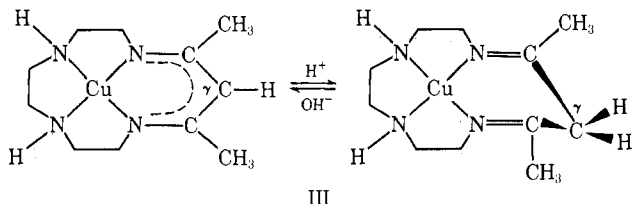


ATH ligand. This large difference is believed to be related to steric strain introduced into the six-membered chelate ring by coordination to the slightly larger copper(II) ion. The strain is expected to be greater in AT complexes since this form of the ligand contains a rigid planar six-membered ring. Steric strain should be somewhat relieved by protonation of the γ carbon (III), causing a change in hybridization



III

from sp^2 to sp^3 and allowing the $-CH_2-$ group to bend out of the plane containing the copper(II) ion and

imines. The lesser rigidity of the protonated six-membered ring may permit the $N \cdots N$ distance in that ring to increase, thus relieving some of the strain due to the relative smallness of the "hole" in the macrocycle. In addition to steric strain, electron-electron repulsion effects between the uninegative partially delocalized ring of the AT ligand and the metal ion may be such that the copper(II) ion acts as a poorer electron sink than nickel(II). The problems associated with steric constraints in these systems will be discussed in more detail in a forthcoming paper on nickel(II) and copper(II) complexes containing larger macrocyclic ligands similar to those described here.

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CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210, AND THE DEPARTMENT OF CHEMISTRY, VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY, BLACKSBURG, VIRGINIA 24061

Chemically Reduced Derivatives of the Nickel(II) and Copper(II) Complexes of the Cyclotetrameric Schiff Base of *o*-Aminobenzaldehyde

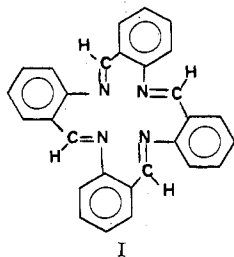
By VLADIMIR KATOVIĆ,^{1a} LARRY T. TAYLOR, FRED L. URBACH, WILLARD H. WHITE, AND DARYLE H. BUSCH*^{1b}

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Nickel(II) and copper(II) complexes containing a cyclotetrameric Schiff base ligand, TAAB, may be chemically reduced by hydrogen at relatively low pressures to yield very different materials, depending on the metal ion. The azomethine linkages are hydrogenated in the case of the nickel complex and the product has been formulated as $Ni(H_8TAAB)X_2 \cdot nH_2O$, where $X^- = ClO_4^-, BF_4^-, PF_6^-, NO_3^-, NCS^-, Cl^-, Br^-,$ and I^- . The copper complex undergoes a one-electron reduction followed by rearrangement to $[Cu^{III}(TAAB^{2-})]X$, where $X^- = Cl^-$ and PF_6^- . The parent copper complex is also reduced by elemental mercury to yield $[Cu^{III}(TAAB^{2-})](HgCl_2) \cdot 3H_2O$. The materials have been characterized by elemental analysis, magnetic susceptibility measurements, infrared and visible spectra, and X-ray powder diffraction measurements. A partially solvolyzed product, $[Cu(TAAB)(OCH_3)]Cl \cdot 0.5H_2O$, has also been isolated by allowing the reduced copper complex to air oxidize slowly in solution.

Introduction

The complexes derived from the cyclotetrameric Schiff base of *o*-aminobenzaldehyde (TAAB, structure I) are proving to be remarkable in a variety of ways.

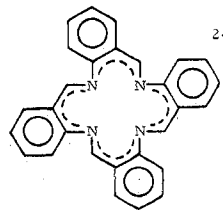


I

With the sole exception of the porphyrins and phthalocyanines they are the best characterized and most stable derivatives of a 16-membered macrocyclic ligand. This ligand TAAB is uncharged and belongs to the family of alternating unsaturated cycles that are non-aromatic; it is a 16-annulene. We have indicated in an earlier communication that electrochemical reduc-

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tion² of the complexes of TAAB yields products that are aromatic dianions (structure II), that is, porphyrin



II

analogs. The stability and properties of this new ligand are of much interest.

Electrochemical reduction of metal complexes to produce species that exhibit mutual ligand-metal ion oxidation state stabilization is an area that has seen intense research activity.³ On the other hand, chem-

(2) N. E. Tokel, V. Katovic, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).

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TABLE I
 ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES

Compound	% C		% H		% N		% halogen		% P		% S		% Ni	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(H ₅ TAAB)(BF ₄) ₂ ·3H ₂ O	47.57	47.54	4.65	4.58	7.93	8.01	8.31	8.85
Ni(H ₅ TAAB)(NO ₃) ₂ ·2H ₂ O	52.61	52.57	5.05	5.25	13.15	13.04	9.18	9.33
Ni(H ₅ TAAB)(NO ₂) ₂ ·H ₂ O	57.07	56.91	5.13	5.29	14.26	14.19	9.96	10.12
Ni(H ₅ TAAB)(ClO ₄) ₂ ·3H ₂ O	45.93	45.05	4.68	5.06	7.65	7.30	9.68	9.17	8.02	8.30
Ni(H ₅ TAAB)(PF ₆) ₂ ·H ₂ O	42.72	42.59	3.84	3.98	7.12	6.92	28.96	28.75	7.87	7.83	7.46	7.41
Ni(H ₅ TAAB)(NCS) ₂ ·H ₂ O	58.74	58.66	4.93	5.17	13.70	13.30	10.45	10.19	9.57	9.97
Ni(H ₅ TAAB)Cl ₂ ·H ₂ O	59.18	58.54	5.32	5.59	9.86	9.30	12.48	13.23	10.33	10.87
Ni(H ₅ TAAB)Br ₂ ·0.5H ₂ O	51.95	52.00	4.53	4.98	8.65	8.28	24.67	24.30	9.06	8.65
Ni(H ₅ TAAB)I ₂ ·H ₂ O	44.78	44.51	4.03	4.11	7.46	7.21	33.79	33.02	7.82	7.78
Ni(H ₅ TAAB)(BF ₄) ₂ (HF) ₂ ·5H ₂ O	43.06	42.97	4.90	4.24	7.17	6.88	24.33	24.95	7.52	7.58
		42.69		4.26		7.29	

ical reduction of metal complexes has not been attended with the same degree of success⁴ possibly because of the limited number of distinctive reducing agents available. The nickel(II) and copper(II) complexes of tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine,^{2,5} structure I, hereafter referred to as TAAB, provide an excellent opportunity for the study of both chemical and electrochemical reduction reactions.

Experimental Section

Materials.—*o*-Aminobenzaldehyde was prepared by the method of Smith and Opie.⁶ Ni(TAAB)(BF₄)₂ was prepared using a previously described method.⁷ Cu(TAAB)Cl₂ was prepared from Cu(TAAB)(NO₃)₂ by a metathetical reaction⁸ using an aqueous solution of NaCl. PtO₂ catalyst was purchased from Matheson Coleman and Bell. All other chemicals were of reagent grade or equivalent.

Reduction of Cu(TAAB)Cl₂ with Mercury.—A solution prepared by dissolving Cu(TAAB)Cl₂ (1.0 g) in methanol (100 ml) was shaken in the presence of excess mercury at room temperature. Within 1 hr the solution had turned blue with precipitation of a royal blue solid. After 24 hr the unreacted mercury was removed from the blue solid by decantation. The blue material was filtered in the air, washed with methanol, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr.

Isolation of Cu(TAAB)(HgCl₂)·3H₂O. **Method A.**—The blue product obtained from the reduction of Cu(TAAB)Cl₂ with mercury was suspended in 2000 ml of absolute ethanol with stirring. The insoluble royal blue precipitate was filtered and recrystallized from warm acetone. Crystallization was induced by reducing the volume of the solution, after which the blue crystals were filtered, washed with anhydrous acetone, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr. *Anal.* Calcd for C₂₈H₂₀N₄Cl₂HgCu·3H₂O: C, 40.27; H, 2.90; N, 6.71; Cl, 12.74; Hg, 24.02; Cu, 7.61. Found: C, 40.40; H, 2.69; N, 6.90; Cl, 12.69; Hg, 24.34; Cu, 7.04.

Method B.—To a saturated solution of Cu(TAAB)Cl₂ in methanol was added an aqueous solution of HgCl₂. A blue precipitate formed immediately which was filtered, washed with methanol, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr. *Anal.* Found: C, 40.52; H, 2.55. The X-ray powder pattern of this compound is identical with that of the material obtained by method A.

Reduction of Cu(TAAB)Cl₂ with Hydrogen.—To a solution prepared by dissolving Cu(TAAB)Cl₂ (1.0 g) in methanol (250 ml) was added PtO₂ catalyst (0.005 g). The resulting reaction mixture was placed under 60 psi of H₂ in a Parr low-pressure hydrogenation apparatus. After several minutes the color of the solution changed from yellow-green to royal blue. The uptake of hydrogen was completed within 2 hr. After removal of the catalyst by filtration, a blue crystalline solid was caused to precipitate by reducing the volume of the solvent and cooling the solution. The dark blue material was filtered in the air, re-

crystallized from warm methanol, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr. *Anal.* Calcd for C₂₈H₂₀N₄ClCu: C, 65.75; H, 3.94; N, 10.95; Cl, 6.93. Found: C, 63.57; H, 4.19; N, 10.25; Cl, 7.37.

Preparation of Cu(TAAB)PF₆. **Method A.**—A saturated methanol solution of NH₄PF₆ was added to a saturated solution of Cu(TAAB)Cl in methanol. Blue crystals formed immediately; these were filtered in the air, washed with a minimum amount of methanol, and dried as described above. *Anal.* Calcd for C₂₈H₂₀N₄F₆PCu: C, 54.15; H, 3.25; N, 9.02; F, 18.36; P, 4.99; Cu, 10.23. Found: C, 54.09; H, 3.41; N, 9.04; F, 18.51; P, 4.84; Cu, 9.96.

Method B.—The same material was formed by metathetical reaction of Cu(TAAB)(HgCl₂)·3H₂O with NH₄PF₆ in a methanol solution.

Preparation of [Cu(TAAB)(OCH₃)]Cl·0.5H₂O.—A saturated blue solution of Cu(TAAB)Cl in methanol was exposed to the air. After several days, the color of the solution turned from royal blue to green-red. The volume of the solution was reduced by two-thirds and, after addition of a saturated aqueous solution of LiCl, a green precipitate was obtained. The precipitate proved to be a mixture of Cu(TAAB)Cl₂ and the new substance which could be separated by washing the mixture with water whereupon Cu(TAAB)Cl₂ dissolved. The compound in question was filtered, washed with water, and dried *in vacuo* for 12 hr at room temperature. *Anal.* Calcd for C₂₈H₂₃N₄OClCu·0.5H₂O: C, 63.15; H, 4.40; N, 10.16; Cl, 6.43; -OCH₃, 5.62; Cu, 11.52. Found: C, 63.22; H, 5.05; N, 9.80; Cl, 5.98; -OCH₃, 3.58; Cu, 10.73. $\mu_{\text{eff}} = 1.83$ BM.

Hydrogenation of [Ni(TAAB)](BF₄)₂.—To a solution prepared by dissolving [Ni(TAAB)](BF₄)₂ (1.5 g) in methanol (300 ml) was added PtO₂ catalyst (0.05 g). The resulting mixture was placed under 60 psi of hydrogen in a Parr low-pressure hydrogenation apparatus. The hydrogenation was usually complete within 8–10 hr. However, the quality of the PtO₂ catalyst influenced to a large degree the time required for reduction. As the hydrogenation proceeded, the color of the solution changed from red to blue and, finally, to turquoise. The catalyst was filtered from the solution and the volume of the filtrate was reduced. An aqueous solution of NaBF₄ was added to this solution which subsequently yielded a pale blue crystalline precipitate. This material was filtered and dried at room temperature. The yellow-green filtrate from above was evaporated to a small volume on a rotary evaporator after which a methanol solution of NaBF₄ was added. Upon standing for a few days, green crystals precipitated; these were filtered, washed with water, and dried *in vacuo* over P₄O₁₀ at room temperature for 12 hr.

General Procedure for the Preparation of Other Derivatives of Ni(H₅TAAB)X₂·*n*H₂O.—To a solution prepared by dissolving blue Ni(H₅TAAB)(BF₄)₂·3H₂O (0.3 g) in distilled water (100 ml) was added a saturated aqueous solution of the sodium salt of the required anion. The Cl⁻, Br⁻, I⁻, NCS⁻, PF₆⁻, NO₃⁻, NO₂⁻, and ClO₄⁻ derivatives precipitated after stirring for 0.5 hr. All the products were filtered, recrystallized several times from warm water, filtered again, washed with a small amount of water, and air dried. These procedures gave yields of approximately 90%. Analytical data are given in Table I.

Physical Measurements.—Infrared spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. The spectra were determined as Nujol and halo oil mulls, as well as KBr pellets. Electronic spectra were measured with a Cary Model 14 recording spectrophotometer. Spectra of solid samples were obtained by diffuse transmittance employing halo oil mulls

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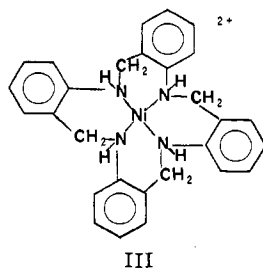
(8) G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

impregnated on Whatman No. 1 filter paper.⁹ Magnetic susceptibilities were measured at room temperature by the Faraday method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The molar diamagnetic corrections for the ligands and anions were calculated from Pascal's constants.¹⁰ Powder diffraction photographs were taken by using nickel-filtered $\text{Cu K}\alpha$ radiation with a Philips powder camera, $\phi = 119.08$ mm, of specimens enclosed in a Lindemann glass capillary of 0.3-mm diameter. Elemental analyses were performed by Bernhardt Microanalytical Laboratories, Elbach über Engelskirchen, West Germany.

Results and Discussion

Chemically Reduced Complexes of $[\text{Ni}(\text{TAAB})]^{2+}$.—The crystal structure of dark red, diamagnetic $[\text{Ni}(\text{TAAB})](\text{BF}_4)_2$ has shown that the four azomethine nitrogen atoms are coordinated to the nickel(II) ion in essentially a square-planar fashion.¹¹ Methanol solutions of this material are susceptible to chemical reduction by elemental hydrogen at relatively low pressures in the presence of a PtO_2 catalyst. In these reductions the amount of hydrogen taken up corresponds to 4 mol of H_2 /mol of complex. A tetrafluoroborate derivative was isolated after the reduction was completed by reducing the volume of the solvent and cooling the resulting solution. Other derivatives (*i.e.*, PF_6^- , ClO_4^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , and NCS^-) were prepared by metathetical reaction in methanol or water using the BF_4^- derivative and an alkali or ammonium salt of the desired anion. Each derivative displayed a pale blue or pale green color and proved to be highly hydrated and air stable in the solid state. In aqueous solution their stabilities toward oxidation are pH dependent. While in acid the complexes may exist indefinitely, but in the presence of base the reduced complexes appear to be rapidly air oxidized with subsequent solvolysis to yield the same product as that obtained by the addition of OH^- to a solution of unreduced tetramer. All the materials are hygroscopic. The analyses in Table I are for the vacuum-dried materials, whereas all physical measurements are performed on previously dried materials which had been subsequently exposed to the laboratory atmosphere.

All reduced $[\text{Ni}(\text{TAAB})]^{2+}$ derivatives can be formulated as $\text{Ni}(\text{H}_8\text{TAAB})\text{X}_2 \cdot n\text{H}_2\text{O}$, structure III, save



a single exception. Two forms (green and blue) of the BF_4^- complex could be isolated from the reaction medium. A blue form corresponds to the formulation described above; however, complete, duplicate elemental analyses excluding oxygen determination rule against this formulation for the green form, which has tentatively been assigned the composition $\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 2\text{HF} \cdot 5\text{H}_2\text{O}$.

A comparison of the infrared spectra of the reduced products with those of the parent $[\text{Ni}(\text{TAAB})]^{2+}$ reveals the following points. (1) The $-\text{C}=\text{N}-$ stretching mode¹² at 1568 cm^{-1} in the spectrum of $[\text{Ni}(\text{TAAB})]$ is missing in the spectra of all reduced derivatives. This indicates hydrogenation of all four Schiff base linkages (Figure 1). (2) The relatively intense band in the



Figure 1.—Infrared spectral bands in the double-bond region for $\text{Ni}(\text{TAAB})^{2+}$ and $\text{Ni}(\text{H}_8\text{TAAB})^{2+}$.

$3550\text{--}3400\text{-cm}^{-1}$ region for the reduced materials is assigned to the symmetric and asymmetric O-H stretching vibrational modes of water. (3) One to three medium sharp bands are observed in the $3250\text{--}3150\text{-cm}^{-1}$ region, depending on the anion present. These have been assigned to the nitrogen-hydrogen stretching modes of the four-coordinated secondary amines that are produced by hydrogenation.

The infrared spectra of the $\text{Ni}(\text{H}_8\text{TAAB})\text{X}_2 \cdot n\text{H}_2\text{O}$, where X has infrared-active modes, show that these anions are not coordinated¹³ in the cases of such poorly coordinating anions as BF_4^- , PF_6^- , and ClO_4^- . The infrared spectrum (KBr pellet, Nujol, and halo oil mulls) of the NO_3^- derivatives reveals four new bands at 1448 , 1370 , 1333 , and 1310 cm^{-1} which are absent in the spectra of the other derivatives. These bands may be assigned to a combination of ionic and monodentate nitrate anions.¹⁴ The abundance of water

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in the crystalline solids suggests that both NO_3^- and H_2O coordinate in the axial sites. The spectrum of the SCN^- derivative has bands at 2092 and 2074 cm^{-1} which have been attributed to the carbon-nitrogen stretching vibration of coordinated N-bonded thiocyanate.¹⁵ Finally, there are no bands in the infrared spectrum that are suggestive of a nickel-hydrogen interaction.

Magnetic susceptibilities have been measured and magnetic moments calculated for each reduced derivative (Table II). The data indicate that there are two

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

Compound	μ_{eff} , BM
$\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ (blue)	3.13
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	3.09
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$	3.26
$\text{Ni}(\text{H}_8\text{TAAB})(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	3.20
$\text{Ni}(\text{H}_8\text{TAAB})(\text{PF}_6)_2 \cdot \text{H}_2\text{O}$	3.06
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NCS})_2 \cdot \text{H}_2\text{O}$	3.25
$\text{Ni}(\text{H}_8\text{TAAB})\text{Cl}_2 \cdot \text{H}_2\text{O}$	3.44
$\text{Ni}(\text{H}_8\text{TAAB})\text{Br}_2 \cdot 0.5\text{H}_2\text{O}$	3.09
$\text{Ni}(\text{H}_8\text{TAAB})\text{I}_2 \cdot \text{H}_2\text{O}$	3.14
$\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 2\text{HF} \cdot 5\text{H}_2\text{O}$	3.27

unpaired electrons associated with each nickel ion. If reduction of the nickel had occurred, a μ_{eff} value considerably below 3.1 BM would be expected. The moments are entirely consistent with the presence of a pseudooctahedral environment about a nickel(II) ion.

Absorption spectra obtained on halo oil mulls were measured in the near-infrared and visible regions. Solution spectral measurements were precluded because of the limited solubilities. The spectra of the derivatives show essentially two identically positioned bands in the 11,500- and 16,700- cm^{-1} regions (Table III). A third,

TABLE III
ELECTRONIC ABSORPTION SPECTRA^{a, b}
OF THE NICKEL(II) COMPLEXES

Compound	ν_1	ν_2	ν_3
$\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ (blue)	9,350 b ^c	11,430	16,950
$\text{Ni}(\text{H}_8\text{TAAB})(\text{PF}_6)_2 \cdot \text{H}_2\text{O}$	9,220 b	11,560	16,670
$\text{Ni}(\text{H}_8\text{TAAB})(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	9,240	11,590	16,670
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	9,170 b	11,700	16,810
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$	10,310	11,700	17,540
$\text{Ni}(\text{H}_8\text{TAAB})(\text{NCS})_2 \cdot \text{H}_2\text{O}^d$	10,360	11,700	16,670
		sh	
$\text{Ni}(\text{H}_8\text{TAAB})\text{Cl}_2 \cdot \text{H}_2\text{O}$	9,620 b	11,330	15,870
$\text{Ni}(\text{H}_8\text{TAAB})\text{Br}_2 \cdot 0.5\text{H}_2\text{O}$	9,430 b	11,360	16,390
$\text{Ni}(\text{H}_8\text{TAAB})\text{I}_2 \cdot \text{H}_2\text{O}$	9,430 b	11,430	16,670
$\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 2\text{HF} \cdot 5\text{H}_2\text{O}$	9,260	12,360	16,260
	vw, b		

^a Spectra of samples taken as halo oil mulls. ^b All bands given in cm^{-1} . ^c Abbreviations: sh, shoulder; vw, very weak; b, broad. ^d Contains a shoulder of weak intensity at 12,050 cm^{-1} .

lowest energy band is observed to range in energy from 8620 to 10,360 cm^{-1} .

These spectra are interpreted on the basis of the assumption that the complexes possess approximate D_{4h} symmetry, following the interpretation applied by Wentworth and Piper¹⁶ for cobalt(III) and chromium(III) systems and later applied to nickel(II)

systems.^{17,18} The average Dq^{xy} for H_8TAAB is 1147 cm^{-1} . $\text{Tris}(\text{ethylenediamine})\text{nickel(II)}$ ¹⁹ shows a Dq value of 1120 cm^{-1} and the unreduced ligand TAAB ¹⁷ exhibits a Dq^{xy} of 1190 cm^{-1} . ν_1 was used to calculate the ligand field strength of the axial groups (Dq^z): H_2O , 714 cm^{-1} ; NCS , 925 cm^{-1} ; NO_2^- , 915 cm^{-1} . The Dq^z for NCS^- compares quite favorably with the value (910 cm^{-1}) obtained for $\text{Ni}(\text{TAAB})(\text{NCS})_2$.¹⁷ The lower Dq^z value obtained for nitrite ion (915 cm^{-1}) suggests that NO_2^- is coordinated through its oxygen atom.¹⁷

The hydrated salts derived from the reduced products are generally pale blue or green. Removal of the water of hydration *in vacuo* over P_4O_{10} in the cases of salts of the noncoordinating anions (BF_4^- , ClO_4^- , PF_6^-) leads to deep violet compounds which are extremely hygroscopic and could not be easily studied although magnetic measurements indicate that they are paramagnetic. Under reduced pressure $\text{Ni}(\text{H}_8\text{TAAB})(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ initially turns violet and then pink. The pink compound is also paramagnetic ($\mu_{\text{eff}} = 3.29$ BM). Weight loss experiments were performed on all hydrated materials and the losses were less than the theoretical percentages for complete removal of all water. The vacuum-dried materials can be formulated as six-coordinate octahedral or high-spin five-coordinate nickel(II) species rather than square-planar complexes in view of their paramagnetic behavior and retention of H_2O .

Chemically Reduced Complexes of $[\text{Cu}(\text{TAAB})]^{2+}$.—An aqueous solution of the chloride derivative of $[\text{Cu}(\text{TAAB})]^{2+}$ can be easily reduced with H_2 , at 4 atm using PtO_2 as a catalyst, to yield a dark royal blue precipitate whose elemental analysis, excluding carbon,²⁰ is in good agreement with the formulation $\text{Cu}(\text{TAAB})\text{Cl}$. A more satisfactory analysis has been obtained for the PF_6^- derivative, prepared by metathesis.

$\text{Cu}(\text{TAAB})\text{Cl}_2$ also undergoes reduction upon contact of its methanol solution with elemental mercury. Extraction of the blue product with ethanol, followed by recrystallization from hot acetone, yields a material whose formula is $\text{Cu}(\text{TAAB})(\text{HgCl}_3) \cdot 3\text{H}_2\text{O}$.²¹ This same material can be prepared independently by reaction of a methanol solution of $\text{Cu}(\text{TAAB})\text{Cl}$ with an aqueous solution of HgCl_2 . The two materials have identical X-ray powder photographs. The PF_6^- derivative can also be prepared by metathesis from $\text{Cu}(\text{TAAB})(\text{HgCl}_3) \cdot 3\text{H}_2\text{O}$ and NH_4PF_6 in methanol solution.

Infrared spectral measurements support the contention that the macrocyclic ligand is not hydrogenated in either of the procedures involving $\text{Cu}(\text{TAAB})\text{Cl}_2$. No bands are observed in the 3600–3100- cm^{-1} region which can be assigned to an N-H stretching vibrational mode. The region between 1650 and 1500 cm^{-1} con-

(17) D. H. Busch, *Helv. Chim. Acta*, Werner Commemoration Volume, 174 (1967).

(18) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

(19) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(20) Repeated analyses failed to yield satisfactory carbon percentages although the samples were clearly homogeneous and yielded derivatives of expected compositions.

(21) This reaction was performed initially by G. L. Eichhorn and R. A. Latif, *J. Amer. Chem. Soc.*, **76**, 5180 (1954). They postulated a dinuclear complex containing a trimeric, noncyclic condensate of *o*-aminobenzaldehyde bound to both copper atoms.

(15) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

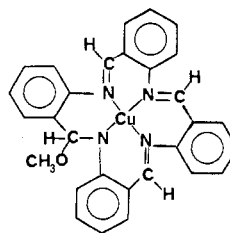
(16) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

tains four major bands in both $\text{Cu}(\text{TAAB})\text{Cl}_2$ and all its reduced products. All four bands are uniformly shifted by approximately 25 cm^{-1} to lower energy in going from the unreduced to the reduced complex. Three of these bands have been assigned as benzene ring vibrational modes whereas the band at 1562 cm^{-1} in $\text{Cu}(\text{TAAB})\text{Cl}_2$ and at 1536 cm^{-1} in the reduced products is attributed to a $-\text{C}=\text{N}-$ stretching mode. The "fingerprint" region for all reduced materials and $\text{Cu}(\text{TAAB})\text{Cl}_2$ is similar except for those bands which can be attributed to the presence of anions.

Magnetic susceptibility measurements show these blue copper complexes to be diamagnetic. This observation, coupled with the fact that the copper to anion ratio is 1:1, suggests $[\text{Cu}^{\text{I}}(\text{TAAB}^0)]^+$ as the proper formulation for these compounds. An alternative representation would be $[\text{Cu}^{\text{III}}(\text{TAAB}^{2-})]^+$ (structure II) as has been proposed from the electrochemical study of the same starting material.² Certainly the shift to lower energy by the so-called $\text{C}=\text{N}$ stretching mode is consistent with a formal two-electron reduction of the TAAB ligand. Further evidence to corroborate the latter assignment is found in the special stability of d^8 systems in a square-planar structure and the destabilization expected of d^{10} systems in that stereochemistry. A square-planar disposition of the four azomethine nitrogens is favored by the TAAB ligand.¹¹

Visible spectra were measured in methanol solution for $\text{Cu}(\text{TAAB})\text{PF}_6$ and $\text{Cu}(\text{TAAB})\text{HgCl}_3 \cdot 3\text{H}_2\text{O}$. The band maxima and corresponding extinction coefficients are as follows: $\text{Cu}(\text{TAAB})\text{PF}_6$, $14,490\text{ cm}^{-1}$ (6410), $28,570\text{ cm}^{-1}$ (13,600), $32,260\text{ cm}^{-1}$ (18,200); $\text{Cu}(\text{TAAB})\text{HgCl}_3 \cdot 3\text{H}_2\text{O}$, $14,080\text{ cm}^{-1}$ (5280), $27,780\text{ cm}^{-1}$ (11,200), $30,770\text{ cm}^{-1}$ (14,400). The extinction coefficients for all bands indicate that the transitions may be parity allowed although the intensity of the $14,000\text{-cm}^{-1}$ band could be abnormally high as a result of "intensity stealing" from the higher energy bands.

The reduced copper complexes are air stable in the solid state and moderately soluble in most polar solvents except water. Iodine or H_2O_2 oxidize these materials to the starting complex $[\text{Cu}^{\text{II}}(\text{TAAB}^0)]^{2+}$. Solutions of the royal blue products discolor over a period of several days on exposure to air. A brown material can be isolated from an aerated methanol solution of $\text{Cu}(\text{TAAB})\text{Cl}$. This material has been formulated as $[\text{Cu}(\text{TAAB})(\text{OCH}_3)]\text{Cl} \cdot 0.5\text{H}_2\text{O}$ (structure IV) and represents an intermediate methanolysis product²² of $[\text{Cu}(\text{TAAB})]^{2+}$. Powder photographs show that this intermediate solvolysis product is not a mixture of



IV

$\text{Cu}(\text{TAAB})\text{Cl}_2$ and $[\text{Cu}(\text{TAAB})(\text{OCH}_3)_2]$. The magnetic moment of 1.83 BM is consistent with our designation of this compound as containing copper(II). Structure II is also supported by infrared spectral measurements in that two electronically different Schiff base linkages are expected (*i.e.*, one typical of $(\text{TAAB})^0$ and one at lower energy characteristic of the adducts such as $[\text{Cu}(\text{TAAB} \cdot 2\text{OCH}_3)]$. The $\text{C}=\text{N}$ stretching frequencies are as follows: $\text{Cu}(\text{TAAB})\text{Cl}_2$, 1562 cm^{-1} ; $\text{Cu}(\text{TAAB})(\text{OCH}_3)_2$, 1526 cm^{-1} ; $\text{Cu}(\text{TAAB})(\text{OCH}_3)\text{Cl} \cdot 0.5\text{H}_2\text{O}$, $1562, 1526\text{ cm}^{-1}$.

The interpretation of the visible spectrum is not straightforward because of relatively low-energy charge-transfer bands. Shoulders are observed at $11,430, 14,390,$ and $20,000\text{ cm}^{-1}$ while a peak is found at $22,220\text{ cm}^{-1}$ (ϵ 6660).

Chemical evidence is also consistent with structure II. Trace quantities of acid and base convert $[\text{Cu}(\text{TAAB})(\text{OCH}_3)]\text{Cl} \cdot 0.5\text{H}_2\text{O}$ to $\text{Cu}(\text{TAAB})\text{Cl}_2$ and $[\text{Cu}(\text{TAAB})(\text{OCH}_3)_2]$, respectively.²²

It is most interesting to realize that the nickel(II) and copper(II) complexes of the macrocycle TAAB yield very different products when subjected to chemical reduction in protonic solvents. The copper complex achieves a favored electronic configuration after having accepted only one electron. It is assumed that the electron densities remain relatively small at this point both in the ring and on the metal atom. Further, it is anticipated that the structure is favored by a considerable stabilization due to the aromatic nature of the ligand (structure II). The contrasting behavior of $\text{Ni}(\text{TAAB})^{2+}$ is associated with the fact that the corresponding stable electronic configuration (d^8 metal ion plus aromatic dianion TAAB^{2-}) would result in the more highly reactive neutral species $\text{Ni}^{\text{II}}(\text{TAAB}^{2-})$. In a separate study²³ it has been found that the substance is unstable in protonic media. Consequently, hydrogenation of the azomethine linkages occurs. The mechanism of the process is not clear at this time.

Acknowledgment.—This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences.

(23) N. E. Tokel, V. Katović, and D. H. Busch, unpublished results.

(22) V. Katović, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, **10**, 458 (1971).