frared work in that the metal-bonded olefin group has the nature of a perturbed CC double bond rather than that of a CC single bond.[12]

The observed frequency lowerings for coordination of the olefinic group of 2-allylpyridine to Cu(I), Pt(II), and Ag(I) are 87, 187, and 58 cm.$^{-1}$, respectively. These shifts are in agreement with other infrared studies of metal olefin complexes. A frequency lowering of 95 cm.$^{-1}$ has been observed for the 1,5-hexadiene complex of CuCl.[13] For norbornadiene complexes of Pt(II) bands at *ca.* 1440 cm.$^{-1}$ have been assigned to the C=C stretching vibration arising from an olefinic group coordinated to Pt(II).[14] The C=C stretching band at 1653 cm.$^{-1}$ for free cyclohexene is lowered to 1582 cm.$^{-1}$ by complex formation to $AgClO_4$.[15] Powell and Sheppard have suggested that the amount of lowering in the C=C stretching mode is proportional to the degree of olefin coordination to the metal.[11] The present infrared study of 2-allylpyridine complexes would indicate, therefore, that the metal–olefin bonding strength increases in the order $Ag(I) < Cu(I) < Pt(II)$.

The strong band at 993 cm.$^{1-}$ for 2-allylpyridine probably arises from both a vinyl out-of-plane CH deformation as well as from the pyridyl ring breathing vibration. In the metal complexes the ring breathing mode is separated from the olefinic deformation and is presumed to shift to higher frequencies as has been observed for metal–pyridine complexes.[10,16] The elevation to higher frequencies in the ring breathing vibration of pyridine complexes has been used to estimate the electron-attracting power of various acceptor molecules, such as Lewis acids.[16] As can be seen in Fig. 1 the spectral pattern of the 2-allylpyridine complexes in this region is too complicated to permit location of the ring breathing band. However, with the exception of the medium intensity band at 992 cm.$^{-1}$ for the Pt(II) complex, the bands in this pattern which appear to be associated with the 993 cm.$^{-1}$ band of the free ligand are found at higher frequencies.

The CH out-of-plane bending vibration of 2-allylpyridine at 756 cm.$^{-1}$ is also shifted to higher frequencies upon complexation. The increase is greatest for $AgNO_3$ (28 cm.$^{-1}$), less so for $PtCl_2$ (17 cm.$^{-1}$), and least for CuCl (11 cm.$^{-1}$). For pyridine complexes increasing frequency of the corresponding CH out-of-plane bending vibration has been associated with increasing N–M bond strength.[17]

The infrared investigation, along with the elementary analyses of the complexes, supports the conclusion that both the olefinic group and the pyridyl nitrogen of 2-allylpyridine are bonded to the metal atoms in the 1:1 complexes with CuCl, $PtCl_2$, and $AgNO_3$. Sublimation of the Pt(II) complex and its molecular weight suggest a monomeric form in which 2-allylpyridine functions as a bidentate ligand.

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Circular Dichroism of Coordination Compounds. II. Some Metal Complexes of 2,2'-Dipyridyl and 1,10-Phenanthroline[1]

By JINSAI HIDAKA and BODIE E. DOUGLAS

Received March 9, 1964

The circular dichroism (CD) and absorption data for the visible and ultraviolet regions are reported for the ions $[Fe(dipy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$, $[Ni(dipy)_3]^{2+}$, $[Ni(phen)_3]^{2+}$, and $[Co(en)_2phen]^{3+}$. The CD bands of these iron(II) complexes in the visible region show much higher intensities than those of most other d^6 metal ion complexes and presumably are caused by charge-transfer processes. The CD curves of $[Co(en)_2phen]^{3+}$ and the nickel(II) complexes are of normal intensity for d–d transitions. The CD bands in the ultraviolet region are attributed to ligand transitions. The great similarity among the very intense CD bands in this region permits the configuration of the complexes to be related.

Introduction

Recently, McCaffery and Mason[2] reported the circular dichroism (CD) curve of $[Ru(phen)_3]^{2+}$ and used the sign of one of the ligand CD bands as the basis for establishing the absolute configuration of the complex ion. Only the CD bands in the region of the ligand absorption were considered.

There have been many reports[3–13] concerning the

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(1) This work was supported by a research grant (AM02219-06S1) from the Division of General Medical Studies, Public Health Service.

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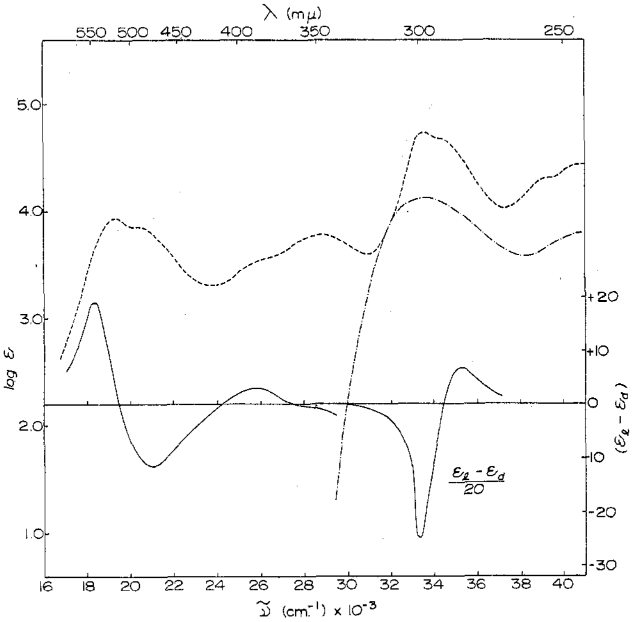

Fig. 1.—(+)$_{589}$-[Fe(dipy)$_3$](ClO$_4$)$_2$: CD curve (———), absorption curve (– – – –); absorption curve of 2,2′-dipyridyl in 1 *N* HCl (- · - ·).

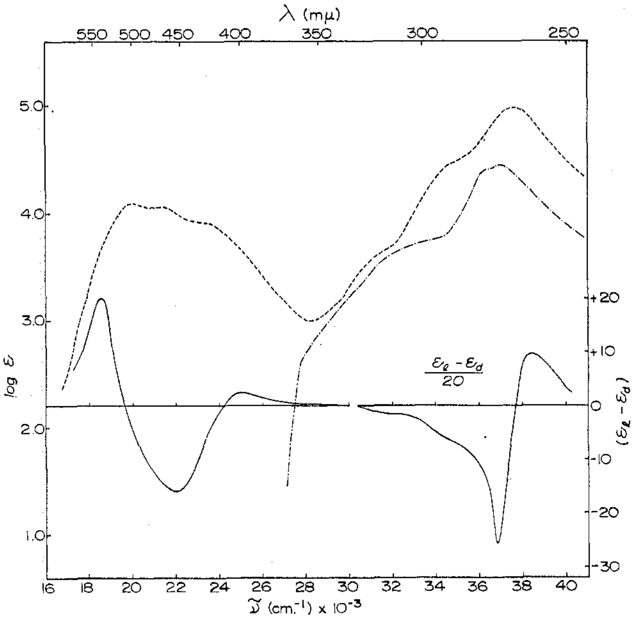

Fig. 2.—(+)$_{589}$-[Fe(phen)$_3$](ClO$_4$)$_2$: CD curve (———), absorption curve (– – – –); absorption curve of 1,10-phenanthroline in 1 *N* HCl (- · - ·).

absorption spectra of metal coordination complexes with 2,2′-dipyridyl (dipy) or 1,10-phenanthroline (phen), especially for the intense bands of the iron(II) complexes in the visible and near-ultraviolet regions and the ligand bands of the metal complexes in the ultraviolet region. It may be expected that the intense absorption bands in the visible region will have components due to the forbidden d–d transitions, but these components are obscured by the much more intense metal-to-ligand charge-transfer bands. The absorption in the ultraviolet region is dominated by the strong ligand absorption. Because of these complexities the absorption bands of the metal complexes of phen and dipy have not been clarified completely up to the present.

The CD curves of [Fe(dipy)$_3$]$^{2+}$, [Fe(phen)$_3$]$^{2+}$, [Ni(dipy)$_3$]$^{2+}$, [Ni(phen)$_3$]$^{2+}$, and [Co(en)$_2$phen]$^{3+}$ are presented here along with their absorption curves. Some suggestions based on the CD data are made concerning the absorption bands.

Experimental

Materials.—The optically active compounds [Fe(dipy)$_3$](ClO$_4$)$_2$·2H$_2$O, [Fe(phen)$_3$](ClO$_4$)$_2$·3H$_2$O, [Ni(dipy)$_3$](ClO$_4$)$_2$·3H$_2$O, and [Ni(phen)$_3$](ClO$_4$)$_2$.3H$_2$O were prepared and resolved following the directions of Dwyer and Gyarfas.[14] Potassium antimonyl *d*-tartrate was used as the resolving agent for the ion [Fe(phen)$_3$]$^{2+}$. After the less soluble diastereoisomer had precipitated, the (+)$_{589}$ complex ion was precipitated as the perchlorate salt by the addition ot sodium perchlorate; $[\alpha]_{589}$ 1400° (obsd.), 1432° (lit.[14]). The (+)$_{589}$-[Fe(dipy)$_3$]$^{2+}$, (+)$_{589}$-[Ni(phen)$_3$]$^{2+}$, and (−)$_{546}$-[Ni(dipy)$_3$]$^{2+}$ ions were separated as the less soluble diastereoisomers using potassium antimonyl *d*-tartrate. The respective specific rotations were: $[\alpha]_{589}$ +4550°, $[\alpha]_{589}$ +1390°, and $[\alpha]_{546}$ −420°. Values reported: +4800°, +1463°, and −480°. The specific rotation of [Ni(dipy)$_3$](ClO$_4$)$_2$·3H$_2$O was measured at 546 mμ because the rotation is near zero at 589 mμ. The [Co(en)$_2$phen]SO$_4$Cl·2H$_2$O was prepared from [Co(en)$_2$(H$_2$O)Cl]SO$_4$·1.5H$_2$O[15] and resolved by Jaeger's method[16] using silver *d*-α-bromocamphcr-π-sulfonate as the resolving agent. The (−)$_{589}$ isomer precipitated as the less soluble diastereoisomer and was converted to the iodide salt. Jaeger reported $[\alpha]_{543}$ −235° compared to our value of −240°. *Anal.* Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(C$_{12}$H$_8$N$_2$)]I$_3$: C, 25.97; H, 3.27; N, 11.36; I, 51.44. Found: C, 26.08; H, 3.24; N, 11.65; I, 51.92.

Measurements.—The solvents employed for the measurements were ice-cold water for the Fe(II) and Co(III) complexes and water–ethanol (1:1) for the Ni(II) complexes. The concentrations for the absorption measurements for the Fe(II) complexes were 10^{-4}–10^{-5} *M* and for the Co(III) and Ni(II) complexes 10^{-3}–10^{-4} *M*, using 1 and 5 cm. cells. The Fe(II) complexes and [Ni(dipy)$_3$]$^{2+}$ racemize so rapidly[17] that their CD curves had to be obtained by taking several readings which were extrapolated to zero time. The [Ni(phen)$_3$]$^{2+}$ complex ion racemizes more slowly and freshly prepared solutions were used to record data over limited wave length regions. Ice-water was circulated through the cell compartment during all measurements. The concentrations for the CD measurements were 10^{-3}–10^{-5} *M* for the Fe(II) complexes, 10^{-2}–10^{-5} *M* for the Ni(II) complexes, and 10^{-2}–10^{-3} *M* for the Co(III) complex. The cell lengths employed were 5, 2, 1, and 0.1 cm.

Absorption spectra were recorded on a Cary Model 14 spectrophotometer. CD curves were recorded on a Baird-Jouan dichrograph. A Rudolph Model 80Q6 polarimeter was used to identify the optically active complexes.

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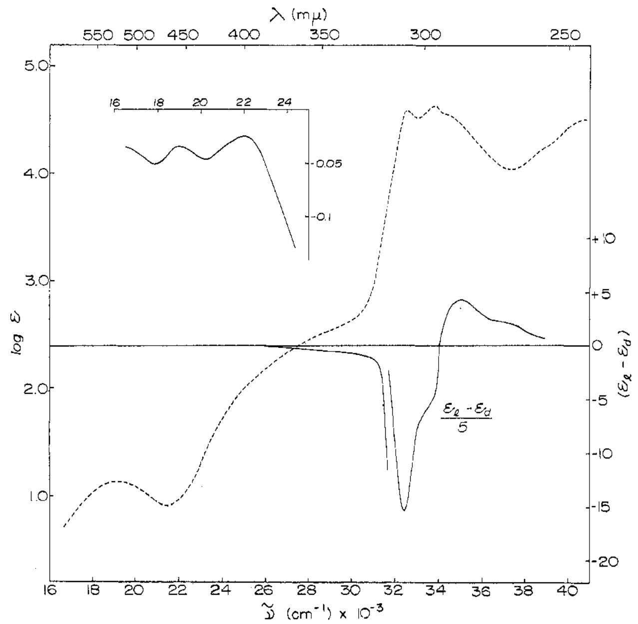

Fig. 3.—(−)$_{546}$-[Ni(dipy)$_3$](ClO$_4$)$_2$: CD curve (———), absorption curve (- - - -).

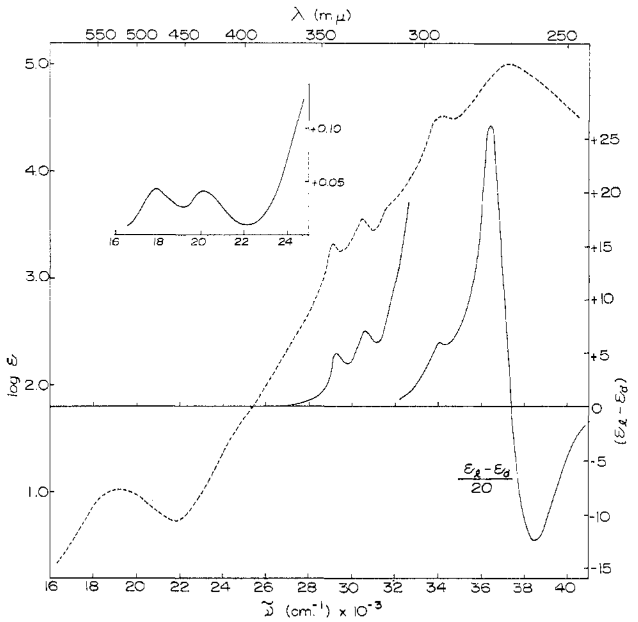

Fig. 4.—(+)$_{589}$-[Ni(phen)$_3$](ClO$_4$)$_2$: CD curve (———), absorption curve (- - - -).

Discussion of Results

The CD and absorption curves of [Fe(dipy)$_3$]$^{2+}$ and [Fe(phen)$_3$]$^{2+}$ are shown in Fig. 1 and 2 and their characteristics are tabulated in Table I. The high intensity of the CD peaks in the 17,000–28,000 cm.$^{-1}$ region for these complexes and the close correspondence with the positions of absorption peaks which have been assigned as Laporte allowed electron transfer from the metal ion to the ligand make it seem reasonable to assume that the CD peaks arise from the same cause. Another possibility is that the d–d transitions in this region gain intensity through mixing with the charge-transfer transitions. It is hoped that these assignments can be clarified by investigations in progress of other complexes involving charge-transfer processes. The negative CD bands at 21,000–22,000 cm.$^{-1}$ are sufficiently unsymmetrical to suggest that more than one component is present, but the absorption bands are too broad and poorly resolved to indicate the number of components.

The two CD peaks in the 19,000 cm.$^{-1}$ region of [Ni(dipy)$_3$]$^{2+}$ (Fig. 3) and [Ni(phen)$_3$]$^{2+}$ (Fig. 4) are of sufficiently low intensity to be assigned to the d–d transitions. The much lower intensity visible absorption bands, as compared to the iron complexes, indicate that the metal to ligand charge-transfer processes are much less important for the nickel complexes.

The visible absorption spectrum of [Co(en)$_3$]$^{3+}$ is very similar to that of [Co(en)$_2$phen]$^{3+}$ (Fig. 5). Each of the complexes has a broad band of about the same intensity at nearly the same frequency. However, the CD curves show greater differences in intensity and the splitting into individual components is different. The transitions in this region can be assigned as metal d–d transitions. The absorption curve in the visible region of [Co(en)$_2$phen]$^{3+}$ is so similar to that of [Co(en)$_3$]$^{3+}$ that one might be led to treat the former complex in terms of D$_3$ symmetry as an approximation. The differences in the CD curves, however, make it clear that the phen is sufficiently different from en to lower the symmetry and change the splitting pattern.

From the great similarities between the absorption curves of the complex ions and free ligands, it is apparent that the absorption for the complexes with phen above 27,500 cm.$^{-1}$ and with dipy above 30,000 cm.$^{-1}$ can be ascribed to the ligands. Although the absorption curves of the ligands dissolved in alcohol and in hydrochloric acid are very similar, the latter are more similar to the curves of the metal complexes, as one might expect. The CD bands in this region are very intense, as expected for ligand transitions which become optically active in the dihedral complexes. The CD peaks of [Co(en)$_2$phen]$^{3+}$ in the ligand band region are even lower in comparison with those of the tris(phen) complexes than would be expected on the basis of the proportions of phen present.

The CD curve of [Ni(phen)$_3$]$^{2+}$ (Fig. 4) shows two positive peaks at 29,200 and 30,600 cm.$^{-1}$. These peaks fall directly beneath peaks in the absorption curve. A negative shoulder (31,250 cm.$^{-1}$) is observed for [Fe(phen)$_3$]$^{2+}$ (Fig. 2) and [Co(en)$_2$phen]$^{3+}$ shows a positive shoulder in the CD curve at about 32,500 cm.$^{-1}$ (Fig. 5). The positions of other CD peaks in this region for [Co(en)$_2$phen]$^{3+}$ cannot be determined because of the greater complexity of the curve and the lower intensity of the CD peaks relative to the absorption bands for this complex. The absence of corresponding peaks in the CD or absorption curves of the dipy complexes suggests that these peaks are associated with the presence of the third benzene ring of phen, giving a more extensive π-system as compared to dipy.

Beneath the main absorption band of phen at about 37,000 cm.$^{-1}$ [Fe(phen)$_3$]$^{2+}$ and [Ni(phen)$_3$]$^{2+}$ show two intense CD peaks of opposite sign. In each case the lower frequency component is more intense. Mason[2]

TABLE I

CIRCULAR DICHROISM AND ABSORPTION DATA[a]

$[Fe(dipy)_3]^{2+}$[b]		*18.35*		*21.0*		*25.95*		*33.3*	*35.15*	
	CD	+19.1		−12.0		+3.2		−>500[c]	+>150[c]	
		19.2		*20.1*	*24.1*	*26.0*	*28.6*	*33.5*	*34.5*	
	Abs.	3.93		3.88	3.36	3.55	3.80	4.81	4.77	
$[Ni(dipy)_3]^{2+}$[d,e]		*17.8*		*20.2*			*32.45*	*33.5*	*35.1*	*(37.5)*
	CD	−0.05		−0.04			−>77[c]	−>30[c]	+>22[c]	−>10[c]
			19.0			*26.5*	*32.55*	*33.85*	*(34.8)*	
	Abs.		1.12			2.26	4.60	4.64	sh	
$[Fe(phen)_3]^{2+}$[b]		*18.5*		*22.2*	*25.0*		*(31.25)*	*(34.5)*	*36.75*	*38.4*
	CD	+20.0		−16.1	+2.4		−sh	−sh	−>520[c]	+>200[c]
		19.6		*21.4*	*23.0*		*31.0*	*34.4*	*37.7*	
	Abs.	4.05		4.0	3.85		3.55	4.41	4.95	
$[Ni(phen)_3]^{2+}$[b,e]		*17.7*		*20.0*		*29.2*	*30.6*	*34.1*	*36.4*	*38.4*
	CD	+0.04		+0.04		+5.1	+7.2	+123	+520	−250
			19.0		*(24.5)*	*29.2*	*30.45*	*31.7*	*34.0*	*37.3*
	Abs.		1.02		sh	3.27	3.46	sh	4.46	4.90
$[Co(en)_2phen]^{3+}$[f]				*20.8*				*(32.5)*	*36.8*	
	CD			−7.8				+sh	+11.4	
				21.5	*28.34*	*29.85*	*31.35*	*32.75*	*36.35*	
	Abs.			2.07	2.88	3.10	3.50	3.82	4.51	
$[Co(en)_3]^{3+}$[f]		*20.5*		*23.5*						
	CD	−1.8		+0.16						
			21.45							
	Abs.		1.94							

[a] The locations of the peaks are given as $\bar{\nu}$ (cm.$^{-1}$) × 10^{-3} in italics. Values are given in parentheses where the peaks are poorly resolved. The intensities are given as ($\epsilon_l - \epsilon_d$) (CD) and log ϵ_{max} (absorption). [b] $(+)_{589}$. [c] Minimum values because of rapid racemization and strong absorption. [d] $(-)_{546}$. [e] Measurements in 1:1 ethanol–water. [f] $(-)_{589}$.

has observed the same pattern for the CD curve of $[Ru(phen)_3]^{2+}$. The CD curves of $[Fe(dipy)_3]^{2+}$ (Fig. 1) and $[Ni(dipy)_3]^{2+}$ (Fig. 3) show similar behavior, but the peaks are at lower frequency corresponding to the position of the main absorption band of dipy. The main CD peaks would seem to arise from a common cause in all of these complexes. Mason assigned these two peaks as p-band excitations which have large zero-order rotational strengths. The CD curve of $[Co(en)_2phen]^{3+}$ in the ligand band region is similar to that of the other complexes, but data could be obtained only through the region of the lower frequency component. This component occurs at almost the same position as that of the iron complex.

There are some differences in the fine structure of the CD bands. The $[Ni(phen)_3]^{2+}$ (Fig. 4) complex ion has a positive CD peak at 34,000 cm.$^{-1}$, directly beneath an absorption peak. The $[Fe(phen)_3]^{2+}$ (Fig. 2) and $[Co(en)_2phen]^{3+}$ (Fig. 5) show shoulders in the CD curve at about the same position. A shoulder is observed at about 33,500 cm.$^{-1}$ for $[Ni(dipy)_3]^{2+}$ (Fig. 3). Presumably the expected splitting of the predominant negative CD band of $[Fe(dipy)_3]^{2+}$ (Fig. 1) is too small to be observed. Mason[2] assigned the low intensity CD peaks for $[Ru(phen)_3]^{2+}$ in this region as ligand transitions which only acquire small first-order rotational strength by mixing with magnetic dipole d–d transitions of the metal.

The CD curves of $[Fe(dipy)_3]^{2+}$ (Fig. 1) and $[Fe(phen)_3]^{2+}$ (Fig. 2) are very similar in the region 24,000–28,000 cm.$^{-1}$, although the absorption curves differ considerably. The absorption peak of $[Fe(dipy)_3]^{2+}$ at 26,000 cm.$^{-1}$ does not seem to have a counterpart for $[Fe(phen)_3]^{2+}$, but the corresponding peak for the phen complex could be obscured by the strong absorption peaks at lower frequencies. Such a peak is expected by comparison with the dipy complex and from the CD peaks in this region for both complexes. The 28,600 cm.$^{-1}$ absorption peak for $[Fe(dipy)_3]^{2+}$ coincides with the trough of the absorption curve for the phen complex. It is at about this point that the ab-

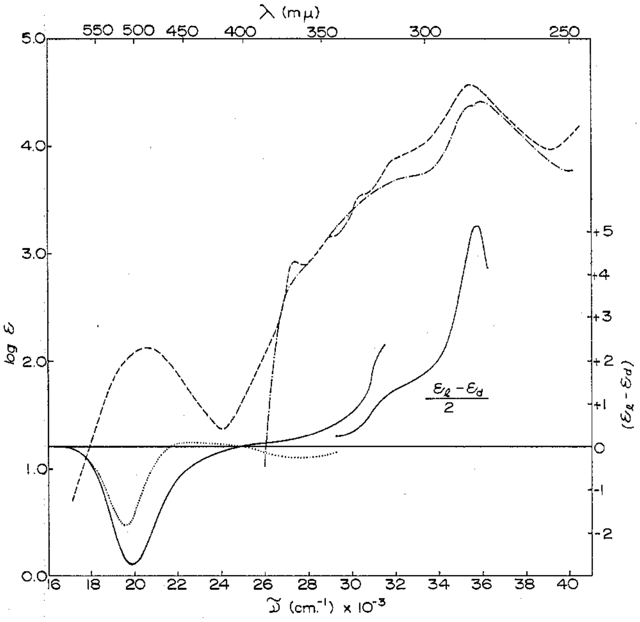

Fig. 5.—$(-)_{589}$-$[Co(en)_2phen]I_3$: CD curve (———), absorption curve (– – – –); absorption curve of 1,10-phenanthroline in 1 *N* HCl (- · · - ·); CD curve of $[Co(en)_3]Cl_3$ (. . . .).

sorption curve for the phen complex begins to follow that of the ligand. The curve of the iron complex does not coincide with that of dipy until about 32,000 cm.$^{-1}$. Thus the absorption of the phen complex in the region of 29,000 cm.$^{-1}$ is almost identical with that of the ligand, but the same is not true for the dipy complex. A change in dipy as a result of coordination is suggested. In solution the benzene rings are not in fixed positions for dipy and solvation should favor a *trans* arrangement. On coordination to a metal ion the two rings must become approximately coplanar with the N atoms in *cis* positions. It is suggested that the 28,600 cm.$^{-1}$ band of $[Fe(dipy)_3]^{2+}$ is associated with this change in the symmetry of the ligand. This would permit new transitions involving the π-system of dipy, similar to those of phen.

The great similarity among the intense CD bands of opposite sign in the ultraviolet region for all of the dipy and phen complexes provides a means of relating the configurations of these complexes. The $(+)_{589}$-$[Fe(phen)_3](ClO_4)_2$, $(+)_{589}$-$[Fe(dipy)_3](ClO_4)_2$, and $(-)_{546}$-$[Ni(dipy)_3](ClO_4)_2$ all have the same sign pattern for the dominant CD peaks and hence are concluded to have the same configuration. The reversed sign pattern of $(+)_{589}$-$[Ni(phen)_3](ClO_4)_2$ indicates that this complex has the opposite configuration. Presumably the configuration of $(-)_{589}$-$[Co(en)_2phen]I_3$ is the same as that of $(+)_{589}$-$[Ni(phen)_3](ClO_4)_2$, although data are not available for the expected higher frequency component of the Co(III) complex.

Mason[2] reported the CD curve for $(-)$-$[Ru(phen)_3](ClO_4)_2$ which is very similar to that for $(+)_{589}$-$[Fe(phen)_3](ClO_4)_2$ except that the signs of the major CD peaks in the low frequency region are reversed. This reversal of signs in one region is surprising in view of the consistency among the complexes reported here. Mason assigned the intense negative band of the CD curve in the main ligand band region as an A_2 component and the positive band as one with E symmetry. He stated that since the A_2 component was negative the complex consisted of a left-handed helix, the same as Λ-$[Co(en)_3]^{3+}$. If Mason's assignment is correct the Λ configuration can be assigned to $(+)_{589}$-$[Fe(phen)_3](ClO_4)_2$, $(+)_{589}$-$[Fe(dipy)_3](ClO_4)_2$, and $(-)_{546}$-$[Ni(dipy)_3](ClO_4)_2$ and the Δ configuration to $(+)_{589}$-$[Ni(phen)_3](ClO_4)_2$ and tentatively to $(-)_{589}$-$[Co(en)_2phen]I_3$.

The solubilities of diastereoisomers have been used to assign the relative configurations of complexes. Even though the antimonyl *d*-tartrate ion was used for the resolution of the tris(phen) and tris(dipy) complexes, the resulting diastereoisomers differ in composition[18] and hence the solubility rule would not be expected to relate the configurations of the phen complexes to the dipy complexes. The solubility rule should be valid for relating the configurations of the phen complexes of Fe(II) and Ni(II) and (separately) the dipy complexes of Fe(II) and Ni(II). The results are consistent with the assignment made based on the CD data. The phen complex of each metal which gives the less soluble diastereoisomer is Δ and the dipy complex of each metal which gives the less soluble diastereoisomer is Λ.

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(18) F. P. Dwyer and E. C. Gyarfas[14] established the compositions of the Fe(II) compounds as $[Fe(dipy)_3]_3(SbOC_4H_4O_6)_4I_2 \cdot 18H_2O$ and $[Fe(phen)_3](SbOC_4H_4O_6)_2 \cdot 4H_2O$.

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Magnetic Properties of Some High-Spin Complexes of Iron(II)

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The magnetic susceptibilities of several high-spin complexes of Fe(II) having the general formula $[Fe(phen)_2X_2]$ (phen = 1,10-phenanthroline; $X^- = Cl^-, Br^-, I^-, N_3^-, SCN^-, SeCN^-$) were determined over the temperature range 100–300°K. The moments found are somewhat lower than those expected for rigorously octahedral complexes and are essentially independent of temperature, except for the thiocyanate and selenocyanate, in which the moment is found to decrease sharply from ~5.0 to ~1.5 B.M. at lower temperatures. Structures are proposed for these complexes, based on X-ray and infrared data.

A series of Fe(II) complexes having the general formula $[Fe(phen)_2X_2]$ (hereafter referred to as the bis complexes; phen = 1,10-phenanthroline) have recently been prepared and their magnetic moments at room temperature reported.[1-3] In all cases, the room temperature moments observed, 5.1–5.3 B.M., are somewhat below that predicted for octahedral, spin-free, d^6 systems when spin–orbit coupling is included.[4,5] This lowering of the moments is at least in part a result of the fact that, in the complexes studied, the symmetry is not truly cubic due to the difference in ligand field strength between phen and X. Thus the moment is partially quenched by the lower symmetry.

Since very little work has been done on the tempera-

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