

Table I. IR Data<sup>a</sup> for Osmium Complexes<sup>b</sup>

| compound  | $\nu(\text{CO})$ | $\nu(\text{CX})$ |
|---|------------------|------------------|
| $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$                | 2012, 1990       | 880, 780, 770    |
| $\text{OsCl}_2(\text{CNCH}_3)(\text{CO})\text{-}$<br>$(\text{PPh}_3)_2$ | 1956             | 2200             |
| $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$                            | 2040, 1975       |                  |
| $\text{OsCl}_2(\text{CS})(\text{CO})(\text{PPh}_3)_2$                   | 2040, 2030, 2020 | 1315             |
| $\text{OsCl}_2(\text{CSe})(\text{CO})(\text{PPh}_3)_2$                  | 2036, 2018       | 1156             |
| $\text{OsCl}_2(\text{CTe})(\text{CO})(\text{PPh}_3)_2$                  | 2040             | 1046             |

<sup>a</sup> In reciprocal centimeters. Measured as Nujol mulls. <sup>b</sup> All compounds have satisfactory C and H analyses.

pure  $\text{TeH}^-$ . The tellurocarbonyl complex forms orange crystals mp 221–223 °C, which are air stable. The corresponding carbonyl, thiocarbonyl, and selenocarbonyl are almost colorless. All the compounds show an exceptionally intense infrared absorption associated with  $\nu(\text{CX})$  (see Table I) dropping from 1315  $\text{cm}^{-1}$  for  $\nu(\text{CS})$  to 1046  $\text{cm}^{-1}$  for  $\nu(\text{CTe})$ .  $\nu(\text{CO})$  remains almost constant throughout the series of compounds.

The stereochemistry of all derivatives is probably as depicted above and this has been confirmed for  $\text{OsCl}_2(\text{CS})(\text{CO})(\text{PPh}_3)_2$  by X-ray crystal structure analysis.<sup>14</sup> Since this is the first complete series of chalcocarbonyl compounds to be described, crystal structure determinations of all members of the series are planned to help evaluate the bonding characteristics of each ligand.

The dichlorocarbene complex promises to have diverse synthetic applications, and the further reactions of I are being studied.

## References and Notes

- Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.
- Butler, I. S.; Cozak, D.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1975**, 103. Clark, G. R.; Grundy, K. R.; Harris, R. O.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1975**, *90*, C37.
- Mansuy, D.; Lange, M.; Chottard, J.-C.; Guerin, P.; Morliere, P.; Brault, D.; Rougé, M. *J. Chem. Soc., Chem. Commun.* **1977**, 648.
- Mansuy, D.; Lange, M.; Chottard, J.-C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781.
- Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Chem. Commun.* **1975**, 929. Fischer, E. O.; Kleine, W.; Kreisli, F. R. *J. Organomet. Chem.* **1976**, *107*, C23.
- Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1.
- Logan, T. J. *J. Org. Chem.* **1963**, *28*, 1129.
- $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  (8.0 g) and  $\text{Hg}(\text{CCl}_3)_2$  (8.0 g) were added to rapidly stirred, boiling toluene (1.2 L) and the resulting solution heated under reflux for 25 min. The solution was then cooled in ice and filtered through a Celite pad. The toluene was removed under reduced pressure and the resulting orange oil crystallized from dichloromethane–ethanol. Recrystallization from benzene–ethanol yielded pure  $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$  (5.5 g, 80%). Anal. Calcd for  $\text{C}_{38}\text{H}_{30}\text{Cl}_4\text{O}_2\text{OsP}_2$ : C, 50.45; H, 3.34. Found: C, 50.90; H, 3.37.
- Crystal data and refinement results for  $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ : orthorhombic;  $a = 19.225$  (2),  $b = 16.675$  (2),  $c = 22.078$  (3) Å; space group  $Pbca$ ;  $Z = 8$ . Intensity data were collected on a four-circle diffractometer and the structure was solved by conventional methods. Least-squares refinement, with anisotropic thermal parameters assigned to the osmium and coordinated phosphorus and chlorine atoms, has given  $R = 0.061$  for 1476 observed reflections. The CO and  $\text{CCl}_2$  groups interchange between two sites, and it was necessary to refine them on the basis of a disordered model. Accordingly, their individual positions are not reliably determined. Details of the structure determination will be published elsewhere.
- Collman, J. P.; Roper, W. R. *J. Am. Chem. Soc.* **1966**, *88*, 3504.
- Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.
- Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
- $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$  (1.5 g) was placed in degassed benzene (55 mL) and  $\text{NaTeH}$  solution<sup>12</sup> (4.8 mL) added. After the mixture was stirred 1 min, most of the benzene was removed under reduced pressure and a black solid obtained by the addition of *n*-hexane. This was chromatographed on silica gel (3 × 42 cm column) using dichloromethane as eluant; the orange band was collected and crystallized using ethanol. To remove the small amount of  $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$  sometimes present in the sample, the material was then dissolved in an acetonitrile–dichloromethane mixture (30:30 mL),  $\text{AgClO}_4$  (0.15 g) added, and the solution heated under reflux for 15 min (this converts the  $\text{OsCl}_2(\text{CTe})(\text{CO})(\text{PPh}_3)_2$  into  $[\text{OsCl}(\text{NCCH}_3)(\text{CTe})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ , the  $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$  remaining unchanged). The precipitated  $\text{AgCl}$  was removed by filtration and ethanol added to the filtrate. The solvent volume was then carefully lowered under reduced pressure to effect the selective crystallization of the  $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$  which was removed by filtration. To the  $[\text{OsCl}(\text{NCCH}_3)(\text{CTe})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  in the filtrate,  $\text{LiCl}$  (0.50 g) in ethanol–water was added and the resulting orange crystals of the regenerated  $\text{OsCl}_2(\text{CTe})(\text{CO})(\text{PPh}_3)_2$  were collected and purified by

chromatography on silica gel (3 × 18 cm column) using dichloromethane as eluant. The orange band was collected and crystallized using ethanol to yield pure  $\text{OsCl}_2(\text{CTe})(\text{CO})(\text{PPh}_3)_2$  (0.45 g, 28%). Anal. Calcd for  $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{O}_2\text{OsP}_2\text{Te}$ : C, 47.88; H, 3.17. Found: C, 47.61; H, 3.39.

(14) Clark, G. R.; Marsden, K., unpublished work.

George R. Clark, Karen Marsden  
Warren R. Roper,\* L. James Wright

Department of Chemistry, University of Auckland  
Auckland, New Zealand

Received September 16, 1979

## Correlation of Circularly Polarized Luminescence Induced in $\text{Tb}(\text{dpm})_3$ by Chiral Solvents with the Absolute Configuration of Those Solvents

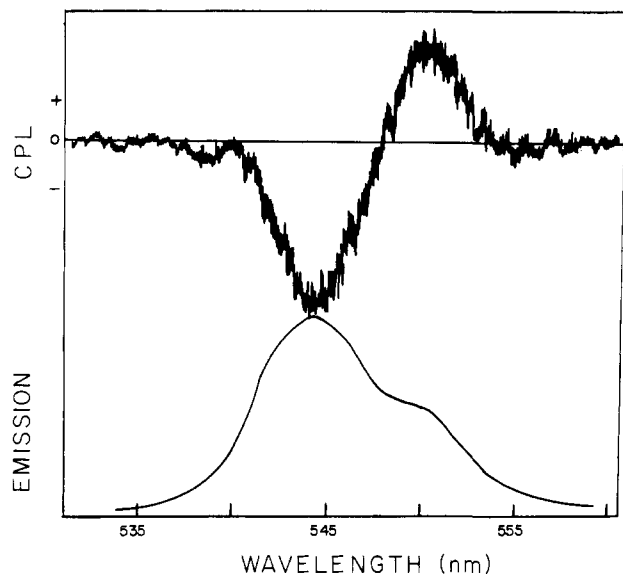
Sir:

The determination of the absolute configuration of a chiral substance is a very important part of the characterization of that molecule. Considerable success has been attained by Nakanishi and Dillon<sup>1</sup> in absolute configurational studies of vicinal glycols with metal derivatives of  $\beta$ -diketones. These workers were able to correlate the sign of circular dichroism peaks appearing  $\sim 300$  nm with the absolute configurations of numerous glycols and amino alcohols. Other workers have examined the circular dichroism induced in the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$  absorption of  $\text{Eu}(\text{III})$  when  $\text{Eu}(\text{fod})_3$  (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) adducts with chiral alcohols were prepared.<sup>2</sup> These methods are attractive in that the experiments are easy to carry out and the results usually adhere to the rules stated by the authors.

When a chiral molecule is also capable of luminescence after being excited by UV light, it is often possible to observe the excited-state analogue of circular dichroism, circularly polarized luminescence (CPL).<sup>3</sup> We have observed earlier that CPL could be induced in achiral  $\text{Eu}(\text{III})$   $\beta$ -diketonate chelates upon complexation with optically active solvents,<sup>4</sup> although we did not attempt to draw correlations between the configuration of the chiral solvent and the signs of the CPL. In the present work, the sign of the CPL induced in  $\text{Tb}(\text{dpm})_3$  (dpm = 2,2,6,6-tetramethylheptane-3,5-dione) is correlated with the absolute configuration of several chiral solvents.<sup>5</sup>

When  $\text{Tb}(\text{dpm})_3$  is dissolved in (*R*)- $\alpha$ -phenethylamine, strong  $\text{Tb}(\text{III})$  luminescence is observed at 545 nm, corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition. This transition is partially circularly polarized, and the particular CPL line shape associated with the CPL induced by the *R* enantiomer is shown in Figure 1.<sup>6</sup> Similar line shapes (although not magnitudes) were obtained when the *R* isomers of 2-aminobutane, 2-aminoheptane,  $\alpha$ -phenethyl alcohol, and propylene glycol were used as solvents for the  $\text{Tb}(\text{dpm})_3$ . Two CPL extrema were observed, and in general, when the *R* enantiomer of the chiral solvent was used, the negative CPL peak was the one located at 544 nm and the positive peak was found at 549 nm. When the *S* enantiomer was used in place of the *R*, the CPL peaks occurred at the same wavelength, had the same intensity, but were of opposite sign.

The CPL spectra of other  $\text{Tb}(\text{III})$  luminescent bands was also recorded, corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ ,  ${}^7\text{F}_4$ , and  ${}^7\text{F}_3$  transitions, but the CPL of these was at least an order of magnitude weaker than the CPL associated with the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  emission. An attempt to compare the CPL of the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$  emission with the induced circular dichroism (CD) of the corresponding  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$  proved unsuccessful owing to the extremely low magnitude of optical activity found with both methods. CD measurements were not pursued further since the low signal-to-noise ratios obtained precluded effective



**Figure 1.** Circularly polarized luminescence (upper) and total luminescence (lower) spectra of  $\text{Tb}(\text{dpm})_3$  dissolved in neat (*R*)- $\alpha$ -phenethylamine. Both intensity scales are completely arbitrary.

evaluation of the sign of induced optical activity with substrate absolute configuration.

No CPL was observed when resolved 2-butanol, 2-octanol, or diethyl tartrate were used as the chiral solvent, and no  $\text{Tb}(\text{III})$  emission was observed when using  $\alpha$ -(1-naphthyl)ethylamine as the solvent (here the solvent totally absorbed the exciting light at 365 nm and thus made it impossible to excite the  $\text{Tb}(\text{III})$  chelate).

It was found that the magnitude of total luminescence (TL) and CPL depended strongly on the nature of the solvent used, and in general the  $\text{Tb}(\text{III})$  emission was at least an order of magnitude more intense in the amine solvents than in the alcohol solvents. Previous work involving emission titrations of  $\text{Eu}(\text{III})$  chelates has established that the luminescence intensity of the lanthanide ion in a tris( $\beta$ -diketone) chelate will increase upon adduct formation with a substrate, and that the increase in luminescent intensity can be related to the formation constant of the chelate: substrate adduct.<sup>7</sup> In the cases where induced CPL was not found in the luminescence of a  $\text{Tb}(\text{dpm})_3$  adduct, it was found that the total emission was simply too weak to be observed.

It is possible to place the CPL results on a quantitative basis by calculating the luminescence dissymmetry factor,  $g_{\text{lum}}$  as defined by Richardson and Riehl:<sup>3</sup>

$$g_{\text{lum}} = \frac{2(\Delta I)}{I} = \frac{2(I_L - I_R)}{(I_L + I_R)} \quad (1)$$

$I_L$  and  $I_R$  refer, respectively, to the intensities of left and right circularly polarized emission,  $\Delta I$  is the differential emission of left and right circularly polarized light, and  $I$  is the mean light intensity. This was done at the two extrema found in the CPL spectra, and the  $g_{\text{lum}}$  values are found in Table I. It may be noted that the induced CPL is greater in the amine solvents than in the alcohol solvents, and this observation is in accord with stronger amine adducts being formed.

**Table I.** Comparison of the Luminescence Dissymmetry Factors Observed in the *R* Enantiomers of Various Chiral Solvents

| solvent                     | $g_{\text{lum}}$ (544 nm) | $g_{\text{lum}}$ (549 nm) |
|-----------------------------|---------------------------|---------------------------|
| $\alpha$ -phenethylamine    | -0.0283                   | +0.0325                   |
| 2-aminobutane               | -0.0134                   | +0.0143                   |
| 2-aminoheptane              | -0.0111                   | +0.0120                   |
| $\alpha$ -phenethyl alcohol | -0.0105                   | +0.00719                  |
| propylene glycol            | -0.00252                  | +0.00112                  |

A clear and detailed understanding of the CPL results is not possible at the present time, but the studies presently underway in this laboratory should provide additional insight into the nature of this problem. The present method appears to offer a simple and fairly convenient method to predict the absolute configuration of a substrate capable of forming an adduct with  $\text{Tb}(\text{dpm})_3$ , and is particularly suited to the study of amine solvents.

**Acknowledgments.** This work was supported by a Cottrell grant from the Research Corporation (No. 8926) and by the National Science Foundation (Grant CHE 78-03402).

## References and Notes

- (1) J. Dillon and K. Nakanishi, *J. Am. Chem. Soc.*, **97**, 5409,5417 (1975); the preceding communications are cited therein.
- (2) N. H. Anderson, B. J. Bottino, A. Moore, and J. R. Shaw, *J. Am. Chem. Soc.*, **96**, 604 (1974).
- (3) F. S. Richardson and J. P. Riehl, *Chem. Rev.*, **77**, 773 (1977).
- (4) H. G. Brittain and R. S. Richardson, *J. Am. Chem. Soc.*, **99**, 65 (1977).
- (5)  $\text{Tb}(\text{dpm})_3$  was prepared in the manner of K. J. Eisentraut and R. E. Sievers, *Inorg. Synth.*, **11**, 94 (1968). Chiral solvents were all obtained from Norse Laboratories.
- (6) The CPL spectrometer was constructed in this laboratory and is similar to the one previously described by C. K. Luk and F. S. Richardson, *J. Am. Chem. Soc.*, **97**, 6666 (1975). The luminescent spectra were recorded by exciting the solutions with the 365-nm output of a 200-W Hg-Xe arc lamp and recording the emission at  $180^\circ$  to the exciting beam. The emission was analyzed by a Spex 1870  $\frac{1}{2}$  meter grating monochromator (15-Å band pass) and detected by an EMI 9798B photomultiplier tube (S-20 response). Our optical modulator is a Model PEMFS-3 (Morvue Electronics).
- (7) (a) H. G. Brittain and F. S. Richardson, *J. Chem. Soc., Dalton Trans.*, 2253 (1976); (b) H. G. Brittain, *J. Am. Chem. Soc.*, **101**, 1733 (1979); (c) H. G. Brittain, *J. Chem. Soc., Dalton Trans.*, 1187 (1979).

Harry G. Brittain

Department of Chemistry, Seton Hall University  
South Orange, New Jersey 07079

Received October 11, 1979

## Orotidine 5'-Monophosphate Decarboxylase Inhibitors Formed by Spontaneous Reaction of Barbituric Acid and Ribose 5-Phosphate, a Surprising Reaction

Sir:

Many drugs used in the treatment of cancer and other proliferative disorders cause an inhibition of RNA and (or) DNA synthesis.<sup>1</sup> We report here determinations of the structures of a series of compounds which result from unusual spontaneous reactions between barbituric acid and D-ribose 5-phosphate in water. All of the products of this reaction thus far tested have been found to behave as potent competitive inhibitors of purified yeast orotidine 5'-monophosphate decarboxylase.<sup>2-4</sup> The decarboxylase catalyzes the final step in the enzymatic sequence for the de novo synthesis of uridine 5'-monophosphate which is eventually incorporated into nucleic acids via its triphosphate.

Barbituric acid (54.1 mg, 0.42 mmol) was incubated with 33.3 mg (0.11 mmol) of D-ribose 5-phosphate disodium salt in 3 mL of deionized water for 2 h at 37 °C, pH 5.5.<sup>2,5</sup> The reaction mixture was then chromatographed on a Sephadex G-10 column (3 × 18 cm) with water, the chromatograph being carried out in a 2 °C cold room to minimize decomposition of the labile product. Monitoring with UV at 260 nm and CD at 290 nm gave the base-line separated peak of product **1** and partly overlapping peaks of barbituric acid and ribose phosphate. The product fraction was lyophilized to afford 39 mg (87%) of practically pure adduct **1**; this was used as such for structural and inhibition studies since it was found that further handling only led to gradual conversion into other products (see below). Adduct **1** strongly and competitively