Complexes of Pyrrole-Derivative Ligands. I.
Planar Nickel(II) Complexes with Tetradentate Ligands

BY JAMES H. WEBER

The 2,2'-[R-bis(nitrilomethylidyne)]dipyrrolonickel(II) complexes and their ligands have been synthesized and characterized. R is an *o*-aryl group or a saturated chain of two to five carbons. All complexes are diamagnetic and planar in the solid phase and in chloroform. The complexes containing the tetramethylene and pentamethylene linkages are monomeric and thus exhibit seven- and eight-membered chelate rings. The following order of ligand field strength for R is observed: trimethylene > tetramethylene > pentamethylene.

Introduction

There has been little information published regarding the nature of the complexes of imines derived from pyrrole-2-aldehyde. Recently, octahedral cobalt(III) complexes of bidentate ligands (structure I, R = alkyl)

I
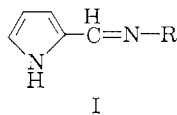
have been assigned a *trans* geometry on the basis of a proton magnetic resonance study.[1] Tanaka and Yamauchi[2] have synthesized copper(II) complexes where R is aryl. Holm, Chakravorty, and Theriot[3] have recently published a thorough report on nickel(II) complexes of ligand structure I. From magnetic moments, electronic spectra, and proton nuclear resonance studies they concluded that a tetrahedral–planar equilibrium exists in solution when R is isopropyl, *sec*-butyl, 3-pentyl, cyclohexyl, and 2-(3-methyl)butyl. The configuration of the complex in solution is planar when R is *n*-propyl and is tetrahedral for the *t*-butyl group. Similarly, copper(II) complexes are nearly planar when R is isopropyl and *n*-butyl, and tetrahedral when R is the *t*-butyl group. Chakravorty, Kalia, and Kannan[4] have studied the ligand field spectra of tris cobalt(III) complexes of structure I, where R = CH₃ and C₃H₇.

The subject of this report is the complexes of nickel(II) with tetradentate diimine pyrrole derivatives (structure II) where R is a bridging alkyl or aryl group.

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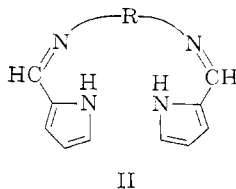
(A sample name for a complex is 2,2'-[ethylenebis-(nitrilomethylidyne)]dipyrrolonickel(II). Other complexes and their ligands are named in an analogous manner.) A previous study of tetradentate pyrrole ligands was published by Pfeiffer, *et al.*,[5] who synthesized nickel(II) and copper(II) complexes where R is ethylene and *o*-phenylene. von Stackelberg[6] confirmed the planar structure of the copper(II) complexes by an X-ray study.

Interesting stereochemical considerations arise as the length of the chain R is increased.[7] From Stuart–Briegleb models it appears that the *o*-phenylene linkage and even the longer ethylene linkage are too short for an unstrained complex. One or two side-chain methyl groups on the ethylene bridging group result in no additional strain, but the *trans*-1,2-cyclohexylene chain increases the strain considerably. In addition, it can be suggested from a study of the models that the trimethylene linkage has the least strain, while the methylene groups of the tetramethylene molecule are very crowded. Even the planar penta- and hexamethylene complexes can be formed with the models, but less nonbonded interaction occurs if a tetrahedral configuration is formed. There has been little conclusive evidence that tetradentate ligands form planar complexes with central rings of seven or more members. Most examples in the literature have not been demonstrated to be planar and/or monomeric. A monomer with a 13-member ring is the largest that has been studied (structure III).[8] When R is pentamethylene
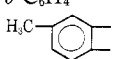
III
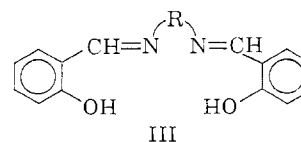
or decamethylene, the copper(II) complex is monomeric as evidenced by a molecular weight determination in pyridine. There is, however, no evidence concerning the configuration of the complex.

(1) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964).
(2) T. Tanaka and O. Yamauchi, *Chem. Pharm. Bull.* (Tokyo), **9**, 588 (1961); **10**, 435 (1962).
(3) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).
(4) A. Chakravorty, R. C. Kalia, and T. S. Kannan, *ibid.*, **5**, 1623 (1966).
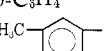(5) P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. Prakt. Chem.*, **149**, 217 (1937).
(6) M. von Stackelberg, *Z. Anorg. Chem.*, **253**, 136 (1947).
(7) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).
(8) P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Ann.*, **503**, 84 (1933).

TABLE I

PREPARATION AND CHARACTERIZATION OF THE PYRROLE-DERIVATIVE LIGANDS[a]

R	Prepn solvent	Recrystn solvent	Mp, °C[b]	—%calcd—			—%found—		
				C	H	N	C	H	N
-CH₂CH₂-	C₂H₅OH	C₂H₅OH	178–180	67.2	6.6	26.2	67.4	6.6	26.2
-CH(CH₃)CH₂-	C₂H₅OH	CH₂Cl₂–C₅H₁₄[c]	136 dec	68.4	7.1	24.5	68.5	7.1	24.5
-C(CH₃)₂CH₂-	C₂H₅OH	CH₂Cl₂–C₆H₁₄	121–122 dec	69.4	7.5	23.1	69.0	7.6	22.8
-CH₂CH₂CH₂-	C₂H₅OH	None	119–120 dec	68.4	7.1	24.5	68.4	7.0	24.7
-CH₂(CH₂)₂CH₂-	C₂H₅OH	None	175–176 dec	69.4	7.5	23.1	69.4	7.8	23.4
-CH₂(CH₂)₃CH₂-	C₂H₅OH	C₂H₅OH–C₆H₁₄	140	70.3	7.9	21.8	70.4	7.9	21.4
-CH(CH₂)₄CH-[d]	H₂O	C₂H₅OH	205 dec	71.6	7.5	20.9	72.0	7.7	20.9
o-C₆H₄	CH₂Cl₂	Xylene	204–205 dec	73.2	5.4	21.4	73.2	5.3	21.3
H₃C-⟨benzene⟩	CH₂Cl₂	Ligroin (60°)	165–167 dec	73.9	5.8	20.3	73.9	5.6	20.6

[a] See structure II. [b] Uncorrected. [c] Hexane. [d] *trans* isomer.

TABLE II

PREPARATION AND CHARACTERIZATION OF THE NICKEL(II) COMPLEXES[a]

R	Prepn method	Recrystn solvent	Color	Mp, °C[b]	—%calcd—			—%found—		
					C	H	N	C	H	N
-CH₂CH₂-	A	CH₂Cl₂–C₆H₁₄[c]	Orange	219	53.2	4.5	20.7	53.5	4.7	20.4
-CH(CH₃)CH₂-	A	CH₂Cl₂–C₆H₁₄	Orange	169	54.8	5.0	19.7	55.1	4.8	20.0
-C(CH₃)₂CH₂-	A	CH₂Cl₂–C₆H₁₄	Orange	163	56.3	5.4	18.8	56.2	5.2	18.9
-CH₂CH₂CH₂-	A	CH₂Cl₂–C₃H₁₄	Orange	175	54.8	5.0	19.7	54.6	4.9	20.0
-CH₂(CH₂)₂CH₂-	A	CH₂Cl₂–C₆H₁₄	Orange	154–155	56.3	5.4	18.8	55.8	5.4	18.9
-CH₂(CH₂)₃CH₂-	B	CH₂Cl₂–C₂H₅OH	Brown	193	57.6	5.8	17.9	58.1	5.9	18.0
-CH(CH₂)₄CH-[d]	A	CH₂Cl₂–C₆H₁₄	Orange	272 dec	59.1	5.6	17.2	59.2	5.6	17.5
o-C₆H₄	A	Toluene	Red	284 dec	60.2	3.8	17.6	59.7	3.8	17.7
H₃C-⟨benzene⟩	A	Toluene	Red	211	61.3	4.2	16.8	61.1	4.3	17.0

[a] See structure II. [b] Uncorrected. [c] Hexane. [d] *trans* isomer.

Experimental Section

Materials.—Pyrrole-2-aldehyde was obtained from the Aldrich Chemical Co.

Magnetic Measurements.—Magnetic measurements were done at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) or distilled, demineralized water as a standard. The solid-state measurements were performed at 8.3 and 10.6 kgauss, and the solution measurements in chloroform, at 14.6 kgauss. Each solid-state value reported was measured at two field strengths and is the average of two or three determinations. Diamagnetic corrections were applied to the complexes before calculating magnetic moments.

Molecular Weights.—Molecular weights were obtained from 0.015 and 0.03 *M* solutions of the complex in toluene at 37°. A Mechrolab 310A osmometer was used.

Spectra.—A Cary 14 spectrophotometer was used at room temperature for spectra in the ultraviolet and visible ranges. The ultraviolet–visible spectra were obtained from $2.5 \times 10^{-5}\ M$ solutions in chloroform. Extinction coefficients agree to 5% or less on duplicate runs. The ligand field spectra were obtained from $2.5 \times 10^{-3}\ M$ solutions in chloroform. Infrared spectra were obtained *via* the mull method using a Perkin-Elmer Model 337 spectrophotometer with an expanded-scale readout.

Analyses.—Analyses were performed by Galbraith Microanalytical Laboratories.

Preparation of Ligands.—With one exception the ligands were prepared by the reaction of pyrrole-2-aldehyde and the appropriate diamine in a 2:1 molar ratio using the appropriate solvent (Table I). The reaction required 1–12 hr at room temperature. Solid ligands were obtained by removing the solvent under reduced pressure using a rotary evaporator. The exception to the general procedure, *trans*-1,2-diaminocyclohexane sulfate, was dissolved in water with a drop of concentrated sulfuric acid and impurities were separated by filtration. Two moles of pyrrole-2-aldehyde per mole of diamine was added to the resulting solution. A precipitatate formed immediately after adjusting the solution to pH 10 with potassium carbonate. After the initial characterization of the Ligands (Table I), the crude ligands were used for further reactions. The ligands when R is aromatic are yellow; all others are white.

Preparation A of Complexes.—After the ligand was dissolved in 95% aqueous ethanol, an equimolar, aqueous solution of nickel(II) acetate tetrahydrate was slowly added. A 3 *M* aqueous solution of sodium carbonate (0.7 mole/mole of ligand) was added dropwise and the solution was stirred at room temperature for 4 hr. The ethanol was removed under reduced pressure using a rotary evaporator. The crude solid thus obtained was recrystallized (Table II). Recrystallized yields range from 30 to 75%.

Preparation B of Complexes.—Based on the method of Holm, *et al.*,[3] the crude ligand (0.01 mole) and potassium *t*-butoxide (0.02 mole) were dissolved separately in anhydrous tetrahydrofuran. After the solution of potassium *t*-butoxide was added to the solution of the ligand, solid tetraethylammonium tetrabromonickelate(II) (0.01 mole) was added. The mixture was stirred 24 hr at room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure using a rotary evaporator. The yield of the recrystallized complex is 55%.
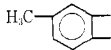
Results and Discussion

Ultraviolet and Visible Spectra.—No agreement has been reached as to the nature of the two transitions which occur in the ultraviolet region in pyrrole and its simple carbonyl derivatives.[9,10] The understanding of the more complicated diimine pyrrole derivatives (structure II) in this report must therefore be qualita-

(9) S. F. Mason in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, pp 59, 60.

(10) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 347–353.

TABLE III

ULTRAVIOLET–VISIBLE SPECTRA OF THE PYRROLE-DERIVATIVE LIGANDS AND THE NICKEL(II) COMPLEXES[a]

Wavelength, mμ (extinction coeff $\times$ 10^{-3})

	Ligand	Nickel(II) complexes
$-CH_2CH_2-$	290 (32.3), 245 sh[b] (10.8)	284 sh (5.9), 321 (24.8), 394 (10.3), 418 sh (7.9)
$-CH(CH_3)CH_2-$	289 (32.0), 245 sh (10.8)	280 sh (6.5), 321 (25.4), 393 (10.6), 419 sh (8.1)
$-C(CH_3)_2CH_2-$	286 (32.1), 245 sh (10.2)	280 sh (6.1), 320 (25.4), 390 (10.6), 413 sh (7.8)
$-CH_2CH_2CH_2-$	287 (33.8), 245 sh (9.4)	270 sh (6.2), 318 (27.4), 380 sh (8.9), 396 (9.4), 437 sh (5.7)
$-CH_2(CH_2)_2CH_2-$	284 (35.0), 245 sh (9.6)	260 sh (6.5), 316 (25.2), 369 sh (9.5), 383 (10.0), 420 sh (6.0)
$-CH_2(CH_3)_2CH_2-$	283 (35.2), 245 sh (9.6)	263 sh (5.6), 316 (24.8), 364 (9.0), 376 (8.8), 417 sh (5.6)
$-CH(CH_2)_4CH-$[c]	280 (32.8), 245 sh (11.2)	279 sh (7.1), 319 (26.6), 389 (11.8)
$o-C_6H_4$	228 sh (9.50), 252 sh (9.1), 309 (35.1), 349 (25.9)	243 (12.6), 336 (39.7), 384 (18.5), 506 (13.1), 547 sh (9.1)
H$_3$C⬡	232 sh (9.7), 250 sh (9.8), 310 (32.6), 350 (24.2)	240 (12.7), 337 (40.4), 383 (19.3), 504 (13.8), 541 sh (9.6)

[a] 2.5 $\times$ 10^{-5} M in chloroform; see structure II.   [b] Shoulder.   [c] *trans* isomer.

tive and be based on empirical data. Each aliphatic diimine in Table III has a maximum at 285 $\pm$ 5 mμ (ϵ 33,600 $\pm$ 1600) and a shoulder near 245 mμ (ϵ 10,000). Because of the magnitude of the extinction coefficient of the more intense band, it is reasonable to assign it to a $\pi \rightarrow \pi^*$ transition. As further evidence it was observed that the maximum in the ethylene compound was shifted from 281 mμ in hexane to 293 mμ in ethanol. The red shift observed when replacing a non-polar with a polar solvent is characteristic of $\pi \rightarrow \pi^*$ transitions.

When the spectra of the aliphatic ligands are compared to those of the corresponding nickel(II) complexes (Table III), a great similarity is observed below 325 mμ (Figure 1). A band in the complex at 318 $\pm$ 3 mμ (ϵ 26,100 $\pm$ 1300) with a shoulder near 270 mμ (ϵ 6500) appears in each spectrum. When the shape of this band is compared to the ligand band near 285 mμ, it appears that the erstwhile ligand $\pi \rightarrow \pi^*$ transition has undergone a red shift. This observation agrees with the conclusion that the formation of planar nickel(II) complexes with tetradentate ligands in the analogous salicylaldehyde system (structure III) results in a red shift of the $\pi \rightarrow \pi^*$ transition relative to the ligand value.[11] The bands in the nickel(II) complexes above 325 mμ could be attributed to additional $\pi \rightarrow \pi^*$ transitions involving metal and ligand orbitals.[11] This is not an absolute assignment, but it is clear that metal–ligand interaction is involved. The bands are not d–d transitions (see below) and are not transitions within the ligand. The higher wavelength bands are of particular empirical interest because they follow a trend with respect to the length of the bridging R group. When R is a two-member chain, maxima occur at 392 $\pm$ 3 mμ and 416 $\pm$ 3 mμ. Maxima occur at 380, 396, and 437 mμ in the trimethylene complex and occur at even lower wavelength in the tetra- and pentamethylene complexes.

The spectra of the aromatic ligands are complicated by the benzenoid bands which appear, for example, at 256 and 324 mμ in both salicylaldehyde and its N-methylimine.[12,13] The additional conjugation in the
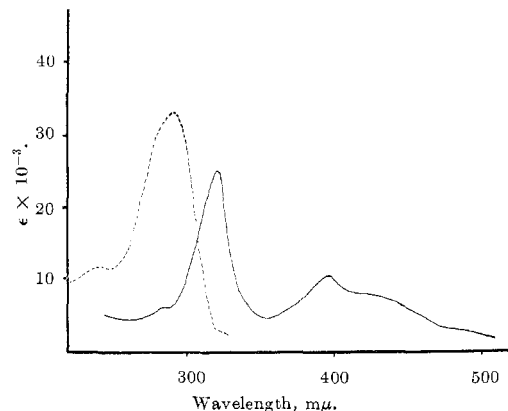
(11) S. M. Crawford, *Spectrochim. Acta*, **19**, 255 (1963).
(12) J. Ferguson, *ibid.*, **17**, 316 (1961).
(13) S. V. Sheat and T. N. Waters, *J. Inorg. Nucl. Chem.*, **26**, 1221 (1964).

Figure 1.—Ultraviolet–visible spectra of 2,2'-[ethylenebis-(nitrilomethylidyne)]dipyrrolonickel(II) (———) and its ligand (---------).

ligands with aromatic R will result in a red shift of the $\pi \rightarrow \pi^*$ transition observed in the aliphatic ligands. Comparison of the spectra of the aliphatic and aromatic ligands (Figures 1 and 2) shows that the maxima at 290 and 309 mμ, respectively, have similar shapes and both may correspond to a $\pi \rightarrow \pi^*$ transition. In Figure 2 (as in the aliphatic system in Figure 1) it appears that the ligand $\pi \rightarrow \pi^*$ transition undergoes a red shift upon complexation.[11] The additional bands in the complex above 400 mμ may result from $\pi \rightarrow \pi^*$ transitions involving metal and ligand orbitals.[11]
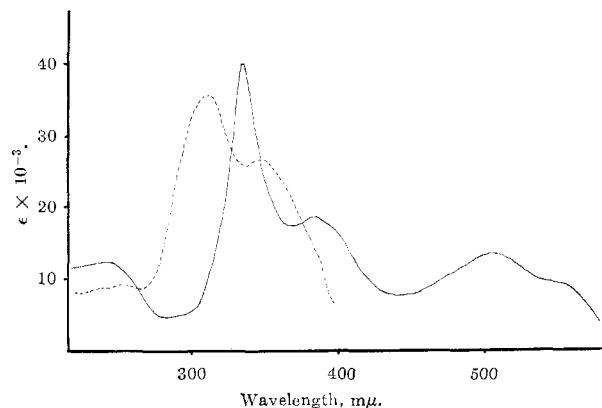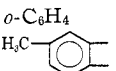

Figure 2.—Ultraviolet–visible spectra of 2,2'-[o-phenylenebis-(nitrilomethylidyne)]dipyrrolonickel(II) (———) and its ligand (---------).

Infrared Spectra.—Initial identification of each ligand and complex was made on the basis of infrared spectra. The ligands are characterized by an N–H stretching vibration doublet centered near 3130 cm^{-1} which disappears upon complex formation. In addition, the ligand C=N stretching frequency at 1636 ± 11 cm^{-1} with aliphatic R and near 1615 cm^{-1} with aromatic R is shifted downward 50 ± 12 and 84 cm^{-1}, respectively, upon complex formation (Table IV).

TABLE IV

INFRARED BANDS OF THE PYRROLE-DERIVATIVE LIGANDS AND THE NICKEL(II) COMPLEXES

| | νC=N, cm^{-1} | | |
R	Ligand	Nickel(II) complex	Δ^a
–CH$_2$CH$_2$–	1638	1587	51
–CH(CH$_3$)CH$_2$–	1626	1573	53
–C(CH$_3$)$_2$CH$_2$–	1633	1571	62
–CH(CH$_2$)$_4$CH–^{b}	1631	1583	48
–CH$_2$CH$_2$CH$_2$–	1635	1596	39
–CH$_2$(CH$_2$)$_2$CH$_2$–	1642	1590	52
–CH$_2$(CH$_2$)$_3$CH$_2$–	1647	1588	59
o-C$_6$H$_4$	1615	1531	84
H$_3$C—⟨○⟩—	1615	1531	84

^{a} νC=N(ligand) − νC=N(complex); see structure II. ^{b} *trans* isomer.

Increasing conjugation of the C=N group with other unsaturated groups in a ligand, as well as metal–ligand π bonding in the complex, lowers the energy of the C=N stretching vibration.[14] The behavior of the compounds with aromatic linkages can be explained on this basis. The C=N stretching vibration frequency of these ligands is lower than that of the aliphatic ligands. Furthermore, the ligand will become no more coplanar upon complexation so that the 84-cm^{-1} downward shift can be essentially attributed to metal–ligand π bonding. The situation is much more complicated with the aliphatic ligands and the corresponding nickel-(II) complexes. It is interesting that the C=N stretching vibration of the aliphatic ligands shows a trend toward increasing frequency as the R chain length is increased. From the above argument it is suggested that the C=N and pyrrole groups become less coplanar as the chain length increases. From models it is seen that, when R is a chain of three or more carbons, the two pyrrole rings can undergo an intramolecular interaction in at least one conformation resulting in decreased coplanarity. Intermolecular interactions may also tend to disrupt the N–H···N hydrogen bonds which increase the pyrrole C=N coplanarity. In the aliphatic complexes the rough trend in the shift of the C=N stretching vibration frequency is parallel to the difficulty in forming the models. The trimethylene ligand, which forms the least strained complex with the models, has the smallest shift (39 cm^{-1}) in the C=N stretching vibration frequency. Complex formation with other aliphatic ligands results in a shift of 55 ± 7 cm^{-1}. The lowering of the C=N stretching vibration fre-

(14) H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, **5**, 1172 (1966).

quency may be the result of concurrent increase in the coplanarity of the C=N and pyrrole groups and the advent of metal–ligand π bonding. Although it is difficult to separate unequivocally the two causes of the frequency shift, it is probable that both occur in this system.

Configuration of the Complexes.—It is learned from magnetic susceptibility measurements at two magnetic field strengths that each complex is diamagnetic in the solid state. Each complex is also diamagnetic in chloroform. Low solubility prevented a proton resonance study. The molecular weights of the tetramethylene and pentamethylene complexes were each determined in 0.03 and 0.015 M toluene solutions. The average experimental values for the tetramethylene and pentamethylene derivatives, respectively, are 280 (calculated value, 298) and 301 (calculated value, 312). From the magnetic and osmometry experiments it is concluded that the complexes are square-planar in the solid and solution phase and monomeric in solution. These two complexes are rare examples of well-defined seven- and eight-membered rings in planar systems. It should be pointed out here that many complexes with tetradentate ligands containing long central chains are dimeric.[15] Structure IV is a schematic representation of a dimer showing only metal and donor atoms.

IV
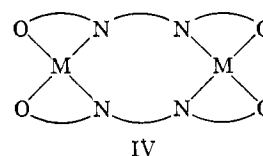
Further evidence for the square-planar configuration is obtained from the ligand field spectra of three of the complexes. The single band observed as a shoulder for the tri-, tetra-, and pentamethylene complexes can be attributed to the only spin-allowed transition in square-planar complexes, $^1A_1 \rightarrow {}^1B_1$.[16] The range of frequencies and extinction coefficients is in agreement with previous studies on neutral square-planar nickel-(II) complexes.[3,16,17] The trimethylene ligand produces the strongest observed ligand field with a frequency of 20,800 ± 400 cm^{-1}. (This band could not be accurately measured, and an accurate extinction coefficient could not be obtained.) The weaker tetra- and pentamethylene ligands result in ligand field splittings of 19,600 cm^{-1} (ϵ 180) and 19,050 cm^{-1} (ϵ 160), respectively. The total range of observed frequencies is about 1800 cm^{-1}. A value of 19,200 cm^{-1} (ϵ 190) was obtained for the planar nickel(II) complex of N-n-propyl(pyrrole-2-methylenimine)[3] (structure I, R = n-propyl). Because of small steric effects this value is probably as high as any for the aliphatic bidentate ligands, but it is less than all but the relatively weak pentamethylene ligand of the tetradentate series.

Holm,[17] in the study of an analogous series of nickel-

(15) T. D. O'Brien in "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 253.
(16) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).
(17) R. H. Holm, *J. Am. Chem. Soc.*, **82**, 632 (1960).

(II) complexes derived from diimine ligands of salicyl-aldehyde (structure III), observed the following order of ligand field strength for R bridging groups: $-CH_2-CH_2- > -CH_2CH_2CH_2- > -CH_2(CH_2)_2CH_2-$. The trend agrees with the order in this work in that chain lengthening in the central ring lowers the ligand field strength of the ligand. At the only two points of comparison, the tri- and tetramethylene bridges, the pyrrole-derivative ligands are stronger than the corresponding salicylaldiimine ones by about 3800 cm^{-1}. If this value is applied to the complexes reported here, the ligand field transition of ligands with a two-carbon chain would be extrapolated to near 460 mμ and would consequently be covered by a more intense band.

Conclusions.—It has been possible to synthesize and characterize planar nickel(II) complexes of tetradentate ligands which have the unusual central ring sizes of seven and eight. From ligand field spectra it has been shown that the ligand field decreases in the monomeric planar complexes as the size of the central ring increases. These tetradentate ligands containing four nitrogen donor atoms are stronger than the bidentate pyrrole-2-methylenimine ligands and are stronger than ligands in the salicylaldehyde system containing two oxygen and two nitrogen donor atoms.

Metal Complexes of N,N,N',N'-Tetramethyldiamines. I. Nickel(II) and Cobalt(II) Complexes

By L. SACCONI, I. BERTINI, and F. MANI

Complexes of N,N,N',N'-tetramethylated ethylenediamine (Me$_4$en), 1,2-propylenediamine (Me$_4$pn), and trimethylenediamine (Me$_4$tn) with nickel(II) and cobalt(II) salts have been prepared and investigated. Compounds of the type M(diamine)X$_2$ (M = Co, Ni and X = Cl, Br, I, NO$_3$, NCS) with tetrahedral and octahedral structures were obtained. The stereochemistry of the complexes, both in the solid state and in solution, is discussed on the basis of their magnetic and spectral properties. The tendency of the diamines to form tetrahedral complexes is found to increase in the order Me$_4$en < Me$_4$pn < Me$_4$tn.

Introduction

Many compounds of nickel(II) with N- and C-substituted ethylenediamines have been described and studied.[1,2] These have been found to have a planar or an octahedral structure. The latter configuration has also been assigned to some nickel(II) derivatives of C-substituted ethylenediamines (phenylethylenediamine, stilbenediamine) which were originally considered to be tetrahedral.[3] To our knowledge, however, no systematic investigation has been made on the ability of N,N,N',N'-tetramethylated ethylenediamine (Me$_4$en), 1,2-propylenediamine (Me$_4$pn), and trimethylenediamine (Me$_4$tn) to form complexes with nickel(II) and cobalt(II) salts. Only the complex Ni-

(Me$_4$en)(NO$_2$)$_2$ has recently been prepared[4] and it has been found to have hexacoordinate structure with two bidentate nitro groups.[5]

We have found that, in anhydrous and noncoordinating solvents, nickel(II) and cobalt(II) halides, nitrates, and thiocyanates react with Me$_4$en, Me$_4$pn, and Me$_4$tn to give complexes of the general formula M(diamine)X$_2$.[6] The stereochemistry and the properties of these complexes have been studied, and the results are reported in this paper.

Experimental Section

Preparation of the Compounds.—The diamines were methylated, with a mixture of formic acid and formaldehyde, using standard methods. All of the complexes were prepared by the same general method. A solution of 10 mmoles of the diamine ligand in 20 ml of dry butanol was added slowly to a hot solution of 10 mmoles of the appropriate metal salt in 50 ml of butyl alcohol, which had previously been distilled over BaO. After boiling for some minutes, the solution was filtered and concentrated, and a precipitate was generally obtained. In some cases cyclohexane was added to promote precipitation. The crystals were collected by filtration and dried in a stream of dry nitrogen. The analytical data are reported in Table I.

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