Reactions of Coordinated Ligands. X. The Formation and Properties of a Tetradentate Macrocyclic Ligand by the Self-Condensation of o-Aminobenzaldehyde in the Presence of Metal Ions

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The self-condensation of o-aminobenzaldehyde in the presence of nickel(II) and copper(II) ions has been shown to produce a tetradentate, closed macrocyclic ligand, tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine. The four donor nitrogen atoms coordinate to the metal atom in a planar manner. These new complexes have been characterized by elemental analysis, infrared spectra, magnetic moments, and visible reflectance spectra. The variation of the physical properties of the nickel(II) complexes with the nature of monodentate ligands bound above and below the plane has been investigated. The coordination template hypothesis has been invoked to explain the formation of these macrocyclic chelate compounds.

Introduction

It is well known that many compounds important to living systems contain a metal atom surrounded by a conjugated macrocyclic ligand with four nitrogen atoms functioning as donors. In the metalloporphyrins, these nitrogen donors are present as members of four pyrrole units linked at their α-carbon atoms to form the more or less planar porphyrin ring system. The corrin ring of vitamin B_{12} is similar but less symmetrical. This type of chelation gives rise to great thermodynamic and kinetic stability for the metal-ligand linkage. In such systems biological activity may be associated with alterations of the metal atom itself, with substitution reactions involving the more labile extraplanar ligands, or with substituents attached to the ring system.[1,2] The function of these natural macrocyclic complexes is greatly varied[3-5] and the contribution of the metal ion to this function has not been fully elucidated.

It would seem most reasonable to attempt the full elucidation of the behavior of metal ions under the influence of macrocyclic ligands and extraplanar monodentate ligands with systems less complicated than those occurring in nature. Until quite recently,[6] very few examples of synthetic tetradentate, planar, macrocyclic ligands were known. Phthalocyanines[7] and synthetic porphins[8,9] have provided exceptions, for these have been known for many years. As a result of synthetic developments in these and a few other laboratories, a broad variety of fully cyclic ligands is becoming available.
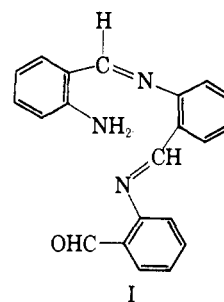
Johnson, Kay, and Rodrigo[10,11] have synthesized some macrocyclic ligands closely related to the corrin system but differing in the degree of saturation of the macrocycle and/or by replacement of a –CH– bridge with –O–, –NH–, or –S–.

The use of metal ions to serve as templates for the

synthesis of macrocyclic compounds has resulted in some new cyclic ligand systems. Thompson and Busch[12] utilized the terminal mercapto groups of nickel(II) complexes of the "linear" tetradentate ligand α-diketobismercaptoethylimine[13] in reactions with difunctional alkylating agents. They obtained closed tetradentate macrocyclic ligands containing two nitrogen and two sulfur donor atoms coordinated in a plane about the nickel(II). Curry and Busch[14] synthesized penta- and sexadentate macrocyclic chelate ligands by the reaction of 2,6-diacetylpyridine with triethylenetetramine and tetraethylenepentamine, respectively, in the presence of an iron(II) salt. The ligands were isolated as their iron(III) complexes. The reaction of bis(dimethylglyoximato)nickel(II) with the etherate of boron trifluoride or triphenylboron replaces the hydrogen bridge with BX_2^+ (X = F, C_6H_5), resulting again in a tetradentate macrocyclic ligand coordinated in a plane around the nickel atom.[15,16] Curtis and co-workers have reported the formation of macrocyclic complexes by the reaction of nickel or copper amine complexes with a variety of aliphatic aldehydes and ketones. The process involves a combination of a Schiff base reaction and an aldol-like condensation to produce closed macrocyclic ligand systems containing four donor nitrogen atoms.[17-19] These ligands also are prepared in the form of their planar nickel(II) or copper(II) chelates.

Eichhorn and Latif first investigated the condensation of o-aminobenzaldehyde in the presence of metal ions.[20] On the basis of analytical data for the nitrate

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TABLE I

ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES OF TAAB

Compound	Calculated, %					Found, %				
	C	H	N	Halogen	S	C	H	N	Halogen	S
Ni(TAAB)(ClO$_4$)$_2$	50.14	2.99	8.36	10.60	...	49.97	3.29	8.59	10.57	...
Ni(TAAB)(BF$_4$)$_2$	52.09	3.10	8.68	23.59	...	51.98	3.16	8.47	23.45	...
Ni(TAAB)[B(C$_6$H$_5$)$_4$]$_2$	82.21	5.45	5.05	...	...	82.18	5.62	5.05	...	...
Ni(TAAB)I$_2$	46.34	2.76	7.72	35.03	...	46.53	3.50	7.80	34.92	...
Ni(TAAB)Cl$_2$·H$_2$O	60.04	3.93	10.00	12.69	...	59.51	4.28	9.51	12.71	...
Ni(TAAB)Br$_2$·H$_2$O	51.77	3.39	8.64	24.65	...	51.66	4.21	8.88	24.09	...
Ni(TAAB)(NO$_3$)$_2$	56.49	3.36	14.11	...	...	56.02	3.92	13.61	...	...
Ni(TAAB)(NCS)$_2$	61.35	3.43	14.31	...	10.92	61.03	3.51	14.21	...	10.80

salts, they concluded that their products were complexes of a trimeric condensate, trisanhydro-o-aminobenzaldehyde (I). We have reinvestigated these reactions[21] and conclude that the product obtained from the condensation in the presence of nickel ions is actually a mixture. From this mixture we have isolated a nickel complex containing the closed macrocyclic tetrameric condensate, tetrabenzo[b,f,j,n][1,5,-9,13]tetraazacyclohexadecine (II), referred to as TAAB.
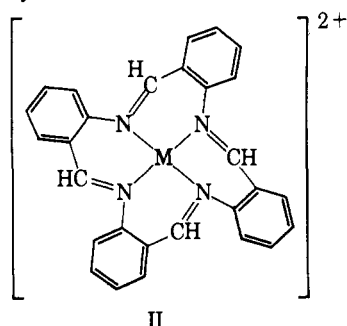
II

An analogous copper(II) complex has also been obtained.

The following discussion describes the synthesis, isolation, characterization, and properties of the nickel and copper complexes containing this macrocyclic ligand. Magnetic, visible, and infrared spectral data are discussed for a variety of "salts" of the nickel complex.

Experimental

Materials.—o-Aminobenzaldehyde was prepared by the method described by Smith and Opie.[22] All other chemicals used were obtained commercially and were of reagent grade or equivalent.

Reaction of o-Aminobenzaldehyde with Nickel(II) Nitrate.— A solution of 2.90 g. (0.024 mole) of freshly prepared o-aminobenzaldehyde in 40 ml. of absolute ethanol was heated and stirred. While the aminobenzaldehyde solution was under reflux, a solution of 1.74 g. of nickel(II) nitrate hexahydrate (0.006 mole) in 30 ml. of absolute ethanol was added. The color of the solution immediately turned from pale yellow to dark brown. After approximately 30 min., an orange precipitate appeared. The solution was stirred and refluxed for a total of 7 hr. After cooling, the solution was filtered and the isolated solid was washed with ethanol and ether and dried in vacuo at room temperature yielding 2.65 g. of orange crystalline material.

Isolation of Tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecinenickel(II) Perchlorate Ni(TAAB)(ClO$_4$)$_2$.—The orange material from above (2.0 g.) was dissolved in water (~200 ml.) at room temperature, and a concentrated aqueous solution of sodium perchlorate was added with stirring to the solution. A bright red precipitate was produced immediately. The solution was filtered and the filtrate was removed from the receiver. The red crystalline product was washed with water and dried in vacuo over P$_4$O$_{10}$ at room temperature yielding 1.0 g. of Ni(TAAB)-(ClO$_4$)$_2$. The filtrate from the original separation was concentrated on a rotary evaporator. A yellow precipitate was produced

which was removed by filtration, washed with water, and dried in vacuo over P$_4$O$_{10}$ at room temperature; yield, 0.8 g.

This yellow compound also contained a self-condensation product of o-aminobenzaldehyde as a ligand, but will be discussed elsewhere.[23]

Preparation of Other Salts of Tetrabenzo[b,f,j,n][1,5,9,13]-tetraazacyclohexadecinenickel(II), Ni(TAAB)X$_2$. General Procedure.—To a saturated solution of the perchlorate salt in water (ca. 1 g. in 500 ml.) at room temperature was added about 10 ml. of a concentrated solution of the sodium salt of the required anion, together with a few drops of the corresponding acid, where available. For example, an aqueous solution of sodium bromide and a few drops of 47% hydrobromic acid were used to prepare the bromide.

In the cases of the thiocyanate, fluoroborate, tetraphenylborate, chloride, and bromide, the salts are almost completely insoluble in the resulting solution and precipitated immediately. For the iodide, precipitation is not immediate. However, this material crystallizes on standing for 2 days at room temperature. The nitrate salt, however, is sufficiently soluble that the solution has to be concentrated by a rotary evaporator to a volume of about 100 ml. before crystallization of the nitrate occurs.

All products are isolated by suction filtration, washed with water, and dried under vacuum at room temperature over P$_4$O$_{10}$. Using these procedures the yield of metathetical product is nearly quantitative. Analytical data are recorded in Table I.

The chloride was also produced by bubbling hydrogen chloride gas into a methanolic solution of the perchlorate. The infrared spectrum of this product was identical with that of samples produced by the more general procedure.

Reaction of o-Aminobenzaldehyde with Copper Nitrate. Tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecinecopper(II) Nitrate, Cu(TAAB)(NO$_3$)$_2$.—A solution of 2.90 g. (0.024 mole) of freshly prepared o-aminobenzaldehyde in 40 ml. of absolute ethanol was heated and stirred. When the aminobenzaldehyde solution was under reflux, a solution of 1.45 g. of copper(II) nitrate trihydrate in 30 ml. (0.006 mole) of absolute ethanol was added. The color of the solution immediately turned from pale yellow to red-brown. After approximately 1 hr., a precipitate appeared. The solution was stirred and refluxed for a total of 9 hr. After cooling, the solution was filtered, and the isolated solid was washed with absolute alcohol and ether and dried in vacuo at room temperature yielding 2.90 g. of dark green microcrystalline Cu-(TAAB)(NO$_3$)$_2$. Anal. Calcd. for C$_{28}$H$_{20}$N$_6$CuO$_6$: C, 56.05; H, 3.36; N, 14.01. Found: C, 56.15; H, 3.38; N, 13.95.

Magnetic Measurements.—Magnetic measurements were made by the Gouy method. The susceptibilities of ligands and anions were calculated from Pascal's constants.[24] The standard used was Hg[Co(NCS)$_4$].

Infrared Spectra.—Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nujol mull and potassium bromide pellet techniques were employed. Polystyrene was used for calibration.

Reflectance Spectra.—Reflectance spectra were obtained with a Cary Model 14 recording spectrophotometer and reflectance attachment. A potassium bromide pellet technique was employed.

Analyses.—Analyses were performed by the Schwarzkopf Microanalytical Laboratories.

Results and Discussion

The reaction of o-aminobenzaldehyde with itself in the presence of nickel(II) or copper(II) ion yields, in

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each case, a cationic complex containing a ligand composed of 4 moles of the self-condensed ligand bound to a single metal ion. In the case of nickel(II), a series of metathetical reactions has led to the isolation of the following series of compounds: Ni(TAAB)(ClO₄)₂, Ni(TAAB)[B(C₆H₅)₄]₂, Ni(TAAB)(BF₄)₂, Ni(TAAB)-Cl₂·H₂O, Ni(TAAB)Br₂·H₂O, Ni(TAAB)I₂, Ni(TAAB)-(NO₃)₂, and Ni(TAAB)(SCN)₂. These materials have been identified and characterized as complexes of the fully cyclized ligand tetrabenzo[b,f,j,n][1,5,9,13]tetra-azacyclohexadecine (II) by elemental analyses, infrared spectra, magnetic moments, and electronic reflectance spectra. The analytical data are presented in Table I. These data clearly show the necessity for formulating the ligand as completely self-condensed in most cases, for only the Cl⁻ and Br⁻ derivatives of Ni(TAAB)²⁺ contain as much as 1 mole of water.

The results of detailed studies on the magnetic properties of the nickel(II) complexes are reported elsewhere[25]; however, these merit mention at this point. The compounds of the formula Ni(TAAB)X₂, where X is ClO₄, BF₄, or B(C₆H₅)₄, are uniformly low spin in configuration and may be taken as containing planar nickel(II) in its usual singlet state. For those cases where X is I, NO₃, and NCS, the moment is about 3.2 B.M., and the compounds thus may be considered to contain axially distorted octahedral or tetragonal nickel(II) in its common triplet ground state. The monohydrated chloride and bromide exhibit intermediate room temperature moments, and from studies on the temperature dependences of the moments, singlet-triplet equilibria have been shown to occur in these cases.[25] In the case of the Cu(TAAB)(NO₃)₂, both the composition and the magnetic moment of 1.84 B.M. prove the presence of copper(II), rather than copper(I) as previously reported.[19]

Strong inference as to the structure of the ligand has been derived from the infrared spectra of the several compounds. In Table II, the infrared absorption bands are tabulated for typical examples of the low-spin (X = ClO₄) and high-spin (X = I) ·nickel(II) derivatives. The absence of the stretching and deformation frequencies expected for the NH₂ group, the absence of the usual C=O stretching frequency of a carbonyl group, and the presence of a strong band at 1570 cm.⁻¹, assignable to the stretching mode of the coordinated and conjugated C=N groups, provide strong evidence for the presence of a closed cyclic product containing Schiff-base linkages. The four bands marked C₆-ring I–IV are the usual modes of *ortho*-disubstituted benzene.

The complete tabulation of infrared data for examples of low-spin and high-spin nickel(II) derivatives serves to illustrate how closely the ligand spectrum replicates throughout the series of compounds. The changes are exceedingly small except for two small regions, one in the range 1235–1250 cm.⁻¹, the other in the range 820–830 cm.⁻¹. In the spectra of the low-spin compounds (ClO₄⁻, BF₄⁻, B(C₆H₅)₄⁻) a medium-strong band occurs at 1250 cm.⁻¹, with no absorption in the range 820–830 cm.⁻¹. The high-spin compounds (I⁻, NO₃⁻, NCS⁻) show a weak broad band at 1235–1240 cm.⁻¹ in place of the aforementioned absorption at 1250 cm.⁻¹ and a medium-strong band in the range 820–

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TABLE II
INFRARED SPECTRA OF REPRESENTATIVE COMPOUNDS, Ni(TAAB)X₂

High-spin example [Ni(TAAB)I₂],[a] cm.⁻¹		Assignment	Low-spin example [Ni(TAAB)(ClO₄)₂],[a] cm.⁻¹	
3020	vw	C–H st	3020	vw
2925	vw	C–H st	2925	vw
1610	vs	C₆-ring I	1614	vs
1589	s	C₆-ring II	1591	vs
1568	vs	C=N	1570	vs
1492	m	C₆-ring III	1492	m
1441	m	C₆-ring IV	1448	m
1404	s		1380	m
1319	m		1320	m
1282	m		1281	m
1239	vwb		1250	m
1198	s		1189	m
1173	sh		1180	w
1122	m		1085[b]	vsb
985	m		961	m
923	m		925	m
824	m			
780	s	C–H def.	786	m
765	s	C–H def.	770	s
			755	s
			621[b]	s
595	w		592	w
532	w		538	w
494	wb		484	m
472	wb		476	m

[a] Abbreviations used: b, broad; m, medium; sh, shoulder; s, strong; vs, very strong; w, weak; vw, very weak. [b] Strong absorptions due to perchlorate.

830 cm.⁻¹. The monohydrated chloride and bromide exhibit both types of absorption in this narrow range. The absorptions due to the water molecules are evident in the spectra of the latter two compounds, occurring as a broad absorption at about 3400 cm.⁻¹ and a weak shoulder at 1650 cm.⁻¹.

The infrared absorption bands of the anions in these complexes show that the perchlorate and fluoroborate are not coordinated.[26] Strong broad bands occur at 1085 and 621 cm.⁻¹ and a medium broad band at 412 cm.⁻¹ for the perchlorate and at 1050, 620, and 412 cm.⁻¹ for the fluoroborate. The nitrate spectrum in a Nujol mull shows strong bands at about 1410 and 1310 cm.⁻¹ and a band of medium intensity at 1065 cm.⁻¹. These features indicate that the nitrate anion is coordinated to the nickel.[27] In a KBr disk, however, a strong absorption was also observed at 1380 cm.⁻¹, while the 1065-cm.⁻¹ absorption was considerably reduced in intensity. This strongly suggests that reaction with the KBr produced some ionic nitrate. The thiocyanate shows a strong C≡N absorption at 2060 cm.⁻¹ suggesting coordination through the nitrogen atom.[28] No absorption due to the C–S stretch could be detected at lower frequencies owing to strong absorptions of the ligand in this region. The absorptions of the nitrate group in the copper compound are similar to those of the nickel compound in Nujol, suggesting coordination of the nitrate in the copper compound. The reflectance spectra of the compounds were measured over the range from 6700 to 29,000 cm.⁻¹ and are reported in Table III. The perchlorate and fluoro-

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(28) P. C. H. Mitchell and R. J. P. Williams, *ibid.*, 1912 (1960).

borate derivatives of Ni(TAAB)$^{2+}$ show one absorption band (ν_5) at about 19,000 cm.$^{-1}$. This result is consistent with the presence of a planar nickel(II) species,[29] and the band is assigned to the transition $^1A_{1g}$ to $^1B_{1g}$. The tetraphenylboron salt also shows this band (ν_5), but, in addition, a very intense, broad absorption (ν_2) at about 9850 cm.$^{-1}$. The latter is probably related to the anion. The spectra of the high-spin iodide, nitrate, and thiocyanate compounds are consistent with an octahedral or tetragonal nickel(II) species, low energy absorptions being observed in the range 8000–10,500 cm.$^{-1}$ (ν_1), in addition to a broad absorption in the range 18,000–20,000 cm.$^{-1}$ (ν_4). These are assigned to $^3B_{1g}$ to $^3B_{2g}$ + ^3E_g and $^3B_{1g}$ to $^3A_{1g}$ + ^3E_g transitions in D_{4h} symmetry. The chloride and bromide have features of both types of spectra, low energy absorptions (ν_1) at 8800 and 8300 cm.$^{-1}$, respectively, and both have broad absorptions between 20,000 and 22,000 cm.$^{-1}$, consisting of two distinct bands (ν_4 and ν_5). The spectra of all the compounds have a strong absorption at 25,000 cm.$^{-1}$, probably due to a ligand transition.

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Table III

Reflectance Spectra^a of the Nickel(II)
Complexes of TAAB

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Compound	ν_1	ν_2	ν_3	ν_4	ν_5
Ni(TAAB)(ClO$_4$)$_2$	....	..	...	....	18,700
Ni(TAAB)(BF$_4$)$_2$	....	..	...	....	18,900
Ni(TAAB)[B(C$_6$H$_5$)$_4$]$_2$	....	9800	...	....	18,900
Ni(TAAB)Br$_2$·H$_2$O	8,300	..	...	20,000	22,000
Ni(TAAB)Cl$_2$·H$_2$O	8,800	..	...	20,000	22,000
Ni(TAAB)I$_2$	8,100	..	...	20,000	....
Ni(TAAB)(NO$_3$)$_2$	8,900	..	...	21,000	...
Ni(TAAB)(NCS)$_2$	10,500	..	11,900 (weak)	18,200	....

^{a} All bands given in cm.$^{-1}$.

These compounds are remarkably stable toward mineral acids, suffering no decomposition in boiling concentrated nitric, hydrochloric, or perchloric acids. Presumably this is associated with the cyclic nature of the ligand and the protective effect of coordination. Since in macrocyclic ligands there are no terminal groups which are capable of stepwise dissociation and protonation in the manner observed for the nickel polyamine complexes,[30] the complexes commonly resist dissociation in strong acid.

The coordinated ligand is sensitive to base. The reaction with base appears to involve the addition of water molecules across the Schiff base linkages to produce α-carbinolamines. This and reduction of the macrocyclic ring are the subjects of continuing investigation.

Reagents such as dimethylglyoxime and cyanide which normally react very quickly with nickel ion do not remove nickel ion from the macrocyclic compounds. The former is without effect while the latter produces the base reaction described above.

Fleischer, in recent X-ray studies,[31] has found that the porphyrin molecule itself is not planar, as had been thought for many years. In nickel etioporphyrin(I),

two of the pyrrole rings are bent up and two bent down from the plane. Copper tetraphenylporphin also has a nonplanar porphyrin, and the phenyl group is tilted both down from the porphyrin ring and out of the plane of the ring.[32] Models seem to indicate a similar situation for the macrocyclic ring reported here. The nitrogen atoms are in a plane around the metal atom; however, the benzene rings situated opposite one another are tilted down from the ring, while the other two slant up. They are also slightly twisted out of the plane of the ring. A single crystal X-ray structure determination should decide whether this is actually the case.[33]

The observed tetramerization of o-aminobenzaldehyde in the presence of metal ions bears a close resemblance to the cyclic tetramerization of phthalonitrile in the presence of metals or metal ions to form phthalocyanines.[34] Reflections on the mechanism of formation of this tetramer are certainly highly speculative at this time; however, it seems reasonable to suppose that the first stages in the building up of the macrocycle may involve a coordinated or uncoordinated amine group reacting with the aldehyde of another coordinated o-aminobenzaldehyde molecule to form a Schiff-base linkage coordinated to the metal through the nitrogen. This procedure may then be repeated until 3 moles of aminobenzaldehyde have reacted. The final ring closure must then involve the reaction of amine and aldehyde groups which are coordinated or very close to the metal atom. This may involve nucleophilic attack by an ionized amino group at the carbon atom of the aldehyde forming an α-carbinolamine intermediate. Subsequent loss of a water molecule would produce the Schiff-base link. The metal ion has a profound influence on the self-condensation of o-aminobenzaldehyde. In the absence of metal ions, a slow self-condensation occurs to form a different material, reported to be the trimer, trisanhydro-o-aminobenzaldehyde[35,36] (I). Seidel[37] also obtained this condensate in the absence of metal ions, but in the presence of zinc chloride, under anhydrous conditions, he obtained a compound reported as C$_7$H$_5$N·0.5ZnCl$_2$. This procedure has been repeated during the work reported herein, and the yellow product has been shown to exhibit an infrared spectrum similar to that obtained for the nickel and copper complexes of the tetrameric macrocycle. This compound should probably be formulated as [Zn(TAAB)][ZnCl$_4$].

The metal ion controlled condensation reactions reported here result in the formation of a species not obtained in the absence of the metal. Presumably these systems provide additional examples of the phenomena, described as coordination template reactions,[6,12,13] wherein the course of reaction of organic molecules is sterically determined by a metal ion.

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