

MLCT excitation are due to the presence of lowest lying, substitution reactive, ligand field excited states, not MLCT states such as those which dominate the visible absorption spectrum.

The progression from relatively photoreactive complexes to unreactive complexes as a function of the MLCT energy occurs rapidly when  $\lambda_{\text{max}}(\text{CT})$  exceeds  $\sim 460$  nm but not instantaneously.<sup>11-13</sup> The observation of an intermediate  $\Phi_{\text{L}}$  value for the pyrazine complex ( $\lambda_{\text{max}}(\text{CT})$  472 nm) may have several explanations, one being that the lowest energy triplet state may have character and reactivity intermediate between the pure charge transfer and pure ligand field state owing to mixing of these two states when they are close in energy.

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(11) The lone exception to the relatively smooth progression of  $\Phi_{\text{L}}$  as a function of  $\lambda_{\text{max}}(\text{CT})$  is the nicotinamide complex, which displays an intermediate value for  $\Phi_{\text{L}}$  despite a  $\lambda_{\text{max}}(\text{CT})$  of 427 nm. However, it has been pointed out (ref 12) that these complexes may have several MLCT states of comparable energy, but the absorption band is especially sensitive to para substituents and much less to meta substituents. Consequently  $\lambda_{\text{max}}(\text{CT})$  may place the nicotinamide complex in an anomalous position, as the strongly delocalizing amide group in the meta site may lower a spectrally unobservable MLCT state to an energy comparable to the lowest ligand field state.

(12) (a) P. C. Ford, D. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968); (b) A. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).

(13) Irradiation of the substitution unreactive isonicotinamide and 4-acetylpyridine complexes with 405-nm light (corresponding to an absorption minimum in the spectra) shows quantum yields of  $(4 \pm 1) \times 10^{-3}$  mol/einstein for each. These values represent enhancements of about 1 order of magnitude over the  $\lambda_{\text{max}}(\text{CT})$  values but are still 1 order of magnitude below the reactivity of  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  at the same wavelength. This result indicates both the presence of a reactive excited state at higher energy (presumably LF in character) and that interconversion of upper to lower states though apparently efficient is not the only significant path of the reactive upper state(s).

(14) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1971-1976.

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## Metal Ion Probes of Molecular Geometry. II. A Direct Spectroscopic Determination of the Absolute Configuration of Hydroxyl Bearing Asymmetric Centers Based on the Shift Reagent, $\text{Eu}(\text{FOD})_3$ <sup>1</sup>

Sir:

Increasingly subtle probes of molecular geometry are required in order to define the configuration of complex natural products and to determine their conformation in solution. Thus far nmr and CD have been the major spectroscopic tools in such studies, and each can be used with metal ion probes by virtue of the magnetic or electronic properties of transition and lanthanide metals.<sup>2</sup> In the study of chiral molecules the circular dichroism induced in the electronic transitions of the metal offers another probe of degree of

(1) For part I of this series, see N. H. Andersen, B. J. Bottino, and S. E. Smith, *J. Chem. Soc., Chem. Commun.*, 1193 (1973). This work is taken in part from the Masters Thesis of B. J. B. (University of Washington, 1972).

(2) The application of lanthanide shift reagents (LSR) in nmr conformational studies is an example of the former.

association,<sup>3</sup> conformation, and (in the present case) absolute configuration.<sup>4</sup>

Present methods for determining the absolute configuration of a hydroxylated center typically<sup>5</sup> involve formation of diastereomeric derivatives followed by spectroscopic measurements<sup>6</sup> or indirect determination of  $\Delta\Delta G^\ddagger$  of diastereomeric transition states.<sup>7</sup> We wish to present a direct spectroscopic method based on the sign of the induced CD of the 525-nm transition of  $\text{Eu}(\text{FOD})_3$  on complexing ligands in which the donor is at a chiral center.

The common nmr shift reagents offer an ideal electrophilic component for complexes with chiral donors. The bulky dionato ligands associated with large paramagnetic shifts should also produce complexes of distinctly dissymmetric polarization for, as an example, ligand geometry I, (which corresponds to an S center in most cases) particularly when two such ligands are incorporated in the complex. With this in mind we have examined the sign of the CD induced at the 525-nm line of  $\text{Eu}(\text{FOD})_3$  during studies of LSR-substrate stoichiometry.<sup>3</sup> Studies of 2-alkanols, menthol, 2-arylcylohexanols,  $\alpha$ -phenethylamine, amphetamine, and a series of sesquiterpene-derived alcohols (II, III, IV, V, and VII) established that a correlation of sign and chirality at the donor-bearing carbon exists. The full results appear in the table. See paragraph at end of paper regarding supplementary material.

We consider this initial data sufficient to conclude that *ligand geometry I* (S, where a steric bulk sequence rule is employed) produces a positive CD for the 2:1 complex with  $\text{Eu}(\text{FOD})_3$ . Such a determination of configuration, in contrast to previous methods,<sup>5-7</sup> does not require derivatization and allows simple recovery of the alcohol tested.<sup>8</sup> Further, the method appears to be applicable to tertiary alcohols as well. Before proceeding with the analysis of the data and a consideration of the apparent exceptions, some warning concerning potential pitfalls in the application of the method will be discussed. First, the absolute values of  $[\theta]$  are small so that measurements require solutions

(3) This technique was used in our studies demonstrating that  $\text{Eu}(\text{FOD})_3$  gives octacoordinate complexes,  $(\text{ROH})_2\text{Eu}(\text{FOD})_3$ , with chiral alcohols when  $C_{\text{ROH}}/C_{\text{Eu}} > 2$ : ref 1.

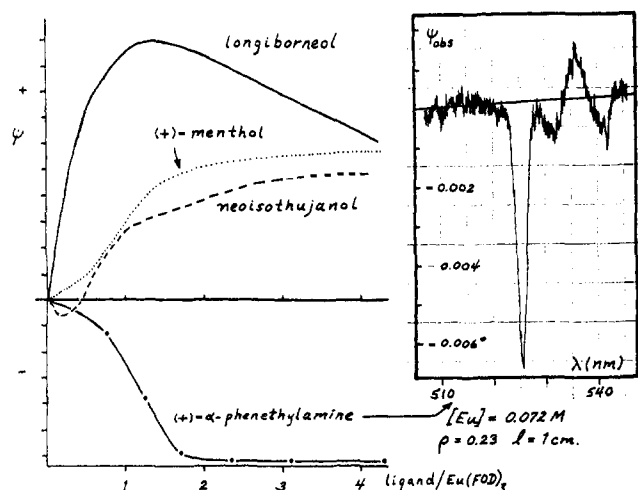
(4) LSR complexes of *vic*-glycols display CD couplets that can be used to assign chirality in much the same way as application of the aromatic exciton method: K. Nakanishi and J. Dillon, *J. Amer. Chem. Soc.*, **93**, 4058 (1971); N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972). The major bands in the uv region are employed for this assignment. Monohydroxylic substances also give CD couplets in this region (ca. 300 nm for Eu). The  $\Delta\Delta\epsilon$  values are too low for easy determination. Our use of LSR complexes is by analogy related to the benzoate rule.<sup>5</sup>

(5) Application of the benzoate rule still requires an examination of a derivative which must be obtained in pure state: J. H. Brewster, *Tetrahedron*, **13**, 106 (1961); *J. Amer. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959). See also the benzoate sector rule: N. Harada, M. Ohashi, and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 7349 (1968); N. Harada and K. Nakanishi, *ibid.*, **90**, 7351 (1968).

(6) Differences in <sup>19</sup>F shifts correlate with configuration of diastereomeric  $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetic esters (MTPA esters): (a) J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, **95**, 512 (1973); (b) G. R. Sullivan, J. A. Dale, and H. Mosher, *J. Org. Chem.*, **38**, 2143 (1973).

(7) The method of Horeau and its recent modifications: A. Horeau, *Tetrahedron Lett.*, 506 (1961); A. Horeau and H. B. Kagan, *Tetrahedron*, **20**, 2431 (1964); R. Weidmann and A. Horeau, *Tetrahedron Lett.*, 2979 (1973); C. J. W. Brooks and J. D. Gilbert, *J. Chem. Soc., Chem. Commun.*, 194 (1973).

(8) The alcohols are recovered from the  $\text{CCl}_4$  solution of the  $\text{Eu}(\text{FOD})_3$  by addition of 3 equiv (related to Eu) of *n*-hexylamine. The resulting mixture is applied to a short column of silica. Elution with benzene yields alcohol completely free of shift reagent by nmr.

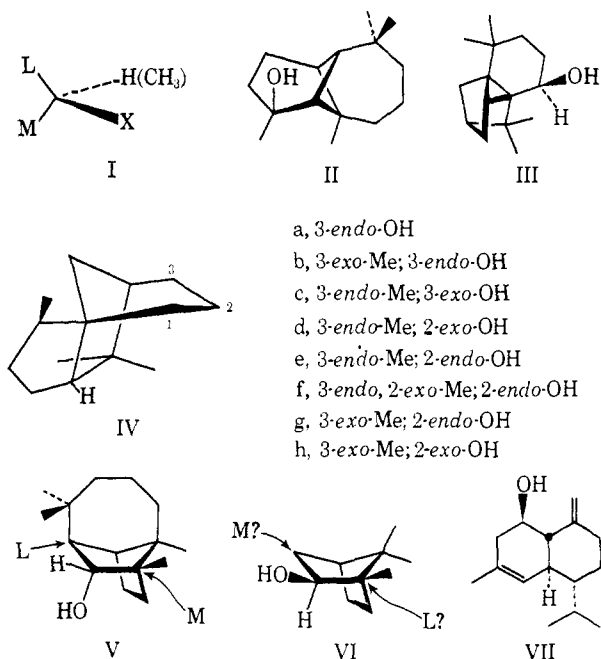


**Figure 1.** The induction of CD at ca. 525 nm on sequential addition of chiral donors to  $\text{Eu}(\text{FOD})_3$ . The solvent is  $\text{CCl}_4$ , except in the case of longiborneol ( $\text{CHCl}_3$ ). The different curves are not to scale. The insert shows an actual trace for the  $\text{Eu}(\text{FOD})_3$ - $\alpha$ -phenethylamine system. Menthol and phenethylamine illustrate cases in which the 1:1 complex has a weaker CD effect of the same sign as the 2:1 complex. The opposite is observed in the case of longiborneol.

0.04–0.17  $M$  in the limiting complex component. This generally implies the use of the less hindered, more soluble, FOD reagents. In addition the narrow lines (see Figure 1) can only be recorded accurately at slow sweeps (<2 nm/min). Second, additional CD bands are induced in this region; we take the largest one observed in the range 523.5–526.5 nm for this correlation. Third, detailed analysis of  $\psi$  induced vs. molar ratio plots (Figure 1) reveals the two stages of complexing<sup>9</sup> and that in certain cases the 1:1 complex can have a CD effect in the opposite sense of the 2:1 complex (for example neoisothujanol in the figure or entries 14 and 28 from the table). It is thus possible for a strong CD effect of a relatively stable 1:1 complex to mask the opposing effect of the 2:1 complex at all molar ratio values studied. In such cases a complete curve analysis is required. Entries 12 and 22, apparent exceptions to the sign rule, likely deviate due to this effect. Fourth, the method should not be applied to polyfunctional compounds since donor groups that are locally symmetric can induce CD effects due to more distant asymmetric centers.

At present, of 32 chiral alcohols examined only two (entries 4 and 8) do not display CD effects large enough for a dependable assignment, 24 correlate based on the normal sequence rule, two (entries 12, 22) appear exceptional due to an unusually strong CD associated with the 1:1 complex. The four remaining examples, the borneols (V, VI), illustrate the need for consideration of steric requirements rather than the Cahn–Ingold–Prelog sequence rule. In the case of the sesquiterpenes we assume that the bulky exo substituent increases the steric requirement of the tertiary carbon making it “larger than” the quaternary center; thus the large

(9) The determination of sequential binding constants and stoichiometry by the nmr method still appears to be a difficult task with a complicated four-parameter analysis required for each set of proton shifts; see B. L. Shapiro and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **94**, 8185 (1972). In contrast  $\psi_{\text{induced}}$  vs.  $\rho$  plots yield binding constants readily without computer curve fitting due to the expected large difference in  $[\theta]$  for complexes of different stoichiometry: N. H. Andersen and A. Moore, to be submitted for publication.



CD effects observed correlate with the sign rule. For the terpenes we find no obvious steric basis for reversing the normal sequence rule; borneol and isoborneol stand as exceptions to the rule.<sup>10</sup> The more limited data for amines suggest extension of the rule to the amino donor group.

With this method, shift reagent studies can now serve to define both relative and absolute configuration in natural product studies.

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**Supplementary Material Available.** A listing of induced CD for  $\text{Eu}(\text{FOD})_3$ -chiral ligand complexes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-603.

(10) It is worth noting that borneol is the only exception to the MTPA ester correlation.<sup>6b</sup>

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### Organocobalt Cluster Complexes. XIII. Nuclear Magnetic Resonance Spectroscopic Evidence Concerning the Stabilization of (Nonacarbonyltricobalt)carbon Substituted Carbonium Ions<sup>1</sup>

Sir:

We have reported recently<sup>2</sup> concerning the preparation, isolation and reactivity of the carbonium ion salts

(1) Part XII: D. Seyferth, J. E. Hallgren, R. J. Spohn, G. H. Williams, M. O. Nestle, and P. L. K. Hung, *J. Organometal. Chem.*, in press.

(2) D. Seyferth, G. H. Williams, and J. E. Hallgren, *J. Amer. Chem. Soc.*, **95**, 266 (1973).