α-Amino Ether and Carbinolamine Derivatives of the Nickel(II) Complex of the Cyclotetrameric Schiff Base of *o*-Aminobenzaldehyde

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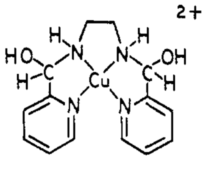
Abstract: The reaction of a cyclotetrameric Schiff base nickel(II) complex (**5**) with alkoxide ions results in the incorporation of two alkoxyl functions into the complex as shown by analytical, molecular weight, and mass spectral data. The resulting inner chelates have been formulated as the partially solvolyzed complexes containing two ionized α-amino ether functions stabilized by the macrocyclic chelate ring. This result is based on infrared, visible, and nmr spectral evidence. With hydroxide ion as the nucleophile, a discrete α-carbinolamine derivative is not obtained owing to further reactions and an apparent instability of this derivative.

The metal ion labilization of a Schiff base toward hydrolysis *via* chelate formation has been demonstrated with a variety of ligands and metal ions.[2] These hydrolysis reactions result in either the production of a carbinolamine intermediate (**1**) or complete reversal of the Schiff base formation leading to regeneration of the primary amine (**2**) and the aldehyde or ketone (**3**). In such metal-ion-catalyzed reactions,

$$\underset{\mathbf{1}}{R_1R_2C{=}NR_3 \rightleftharpoons R_1R_2C(OH)NHR_3} \rightleftharpoons \underset{\mathbf{2}}{R_3NH_2} + \underset{\mathbf{3}}{R_1R_2C{=}O}$$

intermediate solvolysis products, *i.e.*, carbinolamines (**1**) or carbinolamine ethers ($R_1R_2C(OR_4)NHR_3$), rarely have been isolated and characterized.

A partial hydrolysis product of the tetradentate ligand N,N′-bis(2′-pyridylmethylene)-1,2-ethanediamine has been isolated as the copper(II) chloride derivative.[3] Infrared evidence indicated water had added across both azomethine bonds to give the complex denoted in **4**. Alcohols also react with the parent copper complex, but only one azomethine linkage is attacked.[4] An X-ray structural determination has confirmed this formulation as well as revealed that the partially solvolyzed copper(II) complex is five-coordinate.[5]



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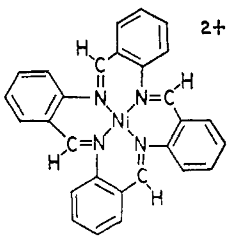
The macrocyclic Schiff base chelates[6,7] derived from *o*-aminobenzaldehyde are of particular interest in regard to this subject. The self-condensation reaction of *o*-aminobenzaldehyde in the presence of nickel(II) ions has been shown to yield two products, one of which is a nickel(II) complex of the closed macrocyclic tetrameric condensate, tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13] tetraazacyclohexadecine (**5**), referred to as TAAB. The other product was determined to be a nickel(II) complex containing an analogous closed trimeric condensate, hereafter referred to as TRI. This paper describes the preparation and characterization of the partially solvolyzed products of $[Ni(TAAB)]^{2+}$.



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Experimental Section

Materials. *o*-Aminobenzaldehyde was prepared by the method of Smith and Opie.[8] The preparation of $[Ni(TAAB)](BF_4)_2$ was similar to the previously described preparation[6] of $[Ni(TAAB)](ClO_4)_2$ except that sodium fluoroborate was substituted for sodium perchlorate. All other chemicals were obtained commercially and were of reagent grade or equivalent.

Reaction of Tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecinenickel(II) Fluoroborate with Sodium Ethoxide. To a solution prepared by dissolving 0.70 g (0.03 g-atom) of sodium metal in 175 ml of anhydrous ethanol was slowly added 1.0 g (0.0016 mole) of $[Ni(TAAB)](BF_4)_2$ dissolved in 1200 ml of ethanol. After stirring for 20 min, the solution was filtered and the dark maroon microcrystalline solid was washed with a small amount of ethanol and air-dried at room temperature. *Anal.* Calcd for $C_{32}H_{30}N_4O_2Ni$: C, 68.45; H, 5.35; N, 9.98; Ni, 10.46; $C_2H_5O^-$, 16.06; mol wt, 561. Found: C, 68.26; H, 5.56; N, 10.04; Ni, 10.21; $C_2H_5O^-$, 16.18; mol wt, 560, 547; μ_{eff}, 0.12 BM.

Reaction of Tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecinenickel(II) Fluoroborate with Sodium Methoxide. To a solution prepared by dissolving 2.10 g (0.09 g-atom) of sodium metal in 600 ml of anhydrous methanol was slowly added 3.0 g (0.0047 mole) of

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[1] National Institutes of Health Postdoctoral Fellow, 2-F2-GM-091-02.

[2] C. M. Harris, S. L. Lenzer, and R. L. Martin, *Aust. J. Chem.*, **14**, 420 (1961); G. L. Eichhorn and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 2905 (1953); G. L. Eichhorn and N. D. Marchand, *ibid.*, **78**, 2688 (1956); A. Namahana, *Bull. Chem. Soc. Jap.*, **32**, 1195 (1959).

[3] D. H. Busch and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **78**, 1137 (1956).

[4] C. M. Harris and E. D. McKenzie, *Nature*, **196**, 670 (1962).

[5] B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 798 (1966).

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

[7] G. A. Melson and D. H. Busch, *ibid.*, **87**, 1706 (1965); L. T. Taylor, S. C. Vergez, and D. H. Busch, *ibid.*, **88**, 3171 (1966).

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

[Ni(TAAB)]$(BF_4)_2$ dissolved in 1200 ml of methanol. After stirring for 20 min, the solution was filtered and the dark red solid was washed with methanol and air-dried at room temperature. *Anal.* Calcd for $C_{30}H_{26}N_4O_2Ni$: C, 67.56; H, 4.88; N, 10.50; Ni, 11.01; CH_3O^-, 11.63. Found: C, 67.27; H, 4.97; N, 10.76; Ni, 11.23; CH_3O^-, 11.93; μ_{eff}, 0.54 BM.

Attempted Reactions of Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinenickel(II) Fluoroborate with Hydroxide. (1) To an approximately 0.25 *M* aqueous sodium hydroxide solution (400 ml) was slowly added 1.0 g (0.0016 mole) of Ni(TAAB)$(BF_4)_2$ dissolved in 400 ml of distilled water. After stirring for 30 min, the solution was filtered and the dark maroon solid was washed with water and dried at room temperature. *Anal.* Calcd for [Ni(TAAB + $2OH^-$)]: C, 66.56; H, 4.39; N, 11.09. Found:[9] C, 59.6, 59.0, 57.43; H, 4.25; 4.05, 4.43; N, 9.85, 9.65, 9.53; Na, 0.40.

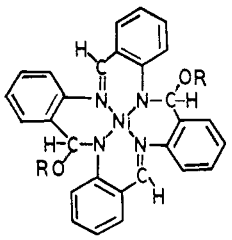
(2) To a solution prepared by adding 30 ml of approximately 1.0 *M* sodium hydroxide to 400 ml of dimethylformamide was slowly added 1.0 g (0.0016 mole) of [Ni(TAAB)]$(BF_4)_2$ dissolved in 300 ml of dimethylformamide. After stirring for 10 min, water was added to the red solution until a definite cloudiness of the solution persisted, after which the solution was cooled overnight. The microcrystalline red solid which formed was filtered and dried at 205° under vacuum in order to remove solvated dimethylformamide. *Anal.* Found: C, 63.12, 63.34; H, 5.30, 5.35; N, 13.13, 13.22; Ni, 13.83, 13.70.

(3) To 700 ml of concentrated ammonium hydroxide was added 1.0 g (0.0016 mole) of [Ni(TAAB)]$(BF_4)_2$ dissolved in 400 ml of distilled water. After stirring for 20 min, the solution was filtered and the dark red solid was washed with water and dried at room temperature. *Anal.* Found: C, 66.95, 69.4, 70.1, 68.8; H, 4.81, 4.90, 4.71, 5.15; N, 14.4, 14.8, 14.74, 15.1.

Physical Measurements. Magnetic susceptibilities were obtained at room temperature by the Faraday method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The molar diamagnetic corrections for the ligands were calculated from Pascal's constants.[10] Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 and Beckman IR-9 recording spectrophotometer. Nujol mull and potassium bromide pellet techniques were employed. Ultraviolet–visible spectra were obtained with a Cary Model 14 recording spectrophotometer. Molecular weight measurements were made with a Mechrolab, Inc. Model 301A vapor pressure osmometer. Chloroform was used as the solvent, and the instrument was calibrated with solutions of benzil of known concentration. Mass spectra were obtained with an AEI MS 9 mass spectrometer. We are indebted to Dr. Peter Thornton, Ohio State University, for this measurement. Nuclear magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer at Case Western Reserve University by Mr. Roger S. Downing and with a Varian HA 60 nmr spectrometer at Battelle Memorial Institute, Columbus, Ohio. We are indebted to Dr. Tom Page for the latter measurements. Analyses were performed by Galbraith Microanalytical Laboratories, Schwarzkopf Microanalytical Laboratories, Micro-Analysis, Inc., and in this laboratory using a F & M carbon, hydrogen, nitrogen analyzer.

Results

The reaction of $[Ni(TAAB)]^{2+}$ with methoxide or ethoxide ions yields the unusual compound **6**, where R = CH_3 or C_2H_5 (the alkoxyl groups have arbitrarily been placed in *trans* position). The resulting inner chelates are soluble in nonpolar solvents and may be viewed as containing two azomethine donors and two ionized α-amino ether donors. It is not possible to achieve the protonated form of the α-amino ether complexes since the presence of acid reverses the addition of alkoxide and regenerates $[Ni(TAAB)]^{2+}$, a behavior typical of α-amino ether compounds.[11] Other than this sensitivity to acid, the partially solvolyzed complexes appear to be quite stable.



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The reactivity of the imine carbon atoms in $[Ni(TAAB)]^{2+}$ toward nucleophilic attack is assisted by the electron-withdrawing influence of the metal ion bound to the adjacent nitrogen atom. The presence of the macrocyclic chelate ring system, however, prevents the complete degradation of the complex by stabilizing the partially solvolyzed product. Further solvolysis would require the disruption of the fused chelate ring system, a highly unfavorable process. The precipitation of the insoluble inner complex after the addition of two alkoxide ions apparently precludes further nucleophilic attack which would lead to the production of anionic chelates.

The experimental data upon which the above conclusions are drawn will now be discussed in detail. The composition of the solvolyzed complexes has been obtained from elemental analyses, including alkoxyl determinations, and is supported by molecular weight determinations in benzene and mass spectral results (*vide infra*).

A comparison of the infrared spectra of the alkoxide adducts with the spectrum of the parent $[Ni(TAAB)]^{2+}$ provides evidence as to the structure of the solvolyzed products. The presence of the alkoxyl groups is indicated[12] by the appearance of absorption bands at 1336, 1358, and 1470 cm^{-1} and in the region 2850–3000 cm^{-1}. No bands appear between 3000 and 4000 cm^{-1} indicating the absence of –NH and –OH groups. The absorption band at 1568 cm^{-1} in the spectrum of $[Ni(TAAB)]^{2+}$ (Figure 1) has been determined by catalytic hydrogenation of $[Ni(TAAB)]^{2+}$ to be the –C=N– stretching vibrational mode.[13] An equally intense band does appear at 1529 cm^{-1} in the spectra of the alkoxide derivatives and is assigned to the stretching vibration of the two remaining azomethine groups. This decreased –C=N– stretching frequency reflects increased electron delocalization within the azomethine containing chelate rings. Two of the four nitrogen donor atoms in the alkoxide derivatives are trigonal and have a filled orbital of π symmetry. As a result the two six-membered chelate rings not involving alkoxyl groups may have an appreciable amount of delocalization. This necessitates a decreased bond order for the remaining azomethine linkages and a lowering of their stretching frequency. The nondiminishing intensity of the –C=N– stretching vibration is probably due to the delocalized dinegative charge on the macrocyclic ligand which allows for a larger change in dipole moment during the stretching vibration.

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(9) Representative analyses found on three independent preparations.

(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.

(11) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

(12) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 197.

(13) F. L. Urbach, G. A. Melson, and D. H. Busch, to be submitted for publication.

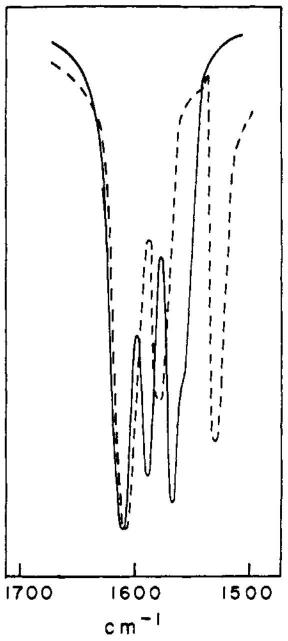


Figure 1. Infrared spectra of [Ni(TAAB)]$(BF_4)_2$ (——) and [Ni(TAAB + $2C_2H_5O^-$)] (- - - -).

Mass spectral data (Figure 2) indicate that **6** represents the correct composition of the solvolyzed tetramer. The most intense mass peaks, however, do not correspond to the intact solvolysis product with two added alkoxide residues but rather to an ion of the formulation $[Ni(TAAB)]^+$. Under the conditions necessary to obtain the mass spectra of these compounds, the alkoxyl groups are for the most part cleaved from the macrocyclic ring. A portion of the adducts does persist, however, and weak signals corresponding to the [Ni(TAAB)] unit plus one and two alkoxide moieties are observed. The ion $[Ni(TAAB)]^+$ suggests the possible existence of a Hückel aromatic ligand derived from TAAB by a two-electron reduction. The suggested material, neutral [Ni(TAAB)], would contain a similar macrocyclic ring to phthalocyanine[14] or porphyrin.[15]

Magnetic susceptibility measurements support **6** as the structure of the solvolyzed products in that the new compounds are diamagnetic, suggesting that the nickel ion resides in a square-planar environment.[16] This result precludes the possibility that the two alkoxyl groups are coordinated to the nickel ion in axial positions since this situation requires that the nickel ion be paramagnetic.[16]

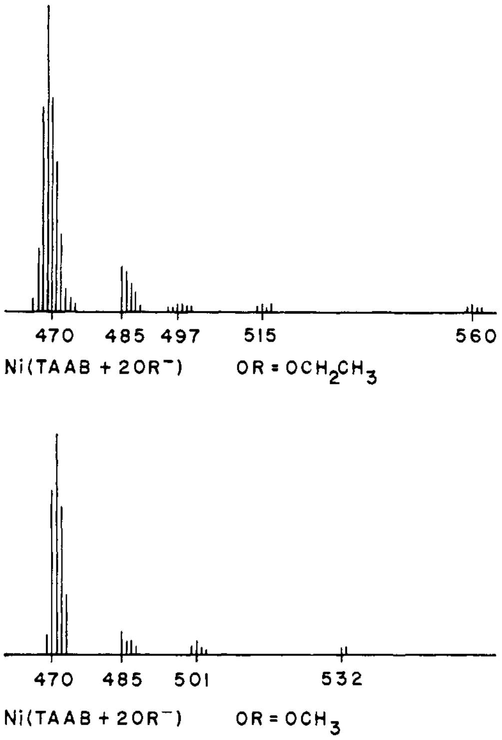


Figure 2. Mass spectra of the alkoxyl derivatives of $[Ni(TAAB)]^{2+}$.

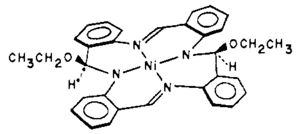
Table I. Electronic Spectra of Alkoxyl Derivatives of $[Ni(TAAB)]^{2+}$

Compound	ν_{max}, cm^{-1} [a]
[Ni(TAAB + $2CH_3O^-$)]	18,200 (9412)
	19,200 sh[b]
	26,800 (13,137)
	38,600 (51,000)
[Ni(TAAB + $2C_2H_5O^-$)]	18,200 (8876)
	19,000 sh
	26,800 (12,690)
	38,500 (51,200)

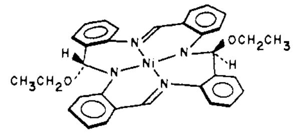
[a] Extinction coefficients in parentheses. [b] Shoulder.

The visible spectra (Table I) provide further evidence that these complexes are square planar. No absorption bands are observed below 18,000 cm⁻¹. The high extinction coefficients for the band maxima indicate they are not due solely to d-d transitions but rather are parity-allowed transitions.[17] 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 alkoxyl derivatives might be interpreted in a similar manner.

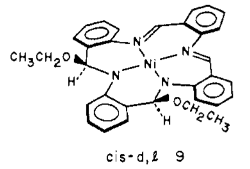
Stereoisomers. The solvolyzed tetramer macrocycles may exist in four stereoisomeric forms shown in **7–10**. The *cis–trans* designation refers to the relative placement of the remaining imine functions, whereas the *d,l* or *meso* designates the relative configurations of the two asymmetric carbons produced by the addi-



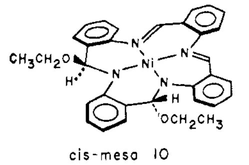
trans-d,ℓ 7



trans-meso 8



cis-d,ℓ 9



cis-meso 10

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(15) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, pp 26, 53.

(16) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 42 (1964).

(17) D. H. Busch, *J. Chem. Educ.*, 41, 77 (1964).

tion of the alkoxide ions. Evidence for the presence of more than one stereoisomer in the ethoxide adduct has been obtained by nmr spectroscopy utilizing a time-averaging computer. In the region 60–90 Hz downfield from TMS, two overlapping triplets of unequal intensity were found indicating the presence of two nonequivalent methyl functions. In each possible stereoisomer, **7–10**, both methyl groups would have identical environments and would give rise to only one triplet. Therefore, it is concluded that the nmr results indicate the presence of at least two stereoisomers. The methylene resonances are of little aid in the detection of stereoisomers since the methylene hydrogens are rendered magnetically nonequivalent by virtue of being attached through the oxygen to an asymmetric carbon atom.[18] The methylene resonances occur as a broad pattern of absorptions between 165 and 270 Hz. The width of this splitting pattern suggests the presence of more than one pair of magnetically nonequivalent methylene groups since similar previously observed methylene patterns only extend over approximately 50 Hz.[19] The derivative prepared with methoxide ion did not have sufficient solubility to obtain an nmr spectrum. Efforts to separate these stereoisomeric forms by column chromatography were unsuccessful.

Attempts to Prepare the α-Carbinolamine Derivative. Repeated attempts were made to synthesize the corresponding hydroxyl derivative (**6**, R = H).

(1) The reaction of $[Ni(TAAB)](BF_4)_2$ with aqueous solutions of alkali metal hydroxides immediately precipitated a maroon powder which behaved as an inner complex. Repeated elemental analyses, however, could not be fitted to any reasonable formulation. The infrared and electronic spectra of the hydrolyzed product were grossly different from the spectra obtained for the alkoxyl derivatives. Acidification of the hydrolysis product yielded a mixture of products which included $[Ni(TRI)]^{2+}$ and $[Ni(TAAB)]^{2+}$, indicating that the hydrolysis of the tetramer had resulted in a mixture of hydrolyzed tetramer and trimer and probably other condensation products (the reaction of $[Ni(TRI)]^{2+}$ with hydroxide ion yields a similarly behaved material).

(2) The reaction of an aqueous solution of $[Ni(TAAB)](BF_4)_2$ with an excess of concentrated ammonium hydroxide precipitated a dark red product. Acidification of this material yields only $[Ni(TAAB)]^{2+}$. Repeated analytical data on independently prepared samples indicated a C/N ratio of approximately 5. Infrared, electronic, and mass spectral data indicate that this compound should be formulated as **6** with –OR replaced by $-NH_2$.[20]

(3) The reaction of $[Ni(TAAB)](BF_4)_2$ with sodium hydroxide in dimethylformamide also gave a dark red material which reverted to $[Ni(TAAB)]^{2+}$ upon acidification. Infrared data indicated that this material contained solvated DMF which could be removed by heating *in vacuo* at 205°. The infrared spectrum of the dried material was essentially the same as the alkoxyl spectra except for 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. Analytical data and electronic and mass spectra indicated that this product is structure **6** with –OR replaced by $-N(CH_3)_2$.[20] This result was confirmed by the fact that the identical compound results from the reaction of an aqueous solution of $[Ni(TAAB)](BF_4)_2$ with dimethylamine. Apparently, DMF is hydrolyzed under these conditions to yield dimethylamine and CO_2; the dimethylamine then adds preferentially across the azomethine linkages. The base hydrolysis of neat DMF has been shown previously to yield $NH(CH_3)_2$ and CO_2.[21] These results illustrate that (1) hydroxide ion does not compete favorably as a nucleophile with ammonia or substituted amines toward addition across the azomethine bonds in the macrocyclic complex and (2) the carbinolamine complexes which do form are unstable, reactive species as evidenced by the appearance of $[Ni(TRI)]^{2+}$ derivatives resulting from the hydrolysis of $[Ni(TAAB)]^{2+}$.

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[18] G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 2628 (1964).

[19] P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1113 (1962), and references therein.

[20] L. T. Taylor, V. Katovic, and D. H. Busch, unpublished results.

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