Nickel(II) and Copper(II) Complexes Containing New Monocyclic and Polycyclic Ligands Derived from the Cyclotetrameric Schiff Base of o-Aminobenzaldehyde

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Nucleophilic addition reactions to cyclotetrameric Schiff base–nickel(II) and –copper(II) complexes have been extended to diol anions, amines, and diamines. The incorporation of two amine or alkoxyl functions into the complex is demonstrated by analytical, molecular weight, and mass spectral data. The resulting inner chelates which are stabilized by the macrocyclic chelate ring have been formulated as the partially solvolyzed complexes containing either two ionized α-amino ether or *gem*-diamine functions. With bis(2-hydroxyethyl)methylamine or bis(2-hydroxyethyl) sulfide as the nucleophile, a new and unusual "basket-like" polycyclic ligand is formed. These results are based on infrared, visible, and mass spectral evidence.

Introduction

Nucleophilic addition reactions involving the azomethine linkage of metal ion coordinated Schiff base ligands are well established.[2] The initial product in such reactions is considered to be a carbinolamine, or some derivative thereof, which is rarely isolated and characterized due to its low thermodynamic stability relative to the free amine and aldehyde or ketone.[3] The stability of the intermediate product has been demonstrated to be considerably enhanced for specific ligand systems in the presence of a metal ion.[4] The cyclotetrameric Schiff base–metal(II) complexes[5,6] derived from o-aminobenzaldehyde (1), hereafter referred to as M(TAAB)$^{2+}$, have been shown readily to yield partially solvolyzed neutral materials containing α-amino ether linkages (2). The attacking nucleophile in

1, M = Ni, Cu   2, R = CH₃, C₂H₅
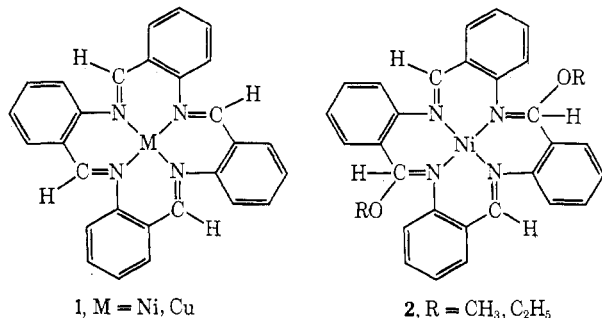
each documented example has been limited to alkoxide or hydroxide ion. This paper describes the preparation and characterization of the partially solvolyzed products of Ni(TAAB)$^{2+}$ and Cu(TAAB)$^{2+}$ employing amines as potential nucleophiles. We also wish to report our findings in more detail concerning the prepa-

ration of polycyclic ligands *via* nucleophilic addition reactions where alkoxide ion serves as the nucleophile.

Experimental Section

Materials.—o-Aminobenzaldehyde was prepared by the method of Smith and Opie.[7] Ni(TAAB)(BF₄)₂ and Cu(TAAB)(NO₃)₂ were prepared employing a previously described method.[8] All other chemicals were obtained from commercial sources and were of reagent grade or equivalent.

Preparation of Complexes. Ni(TAAB)[N(C₂H₅)₂]₂.—A solution prepared by dissolving 0.3 g of Ni(TAAB)(BF₄)₂ in 100 ml of water was added to 100 ml of diethylamine dissolved in 100 ml of water. The color of the solution changed immediately to red, and after stirring for 20 min a red precipitate appeared. The precipitate was filtered, washed with water, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr; yield ∼90%.

Ni(TAAB)[N(CH₃)₂]₂.—A solution of 1.0 g of Ni(TAAB)(BF₄)₂ dissolved in 150 ml of water was added slowly to a solution prepared by dissolving 50 ml of dimethylamine in 500 ml of water. A red precipitate appeared immediately; it was filtered and dried as previously described; yield ∼95%.

Ni(TAAB)(CH₃NCH₂CH₂NHCH₃)₂.—A solution of 0.25 g of Ni(TAAB)(BF₄)₂ in 75 ml of water was added to 50 ml of N,N'-dimethylethylenediamine. A similar isolation and drying procedure was carried out; yield ∼90%.

Ni(TAAB)[NH(CH₂)₅NH₂]₂.—To a solution of 1,5-diaminopentane (25 ml) dissolved in water (10 ml) was added a solution prepared by dissolving 0.25 g of Ni(TAAB)(BF₄)₂ in 25 ml of water. The color of the solution changed to red and after addition of 10 ml of water a red precipitate appeared. Stirring was continued for 1 hr. Red crystals were filtered and dried as previously described; yield ∼80%.

Ni(TAAB)(NHCH₂CH₂CH₂NH₂)₂.—This preparation is the same as above except that 1,3-diaminopropane was used.

Ni(TAAB)[CH₃N(CH₂CH₂O)₂].—Ni(TAAB)(BF₄)₂ (1.0 g) was dissolved in 100 ml of bis(2-hydroxyethyl)methylamine by stirring at room temperature for 10 hr. The resulting solution was filtered and added to another solution prepared by dissolving 0.3 g of sodium metal in 60 ml of bis(2-hydroxyethyl)methylamine. The color of the solution turned to cherry red while the solution was being stirred for 2 hr, after which 100 ml of water was slowly added and a red precipitate appeared. The solution was stirred an additional 30 min, filtered, washed with 1000 ml of water, and dried *in vacuo* over P₄O₁₀ at 100° for 12 hr; yield ∼70%.

Ni(TAAB)[S(CH₂CH₂O)₂].—A previously filtered solution of 0.55 g of Ni(TAAB)(BF₄)₂ dissolved in 50 ml of bis(2-hydroxyethyl) sulfide was added to a solution prepared by dissolving 0.15

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(2) J. P. Collman, *Transition Metal Chem.*, **2**, 2 (1966).

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(4) D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, **78**, 1137 (1956); B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 798 (1966).

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(6) V. Katović, L. T. Taylor, and D. H. Busch, *ibid.*, **91**, 2122 (1969).

(7) L. I. Smith and J. W. Opie, *Org. Syn.*, **28**, 11 (1948).

(8) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4834 (1964).

g of sodium metal in 10 ml of bis(2-hydroxyethyl) sulfide. The intensely red solution was stirred for 2 hr and after the addition of 100 ml of water a red precipitate appeared which was filtered and dried as described above; yield ~80%.

Ni(TAAB)[O(CH₂)₅OH]₂.—A saturated solution of Ni(TAAB)-(BF₄)₂ in 1,5-pentanediol was made by stirring 0.7 g of the complex in 100 ml of the diol for 2 days. The filtered solution from above was added to a solution prepared by dissolving 0.15 g of sodium metal in 100 ml of the diol. The intensely deep red solution was stirred for 2 hr, and after addition of 200 ml of water, a red precipitate appeared which was filtered and dried as described above; yield ~70%.

Cu(TAAB)[N(CH₃)₂]₂.—This preparation is the same as for Ni(TAAB)[N(CH₃)₂]₂ except that Cu(TAAB)(NO₃)₂ was used as the starting complex. An olive green precipitate was obtained, filtered, washed with water, and dried at room temperature for 12 hr *in vacuo*.

Cu(TAAB)[CH₃N(CH₂CH₂O₂)₂].—The preparation of this compound is similar to that described for Ni(TAAB)[CH₃N-(CH₂CH₂O)₂].

Cu(TAAB)[S(CH₂CH₂O)₂].—The preparation of this compound is similar to that described for Ni(TAAB)[S(CH₂CH₂O)₂].

Cu(TAAB)(OCH₃)₂.—One gram of Cu(TAAB)(NO₃)₂ dissolved in 300 ml of anhydrous methanol was slowly added to a solution prepared by dissolving 0.70 g of sodium metal in 175 ml of anhydrous methanol. After stirring for 20 min, the solution was filtered and the dark brown crystalline solid was washed with a small amount of methanol and air dried at room temperature.

Attempted Preparation of Ni(TAAB)(NH₂)₂.—To a concentrated NH₄OH solution (500 ml) was added slowly 1.0 g of Ni-(TAAB)(BF₄)₂ dissolved in 300 ml of water. Immediately a red precipitate appeared. It was filtered, washed with water, and dried *in vacuo* 12 hr over P₄O₁₀ at room temperature. *Anal.* Calcd for Ni(TAAB)[NH₂]₂: C, 66.82; H, 4.81; N, 16.70. Found: C, 66.95, 66.80; H, 4.71, 4.57; N, 14.74, 14.82.

Physical Measurements.—Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nujol and hexachlorobutadiene mulls, as well as KBr pellet techniques, were employed. Ultraviolet–visible spectra were obtained with a Cary Model 14 recording spectrophotometer. Spectra of solid samples were obtained by diffuse transmittance employing Nujol mulls impregnated on Whatman No. 1 filter paper.[9]

Molecular weight measurements were made with a Mechrolab Inc. Model 301A vapor pressure osmometer. Chloroform and 1,2-dichloroethane were used as solvents and the instrument was calibrated with solutions of benzil of known concentrations. Mass spectra were obtained with an AEI MS 9 mass spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday and Gouy methods using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The molar diamagnetic corrections for the ligands were calculated from Pascal's constants.[10] Analyses were performed by Galbraith Microanalytical Laboratories and in this laboratory using an F & M carbon–hydrogen–nitrogen analyzer.

Results and Discussion

Nucleophilic addition reactions of coordinated ligands involving Ni(TAAB)²⁺ complexes have been extended to diol anions, amines, and diamines. Specifically the nucleophiles are ammonia, dimethylamine, diethylamine, *N,N'*-dimethylethylenediamine, *N,N,N'*-trimethylethylenediamine, 1,3-diaminopropane, 1,5-diaminopentane, 1,5-pentanediol anion, bis(2-hydroxyethyl)methylamine dianion, and bis(2-hydroxyethyl) sulfide dianion. Similar reactions involving Cu(TAAB)²⁺

(9) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).
(10) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960.

have been performed with methoxide ion, bis(2-hydroxyethyl)methylamine dianion, bis(2-hydroxyethyl) sulfide dianion, and dimethylamine. In general the reactions are readily carried out at room temperature in aqueous solution by allowing excess nucleophile and M(TAAB)²⁺ to interact. The precipitation of the water-insoluble neutral complex after a second nucleophilic addition apparently precludes further reaction which would lead to the production of anionic chelates.

The resulting neutral complexes are soluble in nonpolar and chlorinated organic solvents and may be viewed as containing two azomethine donors and either two ionized α-amino ether donors (3) (*i.e.*, diol
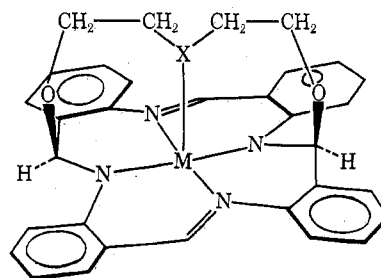
3, M = Ni, Cu
X = S, NCH₃

anion or alkoxide as the nucleophile) or two ionized *gem*-diamine donors (4) (*i.e.*, amine or diamine as the
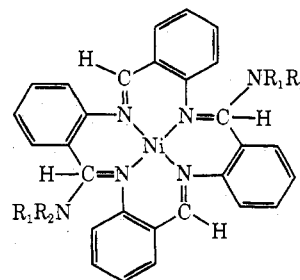
4, R₁ = H, R₂ = H
R₁ = CH₃, R₂ = CH₂CH₂NH(CH₃)
R₁ = CH₃, R₂ = CH₃
R₁ = C₂H₅, R₂ = C₂H₅
R₁ = CH₃, R₂ = CH₂CH₂N(CH₃)₂
R₁ = H, R₂ = CH₂CH₂CH₂NH₂
R₁ = H, R₂ = (CH₂)₅NH₂

nucleophile) where only the ionized amine is coordinated. It is not possible to achieve the protonated form since acid reverses the addition of nucleophile and regenerates M(TAAB)²⁺.

The composition and gross structural features of the solvolyzed products have been ascertained from elemental analysis, molecular weight measurements, magnetic susceptibility measurements, and infrared, visible, and mass spectral results.

Reaction Products Formed *via* Ammonolysis.—Elemental analysis and molecular weight data (Table I) for these intensely red materials indicate that only two Schiff base linkages have undergone ammonolysis. Infrared spectra of these compounds have several features in common: (a) the absence of bands due to

TABLE I
ANALYTICAL DATA FOR THE NICKEL(II) AND COPPER(II) COMPLEXES

	Analyses, %													
Compound	C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	S Calcd	S Found	Ni Calcd	Ni Found	Cu Calcd	Cu Found	Mol wt Calcd	Mol wt Found
Ni(TAAB)[N(CH₃)₂]₂	68.71	68.95	5.77	5.87	15.03	14.76	...	...	10.50	10.32	...	...	559	556^a
Ni(TAAB)[N(C₂H₅)₂]₂	70.25	70.00	6.55	6.67	13.66	13.55	...	...	9.54	9.70	...	...		
Ni(TAAB)[N(CH₃)CH₂CH₂NHCH₃]₂	66.97	66.60	6.57	6.53	17.36	17.07	...	...	9.09	9.25	...	...		
Ni(TAAB)[N(CH₃)CH₂CH₂N(CH₃)₂]₂	67.75	67.64	6.90	6.75	16.64	16.53	...	...	8.72	8.57	...	...	674	680^a
Ni(TAAB)[NHCH₂CH₂CH₂NH₂]₂	66.13	65.92	6.22	6.07	18.45	18.01	...	...	9.56	9.65	...	...		
Ni(TAAB)[NH(CH₂)₅NH₂]₂	67.76	67.24	6.88	7.09	16.64	16.87	...	...	8.72	9.02	...	...		
Ni(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	67.36	67.19	5.32	5.43	11.91	11.82	...	...	9.98	10.10	...	...	588	589–600^b
Ni(TAAB)[OCH₂CH₂SCH₂CH₂O]	64.98	64.70	4.78	4.75	9.48	9.36	5.42	5.27	9.93	9.72	...	...		
Ni(TAAB)[O(CH₂)₃OH]₂	67.35	66.82	6.26	6.32	8.27	8.39	...	...	8.66	8.91				
				6.07		7.99				8.22				
Cu(TAAB)[N(CH₃)₂]₂	67.87	67.69	6.06	5.94	14.89	14.62	...	...	...	...	11.22	11.02	564	550^a
Cu(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	66.81	66.91	5.28	5.38	11.81	11.63	...	...	...	...	10.71	10.78	593	610^b
Cu(TAAB)[OCH₂CH₂SCH₂CH₂O]	64.46	64.24	4.74	4.83	9.40	9.23	5.37	5.17	...	...	10.66	10.46	596	580^b
Cu(TAAB)[OCH₃]₂	66.96	66.39	4.87	4.77	10.41	10.81	...	...	...	...	11.81	12.25		
		66.30		5.08		10.50		...		...		12.11		

^{a} Chloroform. ^{b} 1,2-Dichloroethane.

NO₃⁻ and BF₄⁻, (b) the disappearance of a band at 1568 cm⁻¹ originally present in M(TAAB)²⁺ and assigned to the C=N stretching vibrational mode and the appearance of a new band at 1529 cm⁻¹ which has been assigned as a stretching vibration of the two remaining azomethine linkages, and (c) the presence of bands in the 2950-, 1465-, and 1350-cm⁻¹ regions which can be attributed to aliphatic C–H stretching and bending vibrations.[11] In addition the spectra of a few derivatives have several totally unique bands. The identifying features in the spectra of these derivatives are listed below.

M(TAAB)[N(CH₃)₂]₂: (a) two bands of medium intensity at 2817 and 2770 cm⁻¹ which may be assigned to the symmetric and asymmetric C–H stretching frequencies for *gem*-dimethyl groups attached to nitrogen; (b) the absence of absorptions due to N–H and O–H vibrational modes.

Ni(TAAB)[N(CH₃)CH₂CH₂NH(CH₃)]₂: (a) one medium-intensity sharp band at 3267 cm⁻¹ due to a secondary N–H stretching mode; (b) two strong-intensity bands at 2825 and 2770 cm⁻¹ assigned to the C–H stretching modes of the nitrogen bonded methyl group.

Ni(TAAB)[N(CH₃)CH₂CH₂N(CH₃)₂]₂: (a) the absence of absorptions due to N–H stretching modes in the 3500–3100-cm⁻¹ region; (b) bands characteristic of methyl groups bonded to nitrogen.

Ni(TAAB)[NHCH₂CH₂CH₂NH₂]₂ and Ni(TAAB) [NH(CH₂)₅NH₂]₂: a medium sharp doublet at 3353 and 3322 cm⁻¹ with a shoulder on the low-energy side of the doublet assigned to the symmetric and asymmetric primary N–H and secondary N–H stretching modes.

Ni(TAAB)(NH₂)₂: the presence of two bands at 3355 and 3278 cm⁻¹ due to an NH₂ group. Repeated syntheses and analyses generally failed to establish our success in obtaining pure samples of this compound. We infer its existence on the basis of approximate analyses, expected infrared spectral features, and its mass spectrum. It appears that some of the NH₂ is replaced by OH in the products generally obtained. As shown earlier, the presence of OH in such structures is accompanied by further reactions.[5]

(11) N. B. Colthup, K. H. Daly and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

TABLE II
MASS SPECTRA OF THE NICKEL(II) AND COPPER(II) COMPLEXES

	Assignment^a			
Compd	M-(TAAB)-X₂⁺	M-(TAAB)-X⁺	M-(TAAB)⁺	TAAB⁺
Ni(TAAB)(NH₂)₂	6.2	24.0	100.0	...
Ni(TAAB)[N(CH₃)₂]₂	2.0	9.0	100.0	12.0
Ni(TAAB)[N(C₂H₅)₂]₂	0.7	13.0	100.0	6.0
Ni(TAAB)[N(CH₃)CH₂CH₂NH(CH₃)]₂	2.0	15.0	100.0	...
Ni(TAAB)[N(CH₃)CH₂CH₂N(CH₃)₂]₂	...	7.0	100.0	14.0
Ni(TAAB)[NHCH₂CH₂CH₂NH₂]₂	...	20.0	100.0	13.0
Cu(TAAB)[N(CH₃)₂]₂	3.0	6.0	22.0	100.0
Cu(TAAB)(OCH₃)₂	12.0	6.0	60.0	100.0

^{a} Numbers indicate weighted mass peak intensity.

Mass spectral data (Table II) indicate that **3** represents the correct composition of the solvolyzed tetramer. As was found with the alkoxide adducts, the most intense mass peak does not correspond to the intact solvolysis product but rather to an ion of the formulation Ni(TAAB)⁺. Under conditions required to obtain the mass spectra of these compounds, the nucleophiles are for the most part cleaved from the macrocyclic ring and only weak signals corresponding to the Ni(TAAB) unit plus one and two nucleophile moieties are observed. Those compounds absent from Table II either decomposed before subliming or possessed an extremely low vapor pressure which prevented adequate mass spectral measurement. High-resolution mass measurements have been obtained with Ni(TAAB)[N(C₂H₅)₂]₂. These are in excellent agreement with the proposed formulation and are given in Table III.

TABLE III
HIGH-RESOLUTION MASS MEASUREMENTS OF
Ni(TAAB)[N(C₂H₅)₂]₂

Nominal mass	Mass obsd	Assignment	Mass calcd	ΔM, ppm
614	614.267106	Ni(TAAB)[N(C₂H₅)₂]₂⁺ NiC₃₆H₄₀N₆	614.266727	1
542	542.186536	Ni(TAAB)[N(C₂H₅)₂]⁺ NiC₃₂H₃₀N₆	542.185407	2
470	470.105266	Ni(TAAB)⁺ NiC₂₈H₂₀N₄	470.104087	2.3

The lone ammonolyzed copper complex also exhibits a weak-intensity mass peak assignable to a parent ion (*i.e.*, Cu(TAAB)[N(CH₃)₂]₂⁺). Unlike the nickel compounds, the most intense mass peak corresponds to the metal-free tetrameric macrocyclic ligand.

TABLE IV

ROOM-TEMPERATURE MAGNETIC PROPERTIES OF THE
NICKEL(II) AND COPPER(II) COMPLEXES

Compd	$10 \chi_M$, cgsu	μ_{eff}, BM	Temp, °K
Ni(TAAB)[N(CH₃)₂]₂	+5	...	297
Ni(TAAB)[N(C₂H₅)₂]₂	−173	...	296
Ni(TAAB)[N(CH₃)CH₂CH₂NHCH₃]₂	−193	...	297
Ni(TAAB)[N(CH₃)CH₂CH₂N(CH₃)₂]₂	−166	...	297
Ni(TAAB)[NHCH₂CH₂CH₂NH₂]₂	−255	...	297
Ni(TAAB)[NH(CH₂)₅NH₂]₂	−234	...	297
Ni(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	−92	...	297
Ni(TAAB)[OCH₂CH₂SCH₂CH₂O]	+12	...	296
Ni(TAAB)[O(CH₂)₅OH]₂	+105	1.05	296
Cu(TAAB)[N(CH₃)₂]₂	1703	2.16	297
Cu(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	1570	2.10	296
Cu(TAAB)[OCH₂CH₂SCH₂CH₂O]	1877	2.26	295
Cu(TAAB)[OCH₃]₂	1276	1.90	295

Magnetic susceptibility measurements (Table IV) support **4** as the structure of the solvolyzed products in that the new nickel compounds are diamagnetic or feebly paramagnetic. The slight paramagnetism can

$NH(CH_3)_2$, 1,3-diaminopropane, and 1,5-diaminopentane adducts have similar properties). Ammonolysis of the ligand along with axial perturbation of the metal ion would be considerably less favorable for dimethylamine than for the diamines. Infrared spectra of the 1,3-diaminopropane and 1,5-diaminopentane adducts lend evidence to this conclusion in that the N–H stretching vibration in the free diamine and diamine adduct appear at the same energy. Coordination by the amino group should result in shifting the N–H stretching mode to lower energy.

$Cu(TAAB)[N(CH_3)_2]_2$ has a normal magnetic moment and it is expected to have a structure similar to its nickel analog.

The visible spectra (Table V, Figure 1) provide further evidence concerning the structure of the complexes. No absorption bands are observed below 15,000 cm⁻¹. The spectrum of each compound has three predominant bands in the 6000–30,000-cm⁻¹ region. The high extinction coefficients for these band

TABLE V

ELECTRONIC ABSORPTION SPECTRA (CM⁻¹) OF THE NICKEL(II) AND COPPER(II) COMPLEXES[a,b]

Compd	Medium	ν_1	ν_2	ν_3	ν_4
Ni(TAAB)(NH₂)₂	CHCl₃		18,250 (5800)	19,230 sh	26,880 (11,400)
Ni(TAAB)[N(CH₃)₂]₂	CHCl₃	~15,500 vw	18,250 (10,090)	19,230 sh	26,880 (14,210)
	Nujol	...	17,300	19,300 sh	25,640
Ni(TAAB)[N(C₂H₅)₂]₂	CHCl₃	15,800 (300)	18,200 (6500)	19,400 sh	26,700 (12,300)
	CH₂Cl₂		18,100 (9500)	19,300 sh	26,300 (12,600)
	DMF	15,400 (470)	18,100 (9200)	19,300 sh	26,300 (11,950)
	Nujol	~15,400 vw	17,500	19,500 sh	26,700
Ni(TAAB)[N(CH₃)CH₂CH₂NH(CH₃)]₂	CHCl₃	~15,500 vw	18,200 (9400)	19,200 sh	26,800 (13,200)
	Nujol	~15,400 vw	17,550	18,870 sh	25,600
Ni(TAAB)[N(CH₃)CH₂CH₂N(CH₃)₂]₂	CHCl₃	...	18,200 (9100)	19,200 sh	27,000 (13,600)
Ni(TAAB)[NHCH₂CH₂CH₂NH₂]₂	CHCl₃	~15,500 vw	18,200 (8800)	19,300 sh	26,800 (11,200)
	Nujol	~15,500 vw	17,400	18,200 sh	25,600
Ni(TAAB)[NH(CH₂)₅NH₂]₂	CHCl₃	15,400 (420)	18,200 (8800)	19,300 sh	26,800 (12,600)
Ni(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	CHCl₃	15,800 (700)	18,200 (6500)	19,400 sh	26,700 (12,300)
	Nujol	15,300	18,000	19,000 sh	26,300
Ni(TAAB)[OCH₂CH₂SCH₂CH₂O]	CHCl₃	15,600 (1450)	18,400 (4850)	19,300 sh	27,200 (11,500)
Ni(TAAB)[O(CH₂)₅OH]₂	CHCl₃	15,600 (1200)	18,200 (3300)	19,300 sh	27,400 (12,500)
Cu(TAAB)[N(CH₃)₂]₂	CHCl₃	11,830 (720)	22,000 (17,200)	...	...
Cu(TAAB)[OCH₂CH₂SCH₂CH₂O]	CHCl₃	11,400 (500)	22,000 (11,300)	...	27,000 (5400)
Cu(TAAB)[OCH₃]₂	CHCl₃	11,700 (774)	22,200 (34,000)	...	...
Cu(TAAB)[OCH₂CH₂N(CH₃)CH₂CH₂O]	CHCl₃	11,670 (530)	22,000 (12,200)	...	27,000 (6800)

[a] Abbreviations: sh, shoulder; vw, very weak. [b] Numbers in parentheses are molar extinction coefficients.

be ascribed to temperature-independent paramagnetism and/or insufficient correction for diamagnetism employing Pascal's constants. This result precludes the possibility that the two nucleophiles are strongly coordinated to Ni(TAAB)²⁺ in axial positions since this situation requires the nickel(II) ion to be paramagnetic.[12] Nickel ion in either a four-coordinate square-planar environment or a five- or six-coordinate environment achieved by a weak axial perturbation on the strong square-planar field is consistent with this low magnetic moment.[13] The five- or six-coordinate structure seems unlikely since all compounds have similar chemical and physical properties regardless of the nucleophile (*i.e.*,

maxima indicate they are not due solely to d–d transitions but rather are parity-allowed transitions. The number and positions of the bands correspond well with the metallophthalocyanine[14] and metalloporphyrin[15] spectra and suggest that the electronic spectra of the solvolyzed products might be interpreted in a similar manner since they also possess a highly conjugated ligand system. Using the terminology employed for the porphyrin ring system,[16] ν_2 and ν_3 correspond to the α and β bands, respectively, and ν_4 would be analogous to the Soret band.

The lowest energy band, ν_1, is 10–15 times less intense and considerably broader than the remaining

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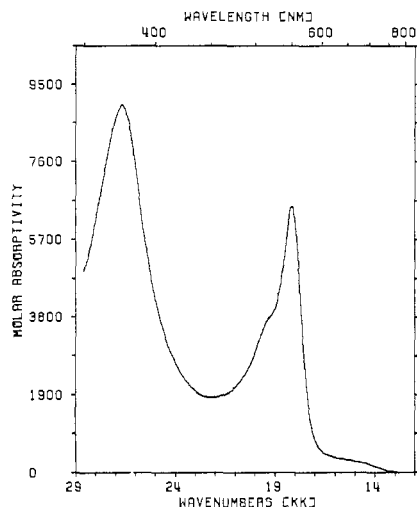(16) M. Gouterman, *J. Mol. Spectrosc.*, **6**, 138 (1961).

Figure 1.—Electronic spectrum of $Ni(TAAB)[N(C_2H_5)_2]_2$ in $CHCl_3$.

three bands. Assignment of this band to an electronic transition is no easy task. The band appears to varying extents in the solution spectra of all materials. In 1,2-dichloroethane this band displays the greatest intensity. We feel that this band may arise in possibly four ways: (1) charge-transfer transition involving the solvent since the position of the band is solvent dependent, (2) d–d transition characteristic of five-coordinate low-spin nickel(II),[17] (3) a parity-allowed transition arising from application of a low-symmetry component on either the α or β band (*i.e.*, the solvolyzed products, at best, have D_{2h} symmetry while the metalloporphyrins have D_{4h} symmetry), and (4) a transition resulting from a new species formed by reaction between the solvent and solvolyzed product (*i.e.*, on standing in chlorinated solvent $M(TAAB)^{2+}$ is regenerated probably due to the slightly acidic nature of the solvents).

Reaction Products Obtained by Alcoholysis.—Analytical data (Table I) indicate that only two azomethine linkages are solvolyzed when $M(TAAB)^{2+}$ reacts with a molar equivalent of either bis(2-hydroxyethyl)methylamine (LN) or bis(2-hydroxyethyl) sulfide (LS). Theoretically the resulting materials may be polymeric with LS or LN bridging two $M(TAAB)^{2+}$ units or monomeric in which each nucleophile is bound to only one $M(TAAB)^{2+}$ unit. Molecular weight measurements in solution indicate the latter to be the case. Decomposition upon sublimation made mass spectral measurements meaningless.

$Ni(TAAB)^{2+}$ was also treated with 1,5-pentanediol to yield the bis-diol adduct. Elemental analysis sup-

ports this assignment along with infrared data which show a medium broad band centered at 3400 cm^{-1} due to a hydrogen-bonded O–H stretching mode. The LN and LS adducts of both copper and nickel complexes show no absorption bands in the O–H stretching region. All three diol adducts have the infrared bands characteristic of other solvolyzed $M(TAAB)^{2+}$. In acid media, the alkoxide group is eliminated, leading to regeneration of $M(TAAB)^{2+}$.

Although the $Ni(TAAB)^{2+}$:nucleophile ratio differs (1:1 or 1:2), all of these materials have somewhat similar magnetic and electronic spectral properties. Each one contains low-spin Ni(II) on the basis of its magnetic susceptibility, and exhibits predominantly three absorption bands in exactly the same positions as found for the other solvolyzed materials.[18] The lowest energy band, ν_1, is considerably enhanced for the LN and LS adducts when compared with other adducts. It is tempting to attribute this transition to low-spin five-coordinate nickel(II) since only one alkoxide ion of each 1,5-pentanediol reacted, whereas both react when a nitrogen or sulfur atom is in the center of the chain. We suggest that weak coordination of this central atom at the axial position holds the diol in such a position that both alkoxide ions of the diol react with two *trans*-azomethine linkages of $M(TAAB)^{2+}$ giving complexes of **3** in which a new and unusual "basket-like" polycyclic ligand has formed. We also suggest that the axial perturbation in the final complexes probably alters the electronic properties produced by the strong in-plane field very little.

The methoxide adduct of $Cu(TAAB)^{2+}$ has also been prepared. The data collected on this material are tabulated in Tables I, II, IV, and V and are consistent with formulation of one $Cu(TAAB)^{2+}$ unit plus two methoxide moieties which is analogous to the methoxide adduct of $Ni(TAAB)^{2+}$ that has been previously[5] reported. A structure similar to that of $Ni(TAAB)(OCH_3)_2$ is postulated.

(18) The magnetic susceptibility of the 1,5-pentanediol derivative consistently reveals the presence of some paramagnetic material. The substance is very sensitive to traces of acid and its solubility characteristics cause it to be extremely difficult to purify. In consequence we conclude that the small apparent magnetic moment is due to the presence of reproducible amounts of impurities. The residual paramagnetism observed for all the remaining compounds is of the magnitude expected to arise from temperature-independent contributions.

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