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Metal Complexes of 2-Allylpyridine[1]

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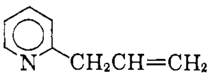
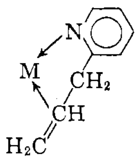
Complexes of 2-allylpyridine with Cu(I), Ag(I), and Pt(II) (1:1) have been prepared. The elementary analyses and the absence of the C=C stretching frequency of the free ligand from the infrared spectra of the complexes suggest that the ligand is coordinated through both the pyridyl nitrogen and the olefinic group. Assignments of most of the infrared bands of 2-allylpyridine have been made from comparisons with other 2-substituted pyridines.

In platinum(II) complexes with allylamines[2] and with an olefinic tertiary arsine[3] both the donor atom (N or As) and the olefinic group in the same ligand are involved in bonding to platinum. For platinum(II) complexes of dimethyl-4-pentenylarsine, which are monomers, chelation of that ligand through As and the olefinic group has been established.[3] With monoallylamines the platinum(II) complexes are dimers which contain allylamine bridging groups.[2]

Molecular models show that 2-allylpyridine (I) can act as a chelating ligand (II). The present work has been carried out to determine whether coordination through the olefinic linkage does occur in metal complexes of 2-allylpyridine.



I



II

Experimental

Starting Materials.—Allyl bromide and 2-bromopyridine, both obtained commercially, were distilled prior to use in the synthesis of 2-allylpyridine. Silver nitrate and picric acid were J. T. Baker Analyzed reagents. Copper(I) chloride[4] and potassium tetrachloroplatinate(II)[5] were prepared by tested synthetic procedures. Most of the other chemicals used were commercially available, reagent grade quality.

Measurements.—Visible and ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer. Infrared spectra were recorded on both a Perkin-Elmer Model 21 (NaCl Littrow prism) and a Beckman IR-8 (filter-grating) spectrophotometer. Infrared spectra of liquids were obtained on films between salt plates and those of solids as mulls of Nujol and halocarbon oil. Uncorrected melting points were determined on a Fisher-Johns electrically-heated aluminum block. A Mechrolab Model 301A osmometer was used for molecular weight determinations. Microanalyses of carbon, hydrogen, nitrogen, and chlorine were performed by Alfred Bernhardt, Max Planck Institut, Mülheim, Germany.

2-Allylpyridine.—The reaction of 2-allylmagnesium bromide with 2-bromopyridine was used to prepare 2-allylpyridine.[6] After the preparation of allylmagnesium bromide,[7] its ethereal solution was immediately siphoned through a sintered glass filter into a second reaction vessel, immersed in an ice bath, into which ethereal solutions of iron(III) chloride and 2-bromopyridine were slowly added. After hydrolysis of the resulting product with an ice–ammonium chloride mixture, ethyl ether was stripped from the organic phase and 2-allylpyridine was distilled under reduced pressure; b.p. 61–64° (14 mm.) [lit.[6] b.p. 63–64° (15 mm.)]; $n^{25}{}_D$ 1.5086 (lit.[6] $n^{2?}{}_D$ 1.513). The ultraviolet spectrum of 2-allylpyridine in absolute methanol contains the following absorption maxima: 2680 Å. (log ϵ_M 3.52), 2615 Å. (log ϵ_M 3.62), 2550 Å. (log ϵ_M 3.58), and 2490 Å. (log ϵ_M 3.56). The infrared spectrum of a film of 2-allylpyridine is tabulated in Table I. The picrate of 2-allylpyridine was prepared in 95% ethanol and recrystallized several times from absolute ethanol, m.p. 157–161°.

Anal. Calcd. for $C_8H_9N \cdot C_6H_3N_3O_7$: C, 48.29; H, 3.47; N, 16.09. Found: C, 48.34; H, 3.47; N, 15.81.

2-Allylpyridinecopper(I) Chloride.—In a preliminary preparation 2.0 ml. (0.015 mole) of 2-allylpyridine was added under nitrogen to 1.45 g. (0.015 mole) of copper(I) chloride. The interaction was exothermic. Absolute ethanol (25 ml.) was then added and the mixture was refluxed for at least 3 hr. to give an amber liquid and a small amount of black tar. The hot reaction mixture was passed through filter paper to give a deep green filtrate from which grayish green crystals precipitated upon cooling to room temperature. After this mixture had been cooled to 0°, it was filtered through sintered glass. The gray-green residue was washed with absolute ethanol and anhydrous ethyl ether and then dried in a vacuum desiccator over $CaCl_2$ at room temperature. The yield of crude C_8H_9NCuCl was 1.12 g. (33% of theoretical).

A better yield of the copper(I) complex was obtained by adding acetonitrile (18 ml.) under nitrogen to copper powder (0.2 g.) and copper(I) chloride (1.0 g., 0.010 mole). After all of the CuCl had dissolved, 2-allylpyridine (1.7 g., 0.014 mole) was added dropwise with stirring at room temperature. Within 1 min. after addition of 2-allylpyridine had been completed, fine crystals precipitated from the reaction mixture, which was warmed for 45 min. to about 65°. After cooling the mixture in an ice bath, the pale greenish residue plus most of the original copper powder were collected on a sintered glass filter and washed with absolute ethanol and anhydrous ethyl ether. After the residue had been dried over $CaCl_2$ in a vacuum desiccator (15–20 mm. pressure) for several hours, the yield of crude C_8H_9NCuCl (subtracting 0.2 g. for the Cu powder) was 1.5 g. (70% of theoretical).

The complex was recrystallized from both benzene and ethyl acetate. During solution of the copper(I) complex in both of these solvents there was some decomposition, since some higher melting (>300°) gray residue always remained on the walls of the vessels after filtering off the hot solutions. The very pale green color of the copper(I) complex, which could not be removed upon repeated crystallization in the presence of air, is probably

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[1] This work was supported by the Atomic Energy Commission, Contract AT(30-1)2274.

[2] R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963).

[3] H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 220 (1961).

[4] W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p. 142.

[5] R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

[6] C. Troyanowsky, *Bull. soc. chim. France*, 420 (1955).

[7] O. Grummitt, E. P. Budewitz, and C. C. Chudd, *Org. Syn.*, **36**, 61 (1956).

TABLE I

INFRARED ABSORPTION BANDS OF 2-ALLYLPYRIDINE AND ITS COMPLEXES

Assignments[8,9,a]	C_8H_9N[b,c]	C_8H_9NCuCl	$C_8H_9NPtCl_2$	$C_8H_9NAgNO_3$[d]
$\nu_{as}(=CH_2)$, ν(ring CH)	3080 m	3050 w	3040 vw	
$\nu(=CH-)$	3010 sh	3010 w		
$\nu_s(=CH_2)$, ν(ring CH)	2990 m	2980 w		
$\nu_{as}(-CH_2-)$	2920 m	2930 vw	2910 w	
$\nu_s(-CH_2-)$	2860 sh	2890 vw		
	1970 vw	2020 vw	2100 vw	
Overtone of $\gamma(=CH_2)$	1835 vw	1835 mw	1855 vw	1920 vw
				1740 w[d]
$\nu(-CH=CH_2)$	1640 m	1553 m	1453 m	1582 m
ν(ring CC, CN)	1592 vs	1597 s	1608 ms	1603 s
ν(ring CC, CN)	1570 ms	1567 ms	1570 w	1562 m
			1536 vw	
ν(ring CC, CN)	1475 s	1475 s	1477 s	1479 s
ν(ring CC, CN), $\beta(-CH_2-)$	1435 vs	1445 s	1443 m	1431 s
$\beta(=CH_2)$		1420 s	1420 w	
	1375 vw	1401 m	1391 w	1401 vs(b)[d]
		1330 mw	1340 w	1357 vs(b)[d]
$\beta(-CH=C-)$	1297 w			1304 vs(b)[d]
β(ring CH)	1285 w	1274 m	1287 m	1269 sh
	1248 vw	1258 w	1255 m	1247 sh
	1218 w			1228 sh
	1198 w	1203 w	1206 w	1193 w
β(ring CH)	1148 m	1160 ms	1171 ms	1156 m
			1163 ms	
β(ring CH)	1110 mw	1095 m	1121 ms	1109 vw
				1080 w
β(ring CH)	1052 m	1046 m	1064 m	1057 ms
Ring breath, $\gamma(-CH=C-)$	993 s	1016 ms	1044 m	1033 s
		1007 w	1012 ms	1028 sh
			992 m	1018 sh
				1012 ms
	966 w	975 w	973 m	981 w
$\gamma(=CH_2)$	916 s(b)	917 s	927 mw	955 vs(b)
		905 ms	916 w	924 m
		885 vw		891 m
	827 w(b)	832 w	826 ms	820 m[d]
	803 vw	819 vw		
γ(ring CH)	756 vs(b)	767 vs	773 vs	784 vs(b)
	703 w	735 w	718 m	752 w
	663 mw	686 mw	666 vw	708 s[d]
		641 mw	655 w	638 ms

[a] ν, stretching vibration; β, in-plane deformation; γ, out-of-plane deformation; as, asymmetric; s, symmetric. [b] Wave numbers in cm.$^{-1}$. [c] Intensities: vs, very strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; sh, shoulder; (b), broad. [d] Anion absorption.

caused by oxidation to a small amount of copper(II). A batch of purified product, recrystallized from ethyl acetate, was dried to constant weight at 50° and 15–20 mm. pressure; m.p. 113–125° dec.

Anal. Calcd. for C_8H_9NCuCl: C, 44.04; H, 4.16; N, 6.42; Cl, 16.25; C/N, 6.86. Found: C, 43.71; H, 4.66; N, 6.32; Cl, 16.23; C/N, 6.92.

Although very low solubility of C_8H_9NCuCl in benzene at 37° prevented reproducible molecular weight determinations, preliminary results were sufficiently low to suggest the presence of either a monomer or a dimer, or a mixture of both.

2-Allylpyridinesilver(I) Nitrate.—Powdered silver nitrate (1.353 g., 0.00796 mole) was added in subdued artificial light to a solution of 0.953 g. (0.00800 mole) of 2-allypyridine in 3 ml. of chloroform. During the addition of $AgNO_3$ appreciable heat was evolved as most of the silver salt appeared to go into solution. After shaking the reaction mixture at 30° for 15 min., a copious white precipitate formed. This was separated from the mother liquor by centrifuging and washed with absolute ethanol and anhydrous ethyl ether. After being air dried a few minutes, the crude product was dried more completely in a vacuum desiccator (15–20 mm. pressure) over $CaCl_2$. The yield of crude $C_8H_9NAgNO_3$ was 1.746 g. (75.9% of theoretical). The silver(I) complex was recrystallized from both absolute ethanol and methanol. A biege sample, recrystallized from ethanol, was dried in a vacuum oven (15–20 mm. pressure) at 50° to constant weight before elementary analysis, m.p. 92–93°.

Anal. Calcd. for $C_8H_9NAgNO_3$: C, 33.24; H, 3.14; N, 9.69; C/N, 3.43. Found: C, 32.98; H, 3.24; N, 9.58; C/N, 3.44.

Dichloro(2-allylpyridine)platinum(II).—Potassium tetrachloroplatinate(II) (2.770 g., 0.00667 mole) was added to 25 ml. of water to give a deep red solution, which was filtered through fluted paper into a solution of 0.823 g. (0.00691 mole) of 2-allylpyridine in 3 ml. of absolute ethanol. An emulsion resulted in which 2-allylpyridine was dispersed throughout the aqueous phase. Within 15 min. after formation of the emulsion the color of the reaction mixture slowly changed from red to orange and an oily orange precipitate started to stick to the sides of the reaction vessel. After the reaction mixture had been shaken another hour at room temperature, 0.9 ml. of

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(8) A. R. Katritzky, *Quart. Rev.* (London), **13**, 353 (1959); A. R. Katritzky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry," Academic Press, Inc., New York, N. Y., 1963, Chapter 10.

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1959, Chapter 3.

12 *M* HCl was slowly added to make the mixture 1% with respect to HCl. Mechanical shaking was continued 23 more hours during which the formerly orange gelatinous precipitate became predominantly yellow and more crystalline. After the reaction mixture had been cooled to 0°, it was filtered through fine sintered glass. The filtrate was a clear orange-red. The residue was washed successively with cold aqueous 0.01 *M* acetic acid, cold water, 50 vol. % aqueous ethanol, 95% ethanol, and anhydrous ethyl ether. After being air dried for a short period, the crude product was dried in a vacuum desiccator (15–20 mm. pressure) over $CaCl_2$ for 36 hr. The yield of sulfur-yellow $C_8H_9NPtCl_2$ was 1.545 g. (60.1% of theoretical). Small amounts of the platinum(II) complex have been recrystallized from acetone, chloroform, and ethanol. The sample for elementary analysis was dried to constant weight between 90 and 100° in a vacuum oven (15–20 mm. pressure) and became yellow-brown.

Anal. Calcd. for $C_8H_9NPtCl_2$: C, 24.95; H, 2.36; N, 3.64. Found: C, 24.80; H, 2.50; N, 3.80.

$C_8H_9NPtCl_2$ has also been purified by sublimation at temperatures above 150° and pressures of less than 1 mm. to give an orange solid, m.p. 183–185°. Upon heating to 90–100° in a vacuum oven, the color becomes light brown with no significant change in weight.

Anal. Calcd. for $C_8H_9NPtCl_2$ (sublimed): C, 24.95; H, 2.36; N, 3.64; Pt, 50.65; Cl, 18.41. Found: C, 25.19; H, 2.21; N, 3.72; Pt, 49.28; Cl, 18.33.

The molecular weight of a 0.44 mg./ml. of benzene solution of $C_8H_9NPtCl_2$ (sublimed) was determined as 330 g./mole, a value lower than the calculated formula weight of 385 g./mole.

Results and Discussion

The infrared absorption bands between 2.5 and 16 μ for 2-allylpyridine are tabulated in Table I. The accuracy of most of the band positions is within ± 0.02 μ (± 5 cm.$^{-1}$ in the vicinity of 1600 cm.$^{-1}$). Since the olefinic group is not in a position to interact with the pyridyl ring through conjugation, the characteristic group frequencies of 2-alkylpyridines and vinyl olefins are expected to appear within their usual ranges. Accordingly, assignments were made with reference to standard compilations.[8,9]

The infrared bands observed in the spectra of 2-allylpyridine complexes of CuCl, $PtCl_2$, and $AgNO_3$ are also given in Table I. The band assignments for the complexes were made by an empirical correlation between the spectrum of liquid 2-allylpyridine and the spectra of mulls of the solid complexes and thus have some degree of uncertainty. It is assumed that upon coordination the pyridyl ring modes of 2-allylpyridine behave similarly to those of pyridine. With respect to metal pyridine complexes infrared studies reveal great similarities between the spectra of the complexes and the spectrum of free pyridine.[10]

For these complexes the infrared regions of greatest interest are shown in Fig. 1. Included for free 2-allylpyridine and its complexes with CuCl and $PtCl_2$ are the ring CC and CN stretching bands in the 1650 to 1450 cm.$^{-1}$ region, the ring breathing vibration at *ca.* 1000 cm.$^{-1}$, and the out-of-plane ring CH deformation at *ca.* 760 cm.$^{-1}$. For the 2-allylpyridine complexes of CuCl, $PtCl_2$, and $AgNO_3$ no band was observed in the vicinity of 1640 cm.$^{-1}$, the position of the C=C stretching vibration for the free ligand. Because of the presence of pyridyl ring bands in the 1600 to 1430 cm.$^{-1}$ region unambiguous assignment of the coordinated C=C stretching mode is difficult. For all of these complexes the strong 1592 cm.$^{-1}$ band for the free ligand is shifted to higher frequencies by *ca.* 5 to 15 cm.$^{-1}$. Such a change has been observed for pyridine complexes where coordinated pyridine is qualitatively distinguished from the free ligand by a shift of the strong 1578 cm.$^{-1}$ band to *ca.* 1600 cm.$^{-1}$.[10] In addition to the pyridyl ring bands moderate bands are found at 1553 cm.$^{-1}$ for the Cu(I) complex, at 1453 cm.$^{-1}$ for the Pt(II) complex, and at 1582 cm.$^{-1}$ for the Ag(I) complex. These bands have been assigned as the C=C stretching vibrations of the coordinated olefin in the respective complexes.

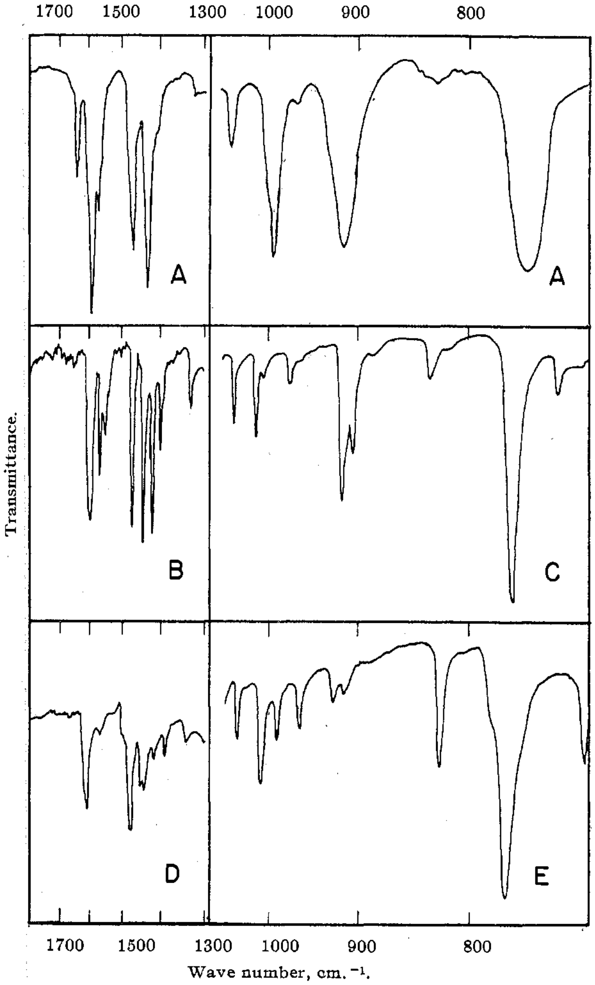

Fig. 1.—Portions of the infrared spectra of a liquid film of 2-allylpyridine (curve A), a halocarbon oil mull of C_8H_9NCuCl (curve B), a Nujol mull of C_8H_9NCuCl (curve C), a halocarbon oil mull of $C_8H_9NPtCl_2$ (curve D), and a Nujol mull of $C_8H_9NPtCl_2$ (curve E).

Infrared examinations of metal olefin complexes show frequency lowerings of 70 to 200 cm.$^{-1}$ with respect to the free olefins for the C=C stretching modes.[11] These shifts arise from coordination of the olefinic linkage to metal atoms. Results of n.m.r. studies on metal olefin complexes are consistent with interpretations of the in-

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(10) N. S. Gill, R. H. Nuttal, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961); P. C. H. Mitchell, *ibid.*, **21**, 382 (1961); A. I. Popov, J. C. Marshall, F. B. Stute, and W. B. Person, *J. Am. Chem. Soc.*, **83**, 3586 (1961).

(11) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958); D. M. Adams and J. Chatt, *Chem. Ind.* (London), 149 (1960).

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.

Acknowledgment.—The authors wish to thank Mr. M. Bollinger of this department for determining molecular weights.

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[12] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

[13] P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **17**, 909 (1961).

[14] R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

[15] H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 249 (1964).

[16] V. N. Filimonov and D. S. Bystrov, *Opt. Spectry.* (USSR), **12**, 31 (1962).

[17] C. Curran and S. Mizushima, "Coupling between C–H Bending Vibrations in Complexes of Pyridine with Metal Halides" in "Advances in Molecular Spectroscopy," Vol. 3, A. Mangini, Ed., The Macmillan Co., New York, N. Y., 1962, p. 961.

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

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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.

[2] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 211 (1963).

[3] K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); K. Yamasaki, H. Yokoi, and K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 137 (1948).

[4] G. L. Roberts and F. H. Field, *J. Am. Chem. Soc.*, **72**, 4232 (1950).