that the bulk of the reaction occurs with methyl-oxygen bond scission, and the carboxyl carbon-oxygen bond breaks only in 2–3% of the events.

When V^{++} is used as the reducing agent, the procedure for separating the fumaric acid is much simpler than with Cr^{++}; the organic acid can be extracted directly from the reaction mixture. Complete hydrolysis of the ester again accompanies electron transfer. The tracer experiment shows that the CH_3-O bond breaks in 95% of the events. With the same reducing agent, but with the methyl maleate half-ester as ligand, bond rupture occurs at the CH_3-O position in 97–98% of the hydrolysis events.

When the phenyl fumarate half-ester is the ligand and V^{++} is the reducing agent, complete hydrolysis of the ester also accompanies electron transfer. In this system, the isotopic compositions of both the phenol and the fumaric acid were determined. The results of a series of experiments are summarized.

Acidity of the solution, M	1	0.50	0.25	0.05
Fraction of phenol enriched	0.071	.094	.105	.118
Fraction of fumaric acid enriched[a]	0.925	.898	.884	.878

[a] As containing one oxygen derived from the solvent.

The isotope balance is good so that the fractions reported can be taken as indicating the fractions of bond rupture at the two positions. It is evident that the course of the reactions can be altered when an alcohol radical such as C_6H_5, which is reluctant to accept substitution is used. It is perhaps even more remarkable that a substantial fraction of the bond breaking occurs at the C_6H_5-O position. The results incidentally show that no exchange of the carboxyl oxygen with the solvent accompanies this type of hydrolysis reaction, in contrast to the behavior demonstrated for a number of other ester hydrolyses.[4]

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(4) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951); references to other work cited by M. L. Bender, R. D. Ginger and J. P. Unik, *ibid.*, **80**, 1044 (1958).

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RECEIVED AUGUST 5, 1959

CHARGE TRANSFER LUMINESCENCE OF A RUTHENIUM(II) CHELATE

Sir:

We would like to report the first example of luminescence resulting from a charge transfer transition in the transition metal chelate tris-2,2′-bipyridine-ruthenium(II). The luminescence of chelates has, in general, been studied as a function of electronic transitions within the ligand itself except for a few isolated cases as for the rare earth chelates with energy transfer and luminescence from f–f transitions[1,2] and for luminescence characteristic of copper(II) in mixtures of copper(II) and aminoanthraquinones,[3] as pointed out by Kasha and McGlynn.[4]

The absorption and fluorescence of tris-5-methyl-1,10-phenanthroline ruthenium chelate have been reported and utilized for a microdetermination of ruthenium[5] although the electronic transition involved has not been discussed. The luminescence shown in Fig. 1 was obtained from a 10^{-4} solution of tris-2,2′-bipyridineruthenium(II) chloride at 77°K. The line-like character of the luminescence is reminiscent of the f–f emission in the rare earth chelates. However, it is a completely different phenomenon produced by an allowed transition whose mean lifetime is less than 10^{-4} sec.[6] As shown by the absorption spectra in Fig. 1 there is no analogous allowed absorption band at the wave length of the luminescence.

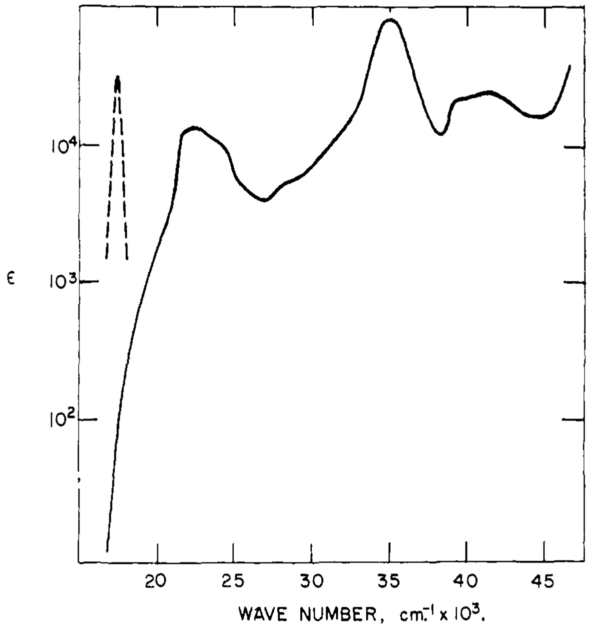

Fig. 1.—Tris-2,2′-bipyridineruthenium(II) chloride: ——— absorption spectra; --------- luminescence spectra (plotted on an arbitrary intensity scale).

We have explained our data in this manner. The broad absorption band between 17,000 and 27,000 cm.$^{-1}$ may be due to a charge transfer absorption ($\epsilon > 10^4$). That is, the d electron from the ruthenium atom may be excited to an antibonding orbital of the bipyridine molecule (d → pi*). Thus we may have a very broad absorption band due to excitation to various vibrationally excited levels of the pi* electronic state and yet have a single emission from the lowest vibrational level of the excited state to the ground d orbital. This may be represented pictorially as shown in Fig. 2.

As predicted there should also be an absorption band from the d orbital to the second antibonding pi orbital. This band was found experimentally to have $\epsilon_{max.}$ at 41250 cm.$^{-1}$ as shown in Fig. 1. The remaining band with $\epsilon_{max.}$ at 35000 cm.$^{-1}$ is of course the pi → pi* transition of bipyridine. Ex-

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(1) S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).

(2) G. A. Crosby and M. Kasha, *Spectrochim. Acta*, **10**, 377 (1958).

(3) A. V. Karyakin and Ya. I. Kalenichenko, *Doklady Akad. Nauk S.S.S.R.*, **66**, 191 (1949).

(4) M. Kasha and S. P. McGlynn, *Ann. Rev. Chem.*, **7**, 403 (1956).

(5) H. Veening, Ph.D. Thesis, Purdue University, 1958. Submitted to *Analytical Chemistry*.

(6) The lifetime estimate was kindly provided by Dr. M. Kasha at the Florida State University.

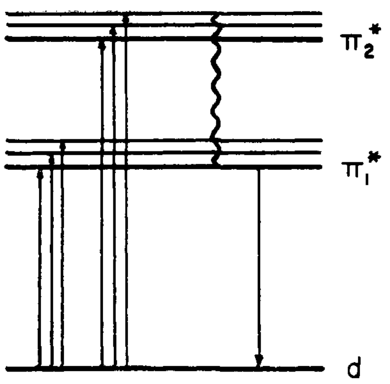

Fig. 2.—Energy scheme for the absorption and luminescence processes for tris-2,2′-bipyridineruthenium(II) chloride.

citation of fluorescence by any of the three absorption bands results in the same characteristic luminescence. Thus we have shown internal conversion from the higher excited level in the ultraviolet to the lowest excited level yielding fluorescence.

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RECEIVED MARCH 18, 1959

OPTICAL ROTATORY DISPERSION STUDIES. XXXI.[1] ANOMALOUS DISPERSION CURVES OF DITHIOCARBAMATES OF α-AMINO ACIDS AND PEPTIDES. STEREOCHEMICAL CORRELATIONS BETWEEN α-HYDROXY AND α-AMINO ACIDS[2]

Sir:

Anomalous Cotton effect curves recently have found extensive applications[3a] in many areas of organic chemistry. Unfortunately, most α-amino acids[3b] and their higher polymers[3c] exhibit only plain dispersion curves[4] over the presently accessible spectral range. We have now discovered that N-dithiocarbalkoxy α-amino acids (I) (dithiocarbamate derivatives) are almost uniquely suited for this purpose and that their use may represent an important advance in α-amino acid or peptide methodology. The preparation[5] of such derivatives is simple and often lends itself to work on a micro-scale.[6]

The long wave length absorption band near 330 mμ of such dithiocarbamates (I) is strongly optically active and leads to Cotton effect curves[4] (Fig. 1). *The sign of the Cotton effect of the dithiocarbamate will indicate the absolute configuration of the α-asymmetric center and all α-amino acids of the* L-*series, which have so far been examined, show a positive Cotton effect, the reverse being true of members of the* D-*series.* This has been tested with the dithiocarbamates of alanine, valine, phenylglycine, isoleucine, alloisoleucine, proline, aspartic acid, glutamic acid and cystine. The nearly identical positive Cotton effect curves of L-isoleucine and L-alloisoleucine demonstrate the unimportance of the β-asymmetric center in this type of analysis. Similarly, N-dithiocarbomethoxy L-alanyl-L-alanine and N-dithiocarbomethoxy L-alanyl-D-alanine exhibit positive Cotton effect curves of virtually identical amplitude. This suggests that the technique may be employed to determine the configuration of the α-asymmetric center of a terminal amino acid in a peptide chain, which may be of importance in antibiotic chemistry.

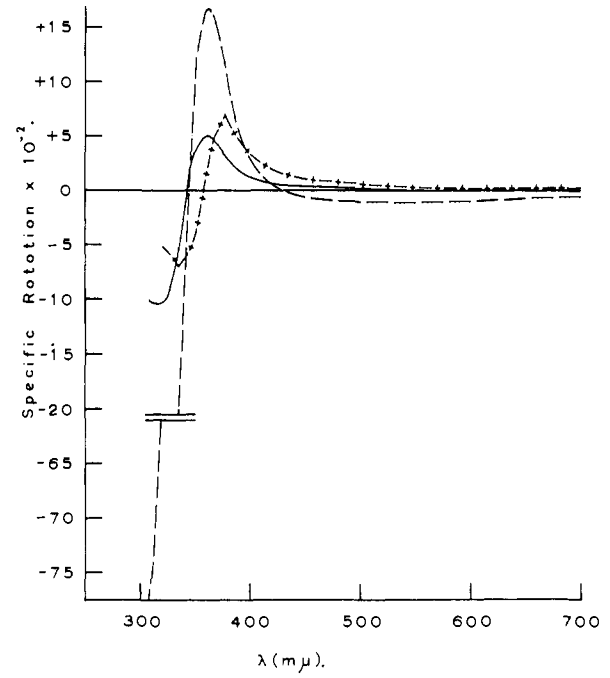
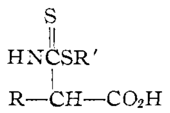


Fig. 1.—Optical rotatory dispersion curves (methanol solution) of N-dithiocarbomethoxy-L-(+)-valine, ———; N,N′-bis-dithiocarbethoxy-L-(−)-cystine, ---------; and L-(−)-malic acid ethyl dithiocarbonate, —+—+—+.

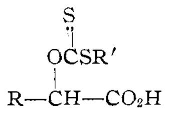
The "optical activity" of the dithiocarbamate is so strong as to overcome the structural factors which often confuse stereochemical correlations of the parent acid based on $[\alpha]_D$ (*e.g.*, L-(+)-alanine *vs.* L-(−)-cystine possessing dispersion curves of opposite sign[3b] while their dithiocarbamates exhibit positive Cotton effect curves).

Xanthate derivatives of certain alcohols have been shown[7] to give anomalous dispersion curves and we have now examined such derivatives (II) of α-hydroxy acids.



$$\begin{array}{c} S \\ \| \\ HNCSR' \\ | \\ R—CH—CO_2H \end{array}$$

I



$$\begin{array}{c} S \\ \| \\ OCSR' \\ | \\ R—CH—CO_2H \end{array}$$

II

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[1] Paper XXX, C. Djerassi, N. Finch and R. Mauli, THIS JOURNAL, **81**, 4997 (1959).

[2] Supported by grant No. CY-2919 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

[3] (a) C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., Chapters 4–14; (b) Sec. 15-4 by J. A. Schellman in ref. 3a; (c) Chapter 17 by E. R. Blout in ref. 3a.

[4] For nomenclature see C. Djerassi and W. Klyne, *Proc. Chem. Soc.*, 55 (1957).

[5] See A. Fredga, *Svensk Kem. Tid.*, **53**, 221 (1941); **54**, 26 (1942).

[6] *E.g.*, 5.8 mg. of L-(−)-proline afforded 2.2 mg. of recrystallized dithiocarbamate.

[7] L. Tschugaeff and A. Ogorodnikoff, *Z. physik. Chem.*, **85**, 481 (1913), and earlier papers; T. M. Lowry and H. Hudson, *Phil. Trans.*, **A232**, 117 (1933).