (b_2 b_3 + a_2 a_3) & (b_3{}^2 - a_2{}^2 - a_1{}^2) \end{bmatrix} \right\} \tag{4}$$

where A = total average absorbance, $\gamma b_3 = 1.151(\epsilon_x - \epsilon_y)lc$ (linear dichroism, LD), $\gamma a_3 = (2\pi/\lambda)(n_x - n_y)l$ (linear birefringence, LB), $\gamma b_2 = -1.151(\epsilon_l - \epsilon_r)lc$ (circular dichroism, CD), $\gamma a_2 = -(2\pi/\lambda)(n_l - n_r)l$ (circular birefringence, ORD), $\gamma b_1 = 1.151(\epsilon_{+45} - \epsilon_{-45})lc$ (LD′), $\gamma a_1 = (2\pi/\lambda)(n_{+45} - n_{-45})l$ (LB′), and $\gamma = 2lc$, ϵ = specific absorbance, n = index of refraction, c = concentration of the active molecules, $1.151 = (\ln 10)/2$, and l = path length.

When dealing with visible light and ordinary materials (the weak interaction limit) all of the birefringence terms and the circular dichroism term will be $\ll 1$, and if LD and LD′ $< \sim 0.2$ no significant errors will be introduced by terminating the series in eq 4 at the second-order term.

Plane Polarized Spectra. If an x or y plane polarized beam of unit intensity is passed through a general anisotropic crystal, eq 2, 3, and 4 give

$$\mathbf{S}_i = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \pm 1 \end{bmatrix}$$

and

$$\mathbf{S}_o = e^{-(\ln 10)A} \begin{bmatrix} 1 + (\gamma^2/2)(b_1{}^2 + b_2{}^2 + b_3{}^2) \pm [-\gamma b_3 + (\gamma^2/2)(a_1 b_2 - a_2 b_1)] \\ -\gamma b_1 + (\gamma^2/2)(a_3 b_2 - a_2 b_3) \pm [\gamma a_2 + (\gamma^2/2)(b_1 b_3 + a_1 a_3)] \\ -\gamma b_2 + (\gamma^2/2)(a_1 b_3 - a_3 b_1) \pm [-\gamma a_1 + (\gamma^2/2)(b_2 b_3 + a_2 a_3)] \\ -\gamma b_3 + (\gamma^2/2)(a_2 b_1 - a_1 b_2) \pm [1 + (\gamma^2/2)(b_3{}^2 - a_1{}^2 - a_2{}^2)] \end{bmatrix} = \mathbf{F}(l) \times \mathbf{S}_i \tag{5}$$

In principle, it would be possible to obtain all seven optical parameters by measuring the four Stokes parameters for both an x polarized and a y polarized beam. However, in practice this would probably not be feasible, and in any event, the usual spectrophotometer measures only the intensity of the exit beam, s_0. Therefore, we will consider only the s_0 terms.

An examination of eq 5 shows that the linear dichroism can be obtained to second-order accuracy from the intensity measurements only if the term $(a_1 b_2 - a_2 b_1)$ vanishes, so that for the x polarized beam

$$s_0 = I_a [1 + (\gamma^2/2)(b_1{}^2 + b_2{}^2 + b_3{}^2) + \gamma b_2]$$

and for the y polarized beam

$$s_0 = I_a [1 + (\gamma^2/2)(b_1{}^2 + b_2{}^2 + b_3{}^2) - \gamma b_2]$$

where $I_a = \exp[-(\ln 10)A]$.

If the crystal is circularly inactive,[11] then $a_2 = b_2 = 0$ and plane polarized spectra are accurate to the second order in any direction. On the other hand if the crystal is circularly active, second-order accuracy is obtained only if it is possible to make $a_1 = b_1 = 0$. If the crystal is uniaxial (hexagonal, tetragonal, or trigonal) this can be easily achieved by placing the unique axis parallel to the laboratory xz (or yz) plane.

The situation is much more restrictive with the optically biaxial, circularly active crystals. If the crystal belongs to one of the orthorhombic point groups 222 or $mm2$, the optic axes must be parallel to one of the crystallographic planes (100), (010), or (001), and second-order accuracy is obtained if the appropriate plane is placed parallel to the laboratory xz (or yz) plane. If the crystal belongs to one of the point groups 1, 2, or m there seems to be no simple way of achieving second-order accuracy and so plane polarized spectra of such crystals should be approached with care when the observed LD is small.

CD Spectra. The conventional Grosjean and Legrand type circular dichroism spectrometer[12] uses a combination of a linear polarizer and a polarization modulator to produce an input beam with a Stokes vector of the form

$$\mathbf{S}_i = \begin{bmatrix} 1 \\ 0 \\ \sin(\delta \sin \omega t) \\ \cos(\delta \sin \omega t) \end{bmatrix} \tag{6}$$

where δ = the maximum phase retardation and ω = the modulation frequency.

If this beam is passed through a general anisotropic crystal slice, the output intensity, s_0, takes on the rather complex form

$$s_0 = I_a [1 + (\gamma^2/2)(b_1{}^2 + b_2{}^2 + b_3{}^2) + \{-\gamma b_2 - (\gamma^2/2)(a_1 b_3 - a_3 b_1)\} \times \sin(\delta \sin \omega t) + \{-\gamma b - (\gamma^2/2)(a_2 b_1 - a_1 b_2)\} \times \cos(\delta \sin \omega t)] \tag{7}$$

The frequency terms in eq 7 can be expanded as

$$\sin(\delta \sin \omega t) = 2J_1(\delta) \sin \omega t + 2J_3(\delta) \sin 3\omega t + 2J_5(\delta) \sin 5\omega t + \cdots$$

and

$$\cos(\delta \sin \omega t) = J_0(\delta) + 2J_2(\delta) \cos 2\omega t + 2J_4(\delta) \cos 4\omega t + \ldots$$

where the J_n are Bessel functions.

The usual procedure is to separate the ac and dc portions of the phototube output and amplify the ac portion with a synchronous amplifier. The out-of-phase cosine terms will be rejected by the amplifier, so that only the sine terms will appear in the output. The output of the machine (the apparent rotation, R_a) is the ratio of the amplified ac component and the dc component, so that

$$R_a \sim \frac{-\gamma b_2 - (\gamma^2/2)(a_1 b_3 - a_3 b_1)}{1 + (\gamma^2/2)(b_1{}^2 + b_2{}^2 + b_3{}^2) + J_0(\delta)[-\gamma b_3 - (\gamma^2/2)(a_2 b_1 - a_1 b_2)]} \tag{8}$$

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

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

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

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

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)

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

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

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

where $S = (\gamma^2/2)(a_2b_3 - a_3b_2)$. 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

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

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

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(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.

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(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).