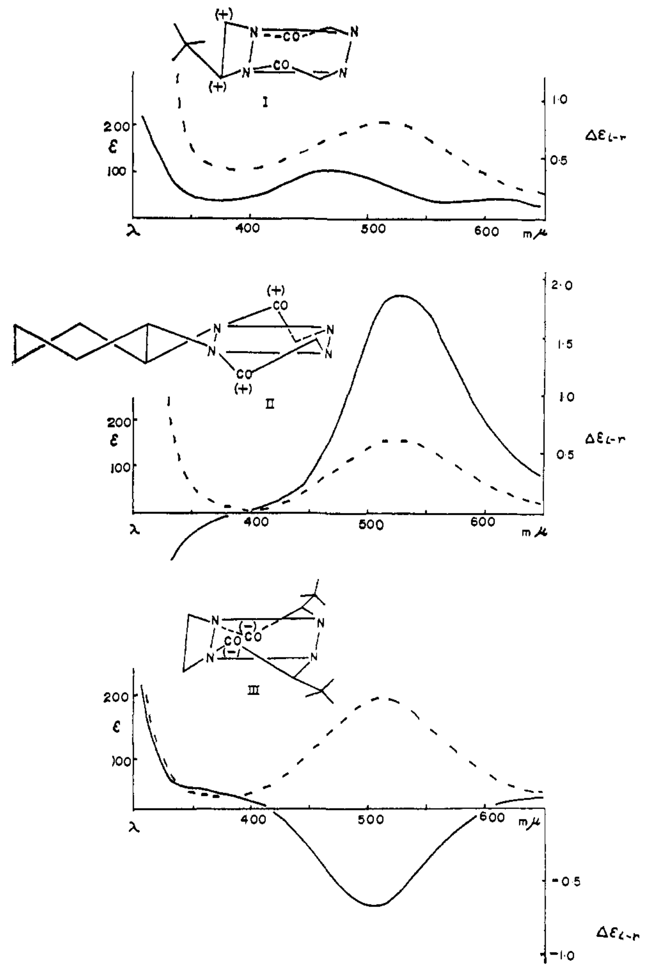
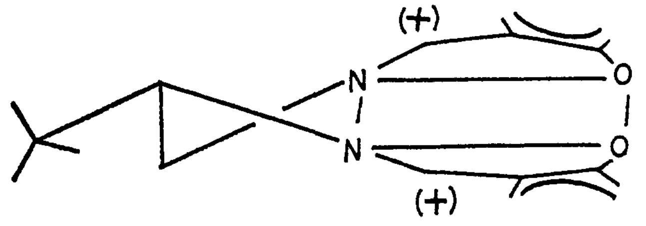
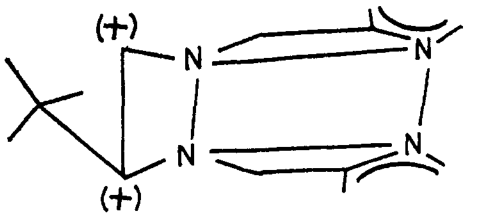




IV



V

Figure 1. Absorption (- - - -) and CD (———) spectra for I, N,N′-bisglycyl-(+)-propane-1,2-diiminecopper(II), II, N,N′-bisglycyl-(−)-cyclohexane-1,2-*trans*-diiminecopper(II), III, N,N′-bis-(+)-alanylethane-1,2-diiminecopper(II). Structures I–III and IV and V (text) show suggested significant octant contributions. CD spectra were measured using a Jasco Model ORD/UV/5 with a cell length of 10 mm at an ambient temperature of 28 ± 1°. The instrument was standardized by means of camphorsulfonic acid. Aqueous solutions were 10^{-1} *M* in NaOH, 10^{-2} *M* in ligand, and 10^{-3} *M* in $CuSO_4$.

increasing contribution to the octants around Cu(II), the CD amplitude of the complexes should be in the order I < III < II. We observe a pronounced positive Cotton effect at 525 mμ, the absorption maximum of II–Cu(II), and a smaller negative Cotton effect at 500 mμ, with an absorption maximum at 510 mμ, for III–Cu(II). Bis-(+)-alaninatocopper(II) has a predominantly negative Cotton effect in this region.[11] The spectrum of I–Cu(II) shows a much smaller positive Cotton effect at about 480 mμ, with an absorption maximum at 510 mμ. A strong positive Cotton effect in bissalicylaldehyde-(−)-propane-1,2-diiminecopper-(II)[12] (IV) may be attributed to the larger terminal and planar chelate rings, these necessarily causing the C=N's to lie in positive octants. This is in contrast to the monohydrate's crystal structure[13] where the orientation is reversed, attributed to the exigencies of packing the methyl substituent and a neighboring water molecule. We would predict anomalous rotatory dispersion to be almost entirely absent in the copper chromophore of N,N′-bis(picolinoyl)propane-1,2-diiminecopper(II)[14] (V), since here the terminal chelate rings should be essentially planar, the residual asymmetry being wholly with the bridging ring, more restricted than in I, and a small positive Cotton effect resulting from the *S* ligand.

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The Application of the Pfeiffer Effect to the Resolution of Dissymmetric Coordination Compounds

Sir:

The Pfeiffer effect[1,2] is the change in optical rotation of an optically active substance (hereinafter called the "environment" compound) in solution upon the addition of a racemic mixture of certain other optically active compounds (until now, complex inorganic compounds). In 1954 Gyarfas and Dwyer[3] postulated that the effect is due to a change in the displacement of an equilibrium between the *dextro* and *levo* enantiomers (in favor of one of them) of an optically labile, racemic complex (where the equilibrium constant is 1) in the presence of an optically active environment.

In support of this idea, Kirschner and coworkers[4–6] have described the increase in Pfeiffer rotation observed for the tris(*o*-phenanthroline) complexes of zinc(II), cadmium(II), and mercury(II), respectively—a series in which the equilibrium constants decrease, which may be indicative of the relative optical lability of these

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Table I. Resolution *via* the Pfeiffer Effect

Initial racemic complex	Environment compd	Pfeiffer rotation (P_{obsd}),[a] deg	Concn of complex,[b] M	Rotation[b] α_{obsd}	$[M]$,[a] deg	% resolution
$[Ni(o\text{-phen})_3]^{2+}$ (0.05 M)	*l*-Malic acid (0.2 M)	2.345	0.048	−1.599	334.2	2.8
$[Ni(dipy)_3]^{2+}$ (0.05 M)	*l*-Malic acid (0.2 M)	0.396	0.048	−0.151	31.46	1.5

[a] 25°, 589 mμ. [b] After resolution.

complexes as well. However, a better test would be to "freeze" the supposedly displaced equilibrium and then study the racemization of the enantiomer trapped in greater concentration. Since the alteration of the equilibrium does not give any indication of the rate at which the interconversion occurs, an attempt was made to find complexes which exhibit the effect but which take some time to achieve the maximum Pfeiffer rotation. The tris(*o*-phenanthroline) and tris(2,2′-dipyridyl) complexes of nickel(II) fall into this category. Dwyer indicated that since the former takes several days to achieve the maximum Pfeiffer rotation, it should be capable of being resolved by conventional means, and this is correct.[7,8] In addition, although the tris(2,2′-dipyridyl) complex of nickel(II) takes only 20 min to achieve its maximum Pfeiffer rotation, it is also capable of being resolved by conventional means.[9]

Most systems which exhibit the Pfeiffer effect attain the maximum Pfeiffer rotation practically instantaneously, and it is interesting to note that none of the racemates of optically active complexes which exhibit an instantaneous Pfeiffer effect has yet been resolved.

In the present work the authors have succeeded in freezing out the nonequimolar mixture of enantiomers from the Pfeiffer-active systems composed initially of DL-$[Ni(o\text{-phen})_3]^{2+}$ (0.05 M) and *levo*-malic acid (0.2 M) in aqueous solution, in one case, and DL-$[Ni(dipy)_3]^{2+}$ (0.05 M) and *l*-malic acid (0.2 M) in the other. The removal of the displaced-equilibrium mixtures from the environment was achieved by precipitation of the complexes as the relatively insoluble perchlorates, by use of sodium perchlorate. The insoluble perchlorates were then redissolved by placing them (as aqueous suspensions) in contact with Amberlite IRA-400 anion-exchange resin in the chloride form. In each case the solution containing the soluble complex (as the chloride) was filtered and its rotation was read by means of a Perkin-Elmer Model 141 photoelectric polarimeter.

Table I lists the observed and Pfeiffer rotations. The observed Pfeiffer rotation is defined[4] as $P_{obsd} = \pm(\alpha_{e+c} - \alpha_e)$, where α_{e+c} is the observed rotation of the Pfeiffer-active system containing both the added racemic complex and the environment compound, α_e is the observed rotation of the environment compound in solution before addition of the racemic complex, and the symbol ± indicates that the sign to be placed in front of the parentheses while calculating the observed Pfeiffer rotation is the same as the sign of α_e.

Figure 1 is a comparison of the first-order racemization curves of the complexes which have been partially resolved by this Pfeiffer-effect technique with the racemization curves of the compounds resolved by conventional means. That these curves are identical provides strong support, in the authors' opinion, for the "equilibrium displacement" mechanism proposed by Gyarfas and Dwyer[3] for the occurrence of the Pfeiffer effect.

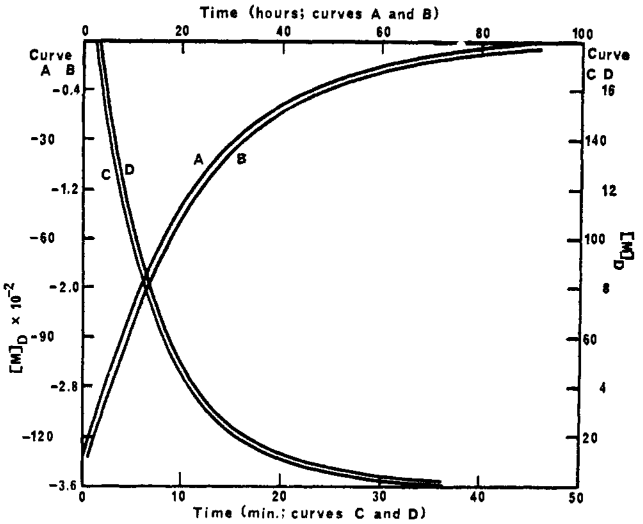

Figure 1. The racemizations in aqueous solution at 25° (1-dm cell) of (A) L-$[Ni(o\text{-phen})_3]^{2+}$ (0.001 M); (B) L-$[Ni(o\text{-phen})_3]^{2+}$ partially resolved by the Pfeiffer-effect technique (0.048 M); (C) L-$[Ni(dipy)_3]^{2+}$ (0.02 M); (D) L-$[Ni(dipy)_3]^{2+}$ partially resolved by the Pfeiffer-effect technique (0.048 M).

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Mono- and Dialkylation of Ethyl Dihaloacetates by Reaction with Organoboranes under the Influence of Potassium *t*-Butoxide. Convenient Procedures for the Conversion of Olefins into the α-Haloalkanoic or Dialkylacetic Acid Esters *via* Hydroboration

Sir:

We wish to report that the facile reaction of organoboranes with ethyl bromoacetate under the influence of potassium *t*-butoxide,[1] which provides a remarkably

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