

- (57) The computation was simplified by truncating the orbitals 33–36, which carry small contributions on the ligands, to that part which is on the metal alone. This truncated wave function was renormalized and then transformed to the local coordinate system ( $x', y', z'$ ) appropriate for the calculation of the overlap integrals.
- (58) M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 198, 1579 (1974); 2611 (1975); J. D. Wilkins and M. G. B. Drew, *J. Organomet. Chem.*, **69**, 111 (1974).
- (59) D. L. Kepert, *J. Chem. Soc., Dalton Trans.*, 617 (1974); 963 (1975); *Inorg. Chem.*, **13**, 2754, 2758 (1974); J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, 546 (1975).
- (60) M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1329 (1972); M. G. B. Drew and C. J. Rix, *J. Organomet. Chem.*, **102**, 467 (1975); A. Mercer and J. Trotter, *Can. J. Chem.*, **52**, 3331 (1974); J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, 546 (1975). Some related structures may be found in M. G. B. Drew, *ibid.*, 626 (1972), and A. P. Wolters, Ph.D. Thesis, University of Reading, 1975, cited in ref 5.
- (61) F. W. B. Einstein and J. S. Field, *J. Chem. Soc., Dalton Trans.*, 1628 (1975).
- (62) E. M. Cradwick and D. Hall, *J. Organomet. Chem.*, **25**, 91 (1970).
- (63) M. G. B. Drew and J. D. Wilkins, *J. Organomet. Chem.*, **69**, 271 (1974).
- (64) M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2664 (1973).
- (65) R. B. Van Dreef, J. J. Stezowski, and R. C. Fay, *J. Am. Chem. Soc.*, **93**, 2887 (1971); D. F. Lewis and R. C. Fay, *ibid.*, **96**, 3843 (1974).
- (66) J. J. Park, D. M. Collins, and L. J. Hoard, *J. Am. Chem. Soc.*, **92**, 3636 (1970).
- (67) T. F. Brennan and I. Bernal, *Inorg. Chim. Acta*, **7**, 283 (1973).
- (68) M. Motevalli and M. B. Hursthouse, unpublished work, cited in ref 5.
- (69) W. A. Dollase, *Acta Crystallogr., Sect. A*, **30**, 513 (1974).
- (70) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
- (71) H. Basch and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).
- (72) V. I. Baranovskii and A. B. Nikolskii, *Teor. Eksp. Khim.*, **3**, 527 (1967).

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## Pfeiffer Effect in Tetrahedral and Negatively Charged Octahedral Coordination Compounds

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The Pfeiffer effect can be utilized to study the optical rotatory and related properties of dissymmetric complexes which are difficult or impossible to resolve because of their optical lability. Most Pfeiffer-active systems are based upon optically active (racemic) six-coordinate complex cations. Examples of Pfeiffer-active systems based upon optically active (racemic) four-coordinate, tetrahedral complexes and negatively charged, octahedral complex anions are reported here, in which both optically active organic compounds and complex inorganic compounds are utilized as environment substances.

### Introduction

The Pfeiffer effect is the change in rotation of a solution of an optically active substance (called the "environment" substance) upon the addition of a racemic mixture of dissymmetric, optically labile, complex inorganic compounds.<sup>2</sup> Many Pfeiffer systems have been reported for cationic octahedral complexes in the presence of organic environments.<sup>3,4</sup> The only previously reported case of a tetrahedral complex exhibiting the Pfeiffer effect is for the bis(8-aminoquinoline)zinc(II) ion.<sup>5</sup> Another tetrahedral complex, bis(8-hydroxyquinoline-5-sulfonato)zinc(II) ion  $[\text{Zn}(\text{QS})_2]^{2-}$ , is reported herein to exhibit the Pfeiffer effect with certain environment substances.

The only negatively charged racemic complexes to show a Pfeiffer effect have been complexes with the oxalate dianion as a bidentate ligand.<sup>3,4,6</sup> The complex anion  $[\text{Ni}(\text{acac})_3]^-$  (acac = acetylacetonato anion) is negatively charged and does not have the oxalate ion as a ligand, and this racemic complex is also reported herein to exhibit the Pfeiffer effect.

The enantiomers of the  $[\text{Co}(\text{en})_3]^{3+}$  ion (en = ethylenediamine) have previously been used as Pfeiffer environments for 1,10-phenanthroline (*o*-phen) complexes and, specifically, for the racemic  $[\text{Zn}(\text{o-phen})_3]^{2+}$  ion.<sup>7</sup> Because of the infrequent use of inorganic complexes as Pfeiffer environments, the (+)<sub>589</sub> $[\text{Co}(\text{en})_3]^{3+}$  enantiomer also is shown herein to be usable as a Pfeiffer environment for the  $[\text{Ni}(\text{acac})_3]^-$  anion.

### Experimental Section

Optical rotations were determined on a Perkin-Elmer 141 photoelectric polarimeter at a wavelength of 589 nm and a temperature of 23 °C. All optical rotatory dispersion and circular dichroism spectra were determined on a Cary 60 recording spectropolarimeter at 23 °C. The nonpolarized absorption spectra were taken on a Cary 14 recording spectrophotometer at 23 °C.

(+)<sub>589</sub> $[\text{Co}(\text{en})_3]^{3+}$ ·H<sub>2</sub>O was prepared and resolved according to methods reported in the literature.<sup>8,9</sup>

The zinc complex  $\text{H}_2[\text{Zn}(\text{QS})_2]$  (QS = 8-hydroxyquinoline-5-sulfonate) was prepared according to the method of Liu and Bailar.<sup>10</sup> The analyses of the complex did not agree with the empirical formula, so a purification procedure was developed. This procedure was to dissolve 10 g of the complex in 200 ml of water and then filter the undissolved material. The filtrate was then made acidic by adding hydrochloric acid until the pH of the filtrate was approximately 3.5. The analyses of the crystals thus obtained were in accord with the empirical formula.

The synthesis of the  $\text{Na}[\text{Ni}(\text{acac})_3]$  complex was first reported by Dwyer and Sargeson.<sup>11</sup> This complex was obtained from Mr. John Klein and Dr. Richard Lintvedt of Wayne State University and was purified according to a variation of a method described by Klein.<sup>12</sup> The complex (5.0 g) was dissolved in 250 ml of water and vigorously stirred for 1 h. It was then filtered and 750 ml of methanol was added to the filtrate. The solution was left to stand overnight and the  $\text{Na}[\text{Ni}(\text{acac})_3]$  precipitate was filtered and washed with methanol and then with ether. It was dried at room temperature over sulfuric acid. This purification separates the inner complex  $[\text{Ni}(\text{acac})_2]$  from  $\text{Na}[\text{Ni}(\text{acac})_3]$ , and the analysis of the complex agreed with the empirical formula.

All solutions used in the Pfeiffer systems were aqueous, and these systems were prepared by mixing an aliquot of a stock solution of the environment substance with an aliquot of the stock solution of the metal complexes. They were then diluted to the appropriate volume.

Aqueous solutions of *d*-cinchonine hydrochloride and *l*-brucine hydrochloride were prepared from *d*-cinchonine and *l*-brucine by adding hydrochloric acid dropwise until the *d*-cinchonine or *l*-brucine dissolved (ca. 1.5 mol of HCl/mol of alkaloid). The pH of these solutions never went below 3.5.

### Results and Discussion

**The  $[\text{Zn}(\text{QS})_2]^{2-}$  Systems.** There is a significant difference between the absorption spectrum of the  $[\text{Zn}(\text{QS})_2]^{2-}$  anion and that of the ligand,  $\text{QS}^{2-}$  (Figure 1). The doublets of the  $\text{QS}^{2-}$  anion at 340 and 250 nm converge to singlet peaks at 365 and 255 nm in the spectrum of the complex  $[\text{Zn}(\text{QS})_2]^{2-}$ . The

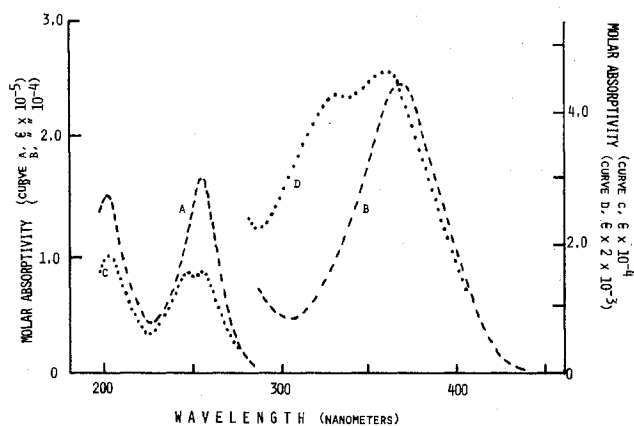


Figure 1. Absorption spectra:  $[\text{Zn}(\text{QS})_2]^{2-}$  (QS = 8-hydroxyquinoline-5-sulfonate), A and B;  $\text{QS}^{2-}$ , C and D.

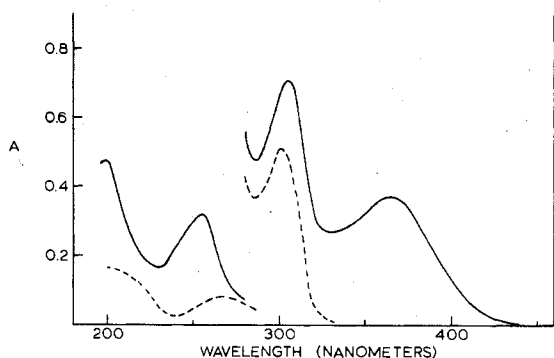


Figure 2. Absorption spectra: 0.6 mM  $[\text{Zn}(\text{QS})_2]^{2-}$  in the presence of 0.15 mM *l*-brucine hydrochloride, —; 0.15 mM *l*-brucine hydrochloride, - - -. Cell lengths: 0.5-cm cell, from 450 to 380 nm; 0.05-cm cell, from 380 to 200 nm.

differences between the spectrum of the ligand anion,  $\text{QS}^{2-}$ , and the complex,  $[\text{Zn}(\text{QS})_2]^{2-}$ , provide verification that the complex has formed.

There is a change in rotation of the aqueous solution of *l*-brucine hydrochloride when the complex  $[\text{Zn}(\text{QS})_2]^{2-}$  is added, which was determined to be due to an equilibrium shift between the enantiomers of the racemic complex and not to "induced" optical activity (outer-sphere complexation) or to a chemical reaction between the complex and environment. This was deduced by comparing the absorption spectrum of the complex with that of the complex in the presence of *l*-brucine hydrochloride. The absorption spectrum of  $[\text{Zn}(\text{QS})_2]^{2-}$  is quite distinguishable in the presence of *l*-brucine hydrochloride, and the two singlet peaks of  $[\text{Zn}(\text{QS})_2]^{2-}$  at 365 and 255 nm are still observable at these wavelengths (Figure 2). Since the absorption spectrum of  $[\text{Zn}(\text{QS})_2]^{2-}$  shows no noticeable change when *l*-brucine hydrochloride is added to the complex, it is concluded that there is no chemical reaction between the complex and the environment substance and that there is no noticeable effect of outer-sphere complexation between them.

The circular dichroism (CD) and optical rotatory dispersion (ORD) curves were determined for the mixture of  $[\text{Zn}(\text{QS})_2]^{2-}$  and *l*-brucine hydrochloride (Figure 3). Two CD peaks were observed at 365 and 260 nm, which coincide with the two absorption peaks of the  $[\text{Zn}(\text{QS})_2]^{2-}$  complex ion. The ORD curve similarly possesses two Cotton effect curves for the two absorption peaks of the  $[\text{Zn}(\text{QS})_2]^{2-}$  complex ion. These peaks were not present before addition of the brucine hydrochloride to the solution of the zinc complex.

From the absorption, CD, and ORD spectra it is concluded that the tetrahedral complex  $[\text{Zn}(\text{QS})_2]^{2-}$  exhibits the Pfeiffer effect in the presence of *l*-brucine hydrochloride.

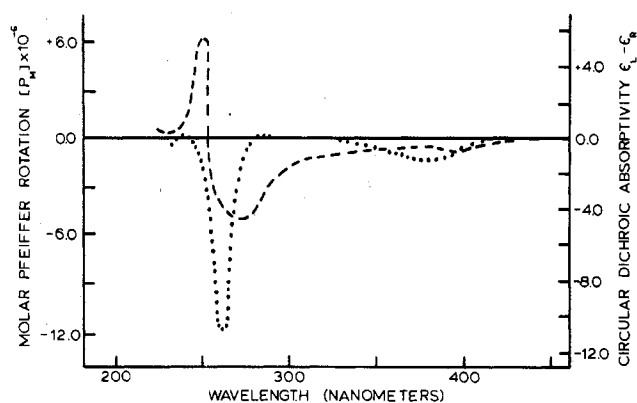


Figure 3. Circular dichroism (····) and Pfeiffer rotatory dispersion (- - -) of  $[\text{Zn}(\text{QS})_2]^{2-}$  in the presence of *l*-brucine hydrochloride.

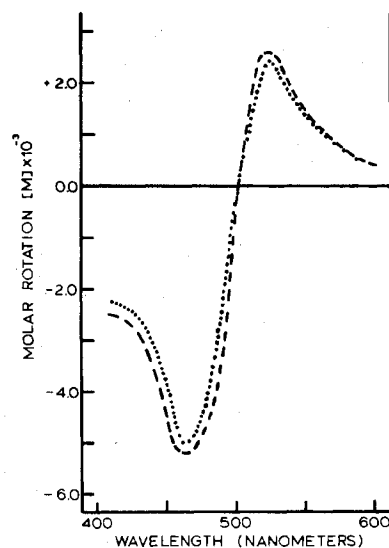
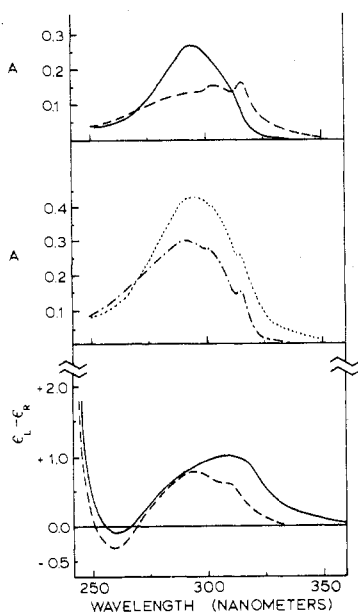


Figure 4. Optical rotation of the  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  ion (- - -) and of the  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  ion in the presence of  $[\text{Zn}(\text{QS})_2]^{2-}$  (····).

**The  $[\text{Zn}(\text{QS})_2]^{2-}$  System with  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$ .** The  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  enantiomer was used as a Pfeiffer environment substance in an attempt to demonstrate the Pfeiffer effect for the  $[\text{Zn}(\text{QS})_2]^{2-}$  ion. Even though the cobalt complex is of opposite charge to the zinc complex, no apparent Pfeiffer effect was observed. There is a change in rotation when the tetrahedral complex  $[\text{Zn}(\text{QS})_2]^{2-}$  is added to the  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  ion, but, upon close inspection, the change in rotation was observed to be due to a change in rotation of the optically active enantiomer,  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$ , itself. The ORD curves of  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  and  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  in the presence of  $[\text{Zn}(\text{QS})_2]^{2-}$  are given in Figure 4. Upon close inspection of these two ORD curves, it can be seen that the change in rotation when  $[\text{Zn}(\text{QS})_2]^{2-}$  is added to  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  is due to a decrease in the magnitude of the rotation of the  $[\text{Co}(\text{en})_3]^{3+}$  cation and not to a Pfeiffer effect. The Cotton effects of both ORD curves cross the zero line at the same wavelength, and the change in the ORD curve for  $(+)\text{}_{589}[\text{Co}(\text{en})_3]^{3+}$  when  $[\text{Zn}(\text{QS})_2]^{2-}$  is added is a symmetrical change. If a Pfeiffer effect had occurred, the additional optical activity due to the increased concentration of one enantiomer of the zinc complex would have produced an unsymmetrical change in the ORD curve of the cobalt complex. This observed slight change in optical rotation of the cobalt complex is probably due to ionic association between the racemate and the environment substance. The ORD of the environment substance is therefore affected, but there is no direct contribution from the racemate to the ORD spectrum because



**Figure 5.** Absorption spectra of 3 mM *d*-cinchonine hydrochloride (—), 1 mM  $[\text{Ni}(\text{acac})_3]^-$  ion (---), and 3 mM *d*-cinchonine hydrochloride in the presence of 1 mM  $[\text{Ni}(\text{acac})_3]^-$  ion (···) and the sum of the absorption spectra of 3 mM *d*-cinchonine hydrochloride plus 1 mM  $[\text{Ni}(\text{acac})_3]^-$  ion (-·-·). Circular dichroism of 6 mM *d*-cinchonine hydrochloride (—) and of 6 mM *d*-cinchonine hydrochloride in the presence of  $[\text{Ni}(\text{acac})_3]^-$  ion (---).

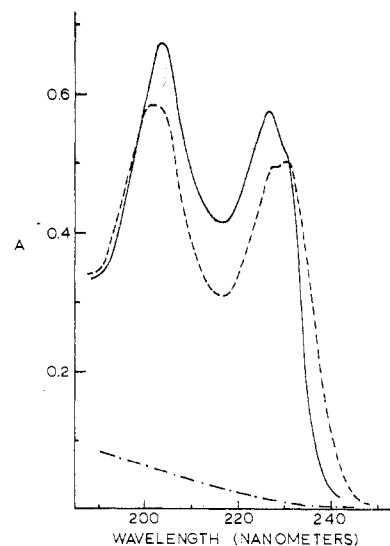
there has not been a shift in its enantiomeric equilibrium. This phenomenon is currently the subject of another investigation.

It has been shown that the tetrahedral complex  $[\text{Zn}(\text{QS})_2]^{2-}$  does exhibit the Pfeiffer effect with an optically active organic compound, *l*-brucine hydrochloride, but there is no observable Pfeiffer effect when the environment substance is the optically active inorganic complex  $(+)\text{Co}(\text{en})_3^{3+}$ .

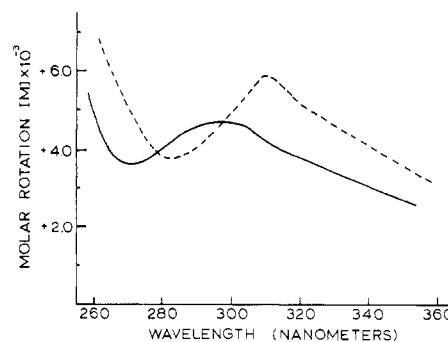
**The  $[\text{Ni}(\text{acac})_3]^-$  Systems.** The racemic complex  $[\text{Ni}(\text{acac})_3]^-$  was used in a Pfeiffer system with the environment substance, *d*-CinHCl (*d*-CinHCl =  $(+)\text{Cin}$ -cinchonine hydrochloride). The absorption spectra of  $\text{Na}[\text{Ni}(\text{acac})_3]$ , *d*-CinHCl, and  $\text{Na}[\text{Ni}(\text{acac})_3]$  in the presence of *d*-CinHCl were taken to determine if there is any interaction of the complex with the environment substance. From 700 to 530 nm there is a broad, low-intensity absorption band for the  $\text{Na}[\text{Ni}(\text{acac})_3]$  and there is no appreciable change in this absorption band when *d*-CinHCl is in the presence of  $\text{Na}[\text{Ni}(\text{acac})_3]$ .

If there is no interaction between  $\text{Na}[\text{Ni}(\text{acac})_3]$  and *d*-CinHCl, the absorption spectrum of  $\text{Na}[\text{Ni}(\text{acac})_3]$  in the presence of *d*-CinHCl should be identical with the absorption spectrum of  $\text{Na}[\text{Ni}(\text{acac})_3]$  added to the absorption spectrum of *d*-CinHCl. However, this is not the case in the wavelength region from 350 to 200 nm where both  $\text{Na}[\text{Ni}(\text{acac})_3]$  and *d*-CinHCl absorb (Figures 5 and 6). In the region from 350 to 275 nm, the absorption of  $\text{Na}[\text{Ni}(\text{acac})_3]$  together with that for *d*-CinHCl in the Pfeiffer system is much less than the sum of the separate absorptions of  $\text{Na}[\text{Ni}(\text{acac})_3]$  and *d*-CinHCl, but there is no shift in the absorption peaks (Figure 5). The *d*-CinHCl band at 240 nm becomes a more pronounced doublet and is shifted to shorter wavelengths, and the band at 200 nm is somewhat broadened and shifted to shorter wavelengths when  $\text{Na}[\text{Ni}(\text{acac})_3]$  is present. The intensity of these two absorption bands is lowered by the presence of  $\text{Na}[\text{Ni}(\text{acac})_3]$  which is opposite to the result found in the region from 350 to 275 nm.

There is a symmetrical decrease in rotation from 600 to 350 nm for *d*-CinHCl upon the addition of  $\text{Na}[\text{Ni}(\text{acac})_3]$ . There is likewise a decrease in rotation at shorter wavelengths, but there is also a shift in the weak Cotton effect curve at about



**Figure 6.** Absorption spectra of 0.5 mM  $[\text{Ni}(\text{acac})_3]^-$  ion in the presence of 1.5 mM *d*-cinchonine hydrochloride (—), of 1.5 mM *d*-cinchonine hydrochloride (---), and of 0.5 mM  $[\text{Ni}(\text{acac})_3]^-$  ion (-·-·). Cell length for all absorption spectra is 0.1 mm.



**Figure 7.** Optical rotation of 6 mM *d*-cinchonine hydrochloride (---) and 6 mM *d*-cinchonine hydrochloride in the presence of 2 mM  $[\text{Ni}(\text{acac})_3]^-$  ion (—).

300 nm to shorter wavelengths. The peak and trough for *d*-CinHCl are at 310 and 285 nm, while the peak and trough for *d*-CinHCl with  $\text{Na}[\text{Ni}(\text{acac})_3]$  are at 300 and 270 nm, respectively (Figure 7).

Below 260 nm, the absorption of *d*-CinHCl is too intense to obtain an ORD spectrum. Since there is no absorption peak for  $\text{Na}[\text{Ni}(\text{acac})_3]$  from 260 to 200 nm, a Cotton effect is not expected for  $\text{Na}[\text{Ni}(\text{acac})_3]$  in this region.

The broad, positive, circular dichroic band at 310 nm for *d*-CinHCl is split into two distinct peaks and is decreased in overall intensity when  $\text{Na}[\text{Ni}(\text{acac})_3]$  is present (Figure 5). Since the absorption spectrum of  $\text{Na}[\text{Ni}(\text{acac})_3]$  in the presence of *d*-CinHCl is less than the sum of the absorption spectra of *d*-CinHCl and  $\text{Na}[\text{Ni}(\text{acac})_3]$ , it is unlikely that the doublet CD peak at 300 nm is due solely to the enrichment of one of the enantiomers of  $\text{Na}[\text{Ni}(\text{acac})_3]$ . This is supported by the fact that there are no other characteristic Cotton effect curves in the ORD (or CD spectra) for  $\text{Na}[\text{Ni}(\text{acac})_3]$  when it is in the presence of *d*-CinHCl.

From all of the above and from a careful analysis of the absorption, CD, and ORD spectra of *d*-CinHCl and  $\text{Na}[\text{Ni}(\text{acac})_3]$  in the presence of *d*-CinHCl, it is concluded, therefore, that a Pfeiffer effect arising from a shift in the enantiomeric equilibrium does not occur in this system but that the observed change in rotation is due to outer-sphere association between *d*-CinHCl and  $\text{Na}[\text{Ni}(\text{acac})_3]$ .

The  $\text{Na}[\text{Ni}(\text{acac})_3]$  complex is sensitive to low pH, and the pH of *d*-CinHCl in the solutions studied was approximately

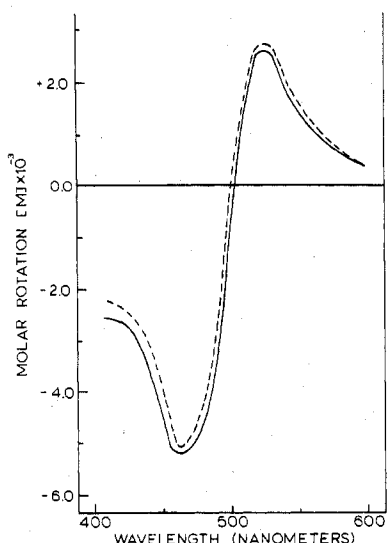


Figure 8. Optical rotation of 30 mM (+)<sub>589</sub>[Co(en)<sub>3</sub>]<sup>3+</sup> ion (—) and of 30 mM (+)<sub>589</sub>[Co(en)<sub>3</sub>]<sup>3+</sup> ion in the presence of 10 mM racemic [Ni(acac)<sub>3</sub>]<sup>-</sup> ion (- - -).

4.3. However, the absorption spectrum of Na[Ni(acac)<sub>3</sub>] in solution at a pH of 4.3 is identical with that obtained in neutral solution, so the observed spectral changes are not a result of the slightly acidic pH of the solution.

The [Ni(acac)<sub>3</sub>]<sup>-</sup> System with (+)<sub>D</sub>[Co(en)<sub>3</sub>]<sup>3+</sup>. When the environment substance, (+)<sub>589</sub>[Co(en)<sub>3</sub>]<sup>3+</sup>, is used with Na-

[Ni(acac)<sub>3</sub>] as a Pfeiffer effect system, the ORD curve of the (+)<sub>589</sub>[Co(en)<sub>3</sub>]<sup>3+</sup> complex shows a nonsymmetrical change, and the crossover point for the Cotton effect is not the same in both cases (Figure 8). Therefore, it is proposed that this is a true Pfeiffer effect system utilizing one enantiomer of a complex ion as an environment substance, which results in the enrichment of one enantiomer of an octahedral, six-coordinate complex anion.<sup>13</sup>

**Acknowledgment.** The authors wish to express their appreciation to the National Science Foundation for a research grant which contributed significantly to the progress of this investigation.

**Registry No.** [Zn(QS)<sub>2</sub>]<sup>2-</sup>, 41133-46-4; (+)<sub>589</sub>[Co(en)<sub>3</sub>]<sup>3+</sup>, 27228-84-8; *d*-CinHCl, 24302-67-8; [Ni(acac)<sub>3</sub>]<sup>-</sup>, 31147-73-6; *l*-brucine hydrochloride, 5786-96-9.

#### References and Notes

- (1) (a) Wayne State University. (b) Centrul de Chimie.
- (2) P. Pfeiffer and K. Quehl, *Ber. Dtsch. Chem. Ges. A*, **64**, 2667 (1931); **65** 560 (1932).
- (3) S. Kirschner and N. Ahmad, *Coord. Chem., Proc. John C. Bailar, Jr., Symp.*, **42** (1969).
- (4) L. A. Meyers, Ph.D. Dissertation, University of Minnesota, 1969.
- (5) V. J. Landis, Ph.D. Dissertation, University of Minnesota, 1957.
- (6) N. Davies and F. Dwyer, *Trans. Faraday Soc.*, **50**, 24 (1953).
- (7) P. E. R. Nordquist, Jr., Ph.D. Dissertation, University of Minnesota, 1964.
- (8) J. B. Work, *Inorg. Synth.*, **2**, 221 (1946).
- (9) J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *ibid.*, **6**, 183 (1960).
- (10) C. F. Liu and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 5432 (1951).
- (11) F. P. Dwyer and A. M. Sargeson, *J. Proc. R. Soc. N.S.W.*, **90**, 29 (1956).
- (12) J. Klein, Masters Thesis, Wayne State University, 1970.
- (13) P. E. Schipper, *Inorg. Chim. Acta*, **12**, 199 (1975).

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## Preparation of the Paramagnetic Alkyls Cp<sub>2</sub>NbMe<sub>2</sub> and (MeCp)<sub>2</sub>TaMe<sub>2</sub> and Some Six- and Eight-Coordinate Phosphine Derivatives of Nb(IV)

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Reactions of Cp<sub>2</sub>NbCl<sub>2</sub> and (MeCp)<sub>2</sub>TaBr<sub>2</sub> (Cp = π-C<sub>5</sub>H<sub>5</sub> and MeCp = π-C<sub>5</sub>H<sub>4</sub>Me) with MeLi in ether give the paramagnetic alkyls Cp<sub>2</sub>NbMe<sub>2</sub> and (MeCp)<sub>2</sub>TaMe<sub>2</sub> as red crystalline solids. Magnetic moments and ESR spectral data are given. The niobium complex violently decomposes at ~130 °C liberating 1.3–1.5 mol of methane/mol of complex. Convenient preparations of NbCl<sub>4</sub> and NbCl<sub>4</sub>(THF)<sub>2</sub> (THF = tetrahydrofuran) are described. Reactions of the tetrahydrofuran complex with triethyl- and trimethylphosphine give NbCl<sub>4</sub>L<sub>2</sub>. Using chelating phosphines the eight-coordinate complexes NbCl<sub>4</sub>(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (R = Me, Et) are isolated as magnetically dilute, blue crystalline solids.

### Introduction

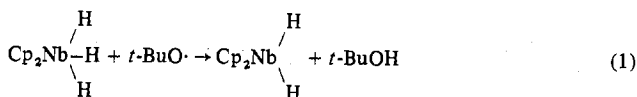
The tetrahalides of niobium in the +4 oxidation state are polymeric, insoluble, diamagnetic, and rather unreactive materials. Nevertheless, a number of adducts of NbX<sub>4</sub> have been isolated<sup>1,2</sup> either by the slow reaction of ligands with the tetrahalides or by reduction of the pentahalides in the presence of excess ligand. We were interested in finding a more convenient route to niobium(IV) complexes and in this paper describe a good preparation of NbCl<sub>4</sub>(THF)<sub>2</sub> and some phosphine derivatives of the types NbCl<sub>4</sub>L<sub>2</sub> (L = PMe<sub>3</sub>, PEt<sub>3</sub>) and NbCl<sub>4</sub>L<sub>4</sub> (where L<sub>2</sub> = R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>, R = Me, Et).

Few organometallic derivatives of niobium(IV) and tantalum(IV) have been prepared. Seigert and deLiefde Meijer<sup>3</sup> reported the preparation of Cp<sub>2</sub>NbPh<sub>2</sub> and recently Klaus<sup>4</sup> has reported the preparation of Nb(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub> from NbCl<sub>5</sub> and Mg(CH<sub>2</sub>Ph)<sub>2</sub>. Preparations of the two paramagnetic com-

plexes Cp<sub>2</sub>NbMe<sub>2</sub> and (MeCp)<sub>2</sub>TaMe<sub>2</sub> are now reported.

### Results and Discussion

**A. Some Organometallic Chemistry Of Nb(IV) and Ta(IV).** In a recent ESR study<sup>5</sup> we observed the formation of the paramagnetic dihydride Cp<sub>2</sub>NbH<sub>2</sub> by the reaction of Cp<sub>2</sub>NbH<sub>3</sub> with photochemically generated *tert*-butoxy radicals according to eq 1. The complex exhibited a beautiful ESR spectrum



in solution at -80 °C. The resonance consisted of ten lines due to coupling of the electron with <sup>93</sup>Nb (*I* = 9/2, 100% abundance) and each of these lines was split into a triplet due to hyperfine coupling of the electron with two hydrogen atoms.