and disappears when the light is extinguished. These esr data are consistent with our assignment of the long wavelength room temperature emission as phosphorescence. The larger g value (2.02) and the bandwidth observed ($\sim$25 G) are characteristic of a delocalized triplet π system. The other signal ($g = 2.003$) is likely due to a solvent radical formed in a solute photosensitized reaction. Such photosensitization generally requires the intermediacy of a triplet species.[14,15]

The rationale for the unique behavior of these biphenyl derivatives is not yet clear but may be due to a mixing of π–π^* and n–π^* states. Such a model has been used to explain the enhanced carbonyl absorption and Cotton effect behavior of IV.[16] The derivatives which do not display this emission (X = single bond, O, S, SO_2) are systems not expected to be capable of such mixing. A full discussion of our findings is deferred to the full paper.

Acknowledgment. We are indebted to the National Science Foundation (M. K. D.) and the North Carolina State University Engineering Foundation (G. H. W.) for partial support of this work.

(14) H. G. Judeikis and S. Siegel, *J. Chem. Phys.*, **43**, 3625 (1965).

(15) K. D. Cadogan and A. C. Albrecht, *ibid.*, **43**, 2550 (1965).

(16) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).

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Solvent Effects and the Circular Dichroism Spectra of Metal Complexes

Sir:

The circular dichroism spectra observed in the regions of the d–d transitions of metal complexes which are dissymmetric only because of their conformational structure or because of vicinal effect dissymmetry are currently the subject of intensive investigation. These studies tacitly assume that the solution circular dichroism spectra of these complexes are largely representative of the spectra which would be observed if these molecules were free of their solvent environment. In the course of our fairly extensive studies of the circular dichroism spectra of polyamine systems, we have found that this assumption is rarely correct. We wish to draw attention to this problem here where we describe perhaps the most spectacular example of solvent variation we have observed.

The complex ion *trans*-(*R*,*R*)-$[Co\text{-}3,2,3\text{-tet}(N_3)_2]^+$ (3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$) has been resolved and its absolute configuration has been unambiguously correlated[1] with the *trans*-(*R*,*R*)-$[Co\text{-}3,2,3\text{-tet-}Cl_2]NO_3$ complex, the absolute structure of which has been determined by X-ray analysis.[2] Figure 1 shows the absorption spectrum of the azido complex in water and dimethyl sulfoxide (DMSO) and the circular dichroism spectra in water, DMSO, and a 1:1 volume solution in water and DMSO. The first two circular dichroism bands at around 15,000 and 17,500 cm^{-1} represent the components of the $^1A_{1g} \rightarrow {}^1E_g$ transition and the (overlapped) band at 20,500 cm^{-1} is the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. All three of these components are derived from the $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic transition which is split by the largely D_{4h} field. It will be evident that the circular dichroism spectra in water and DMSO are practically enantiomorphous for these three components, and it is only in the higher energy regions, due mainly to charge-transfer transitions, that the circular dichroism in the two solvents becomes approximately similar. A tenfold dilution of the solution or the addition of a 1000-fold excess of ClO_4^- ions over the complex ion concentration does not alter the spectrum in DMSO; a 1000-fold excess of Cl^- ions over the complex concentration does lead to a small change in intensity but there is not a change in sign of any of the components. This last observation suggests that ion multiplets do not cause the effects we are observing. This seems to leave either of two possible explanations: (1) that these effects are due to conformational changes or (2) that the conformations do not change from solvent to solvent but that the effects are in some way caused by the solvent.

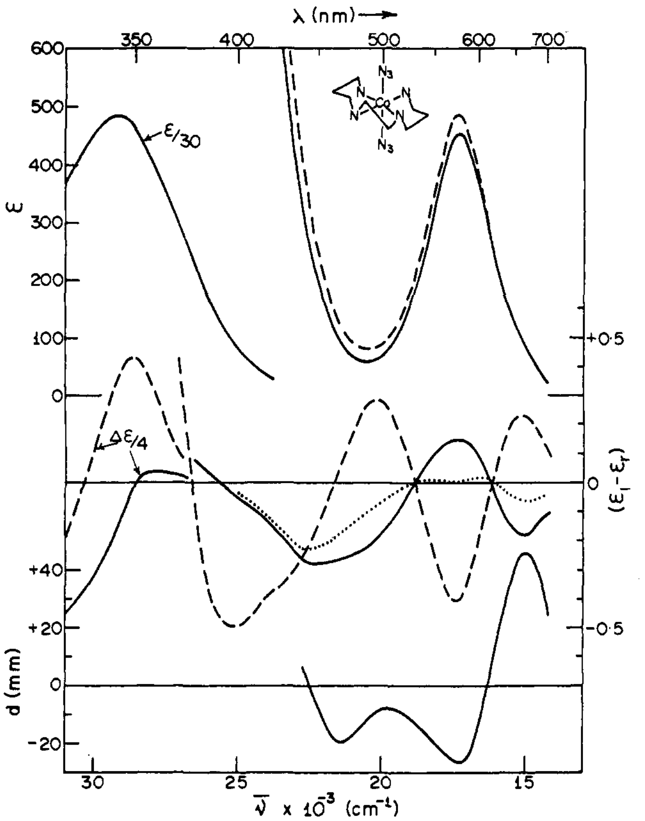

Figure 1. The absorption and circular dichroism spectra of the *trans*-(*R*,*R*)-$[Co\text{-}3,2,3\text{-tet}(N_3)_2]ClO_4$ complex in water (——), DMSO (----), and 50% water–DMSO (····). The KBr disk spectrum (——) is shown at the bottom.

Taking the former postulate first, we note that the two terminal six-membered rings are flexible and that it is conceivable that a conformational equilibrium exists where the terminal rings are flipping from the nonchiral chair to the chiral–skew conformations (Figure 2). It will be evident that, because of the chiral constraints imposed by the inner secondary nitrogen atoms, the outer rings in the skew conformation will have the opposite twist sense to the inner

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(1) B. Bosnich and J. M. Harrowfield, *Inorg. Chem.*, submitted for publication.

(2) N. C. Payne, *ibid.*, in press.

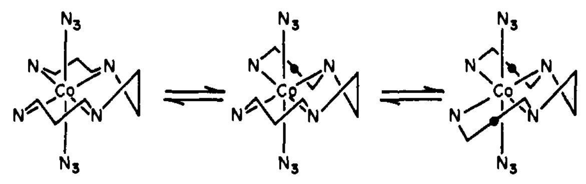

Figure 2.

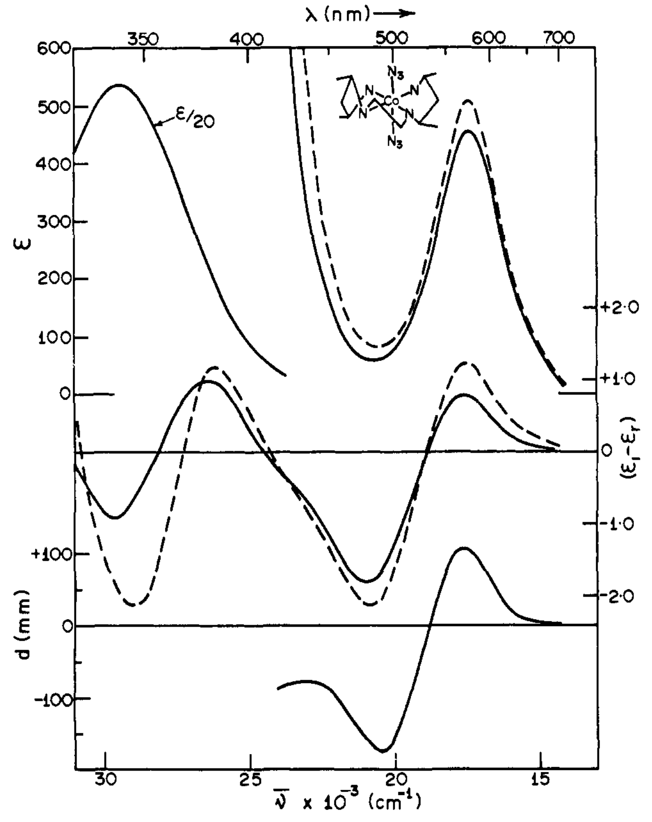

Figure 3. The absorption and circular dichroism spectra of *trans*-(*S*,*S*)-[Co-(*R*,*R*,*R*,*R*)-sk-3,2,3(N_3)$_2$]ClO_4 in water (——) and DMSO (- - - -). The structure of the complex is shown in the inset and the KBr disk spectrum (——) is shown at the bottom.

ring. And, if we make the assumptions, which have been verified in analogous systems,[1] that the circular dichroism is roughly additive for each chiral ring and that a six-membered skew ring imparts roughly the same amount of circular dichroism as a five-membered gauche ring, then it is possible to explain the solvent behavior on this basis. In view of the many examples found in organic chemistry,[3] this explanation seems plausible and appealing but it is almost certainly wrong. The reasons are as follows.

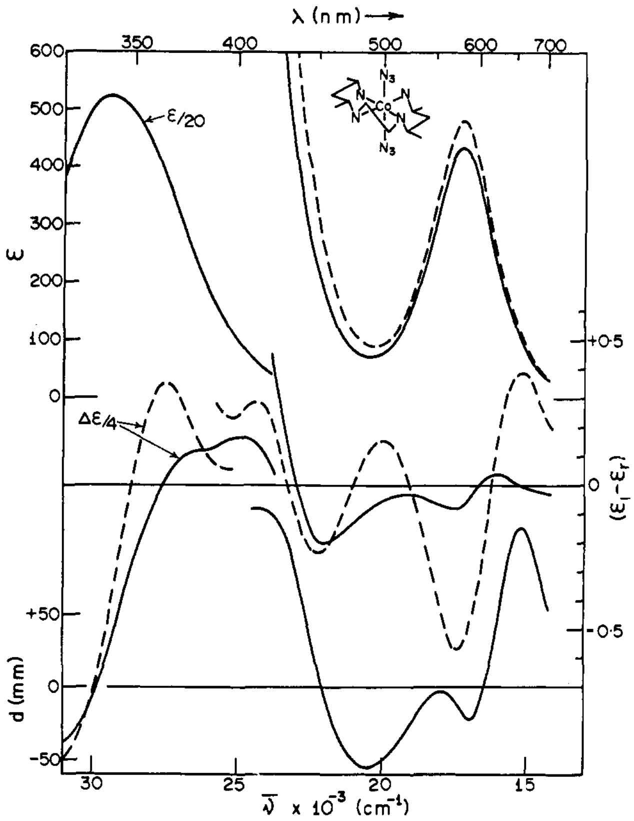

Figure 4. The absorption and circular dichroism spectra of *trans*-(*S*,*S*)-[Co-(*S*,*R*,*R*,*S*)-ch-3,2,3(N_3)$_2$]ClO_4 in water (——) and DMSO (- - - -). The structure of the complex is shown in the inset and the KBr disk spectrum (——) is shown at the bottom.

We have prepared and resolved the two analogous complexes, *trans*-(*S*,*S*)-[Co-(*S*,*R*,*R*,*S*)-ch-3,2,3(N_3)$_2$]ClO_4 and *trans*-(*S*,*S*)-[Co-(*R*,*R*,*R*,*R*)-sk-3,2,3(N_3)$_2$]ClO_4, where the ligand in both cases is $NH_2CH(CH_3)CH_2(CH_3)CHNHCH_2CH_2NHCH(CH_3)CH_2CH(CH_3)NH_2$; the *S*,*R* nomenclature refers to the sequential order of the chiral centers by the standard numbering scheme. These assigned absolute configurations are based on chemical correlations and the circular dichroism shown by the complexes of the ligands. If we assume that the methyl groups attached to the six-membered rings will adopt equatorial dispositions, then the *trans*-(*S*,*S*)-[Co-(*S*,*R*,*R*,S)-ch-3,2,3(N_3)$_2$]$^+$ ion has the two terminal rings in the chair conformation whereas both these two rings are in the skew conformation in the *trans*-(*S*,*S*)-[Co-(*R*,*R*,*R*,*R*)-sk-3,2,3(N_3)$_2$]$^+$ ion (see Figures 3 and 4). Figures 3 and 4 show the absorption and circular dichroism spectra of these two ions in water and DMSO. The circular dichroism of the *trans*-(*S*,*S*)-[Co-(*R*,*R*,*R*,*R*)-sk-3,2,3(N_3)$_2$]$^+$ ion is only slightly dependent on the solvent and the pattern it displays in the $^1T_{1g}$ region is quite distinct from that shown by the *trans*-(*R*,*R*)-[Co-3,2,3-tet(N_3)$_2$]$^+$ ion in any solvent and suggests that the latter is not undergoing a double chair to skew change in these solvents although this observation may not exclude the possibility of only one of the terminal rings flipping. However, this latter possibility seems unlikely since the DMSO spectrum of the *trans*-(*S*,*S*)-[Co(*S*,*R*,*R*,*S*)-ch-3,2,3(N_3)$_2$]$^+$ ion is nearly identical with that of the *trans*-(*R*,*R*)-[Co-3,2,3-tet(N_3)$_2$]$^+$ ion in the same solvent and, although the spectra do not match exactly, both these complexes show a strong solvent dependence and both have a −, +, − pattern under the $^1T_{1g}$ band in water solution. These observations give no substantiation to the conformational equilibrium hypothesis and tend to support the idea that these effects are only due to the solvent.

The spectra of the three complexes described are examples where solution circular dichroism spectra of conformational isomers of metal complexes are unreliable if correlations between circular dichroism and absolute configurations are attempted and attempts to rationalize changes in circular dichroism in various

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(3) A. Moscowitz, K. M. Wellman, and C. Djerassi, *Proc. Nat. Acad. Sci.*, **50**, 779 (1963).

solvents with conformational changes are fraught with ambiguity. We have found this to be true for all the polyamine and amino acid complexes we have investigated and we suppose that the problem is quite general to these systems.

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Solvents of Low Nucleophilicity. XIV. A Nucleophilicity Scale Based on Rates of Reaction of Tetramethylenechloronium Ion with Carboxylic Acids and Its Use in Swain–Scott Type Correlations

Sir:

Various halonium ions recently have been prepared as stable species, some of which undergo extraordinarily facile alkylation reactions.[1] We now report (in Table I) the rate constants for the reaction of tetramethylenehalonium ions with various carboxylic acids in SO_2 at $-65.6 \pm 0.1°$ (eq 1). The logarithms of these rate constants, given in Table I, are particularly significant as possible measures of the nucleophilicities of the carboxylic acids. They are comparable to log k values for solvolysis of *tert*-butyl chloride, used as measures of ionizing power.[2]

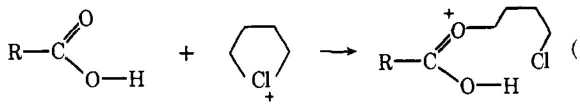
(1)

Table I. Rate Constants for Reactions of Tetramethylenechloronium Ion with Nucleophiles in SO_2, $-65.6 \pm 0.1°$

Nucleophile	$k_{1/2}$, $M^{-1/2}$ sec^{-1} [a]	Log k
HCO_2H	5.6×10^{-2}	-1.25
CH_3CO_2H	4.1×10^{-2}	-1.39
$ClCH_2CO_2H$	4.2×10^{-3}	-2.38
Cl_2CHCO_2H	2.3×10^{-4}	-3.64
CF_3CO_2H	8.7×10^{-6}	-5.06

[a] Calculated from the integrated rate equation for reactions first order in halonium ion and half order in nucleophile. The approximate half-order dependence, demonstrated in six runs for acetic acid, may result from the acid dimer-monomer equilibrium.

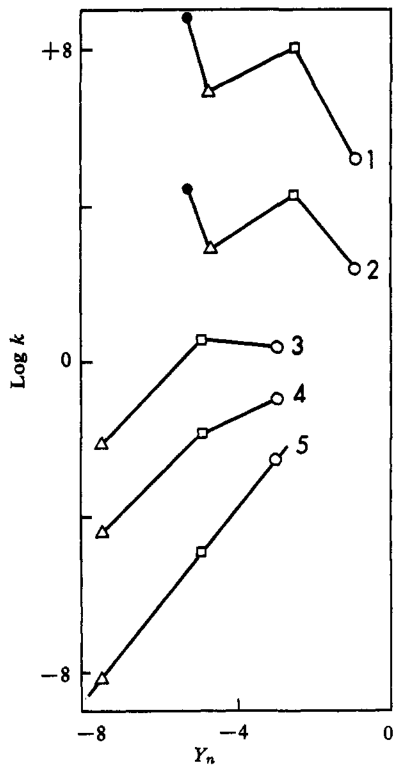

Figure 1. Log k for alkyl tosylates plotted against Y_n for the solvents CF_3CO_3H (○), CH_3CO_2H (△), HCO_2H (□), and EtOH (●). The alkyl tosylates, identification numbers, solvolysis temperatures, and number of log units by which the graph has been displaced upward are, respectively: methyl, 1, 75°, 13 units; ethyl, 2, 75°, 9 units; isopropyl, 3, 25°, 5 units; 3-heptyl, 4, 25°, 2 units; 2-adamantyl, 5, 25°, 0 units.

Winstein, Grunwald, and Jones, and Swain and Scott have considered solvolysis rates to be primarily a function of the nucleophilicity and the ionizing power of the solvent.[3] The Swain-Scott equation may be written in the form

$$\log k_A - \log k_B = sN_A{}^B + mY_A{}^B \qquad (2)$$

In this equation giving logarithms of rate constants, k, for solvolyses in solvents A and B, $N_A{}^B$ and $Y_A{}^B$ are the differences in nucleophilicities and ionizing powers, respectively, between the two solvents, and m and s are sensitivity parameters characteristic of the compound.

Swain, Mosely, and Bown[4] used the relationship of eq 2 in the form given in eq 3. However, the results

$$\log (k/k_0) = c_1d_1 + c_2d_2 \qquad (3)$$

stemming from their assumptions regarding standard reaction parameters were not fully understood.

Accordingly, in addition to developing our own parameters for use in eq 2, we have derived eq 4–7 for converting the Swain–Mosely–Bown parameters into s, N, m, and Y values as defined for eq 2, based on the assumptions that $s = 0$ for *tert*-butyl chloride, $s = 1$ for methyl bromide, and that the N values for acetic and formic acid are equal.

$$Y_{SMB} = d_1 + d_2 \qquad (4)$$

$$m_{SMB} = 0.11(c_1 - c_2) + c_2 \qquad (5)$$

$$N_{SMB}/0.53 = 0.89d_2 - 0.11d_2 \qquad (6)$$

$$s_{SMB} = (c_1 - c_2)/0.53 \qquad (7)$$

For treatment of solvolyses in acid solvents, including trifluoroacetolyses, according to eq 2, availability of data led us to choose the logarithms of the rate constants for the solvolysis of neophyl tosylate (p-$CH_3C_6H_4SO_3$-$CH_2C(CH_3)_2(C_6H_5)$) as the measures of ionizing power. These values, here designated Y_n, have been shown to be

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(1) (a) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970); (b) P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2840 (1970).

(2) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(3) (a) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(4) C. G. Swain, R. B. Mosely, and D. E. Bown, *ibid.*, **77**, 3731 (1955).