compound), displays an anomalous nmr because of a $\sigma-\pi$ transformation in the allyl group[7] induced by cyanide lability.

Reaction with Hydrogen Halides.—Whereas iridium(I)-phosphine complexes readily add hydrogen chloride to give iridium(III) hydrides, the $Ir(CO)_2Cl_2^-$ ion does not react with dry HCl at room temperature. Hydriodic acid in excess will react with $Ir(CO)_2X_2^-$ ions to give $Ir(CO)_2I_4^-$ and hydrogen. When a solution of $[(C_6H_5)_4As][Ir(CO)_2I_2]$ in nitromethane is treated with an equimolar quantity of concentrated aqueous hydriodic acid, a new species is formed with strong carbonyl stretching bands at 2107 and 2056 cm^{-1} and a weak band at 2160 cm^{-1}. These bands may be those of the $HIr(CO)_2I_3^-$ ion, but attempts to isolate this ion as a solid salt were unsuccessful.

Reactions with Acyl Halides.—Acetyl halides add rapidly to $Ir(CO)_2X_2^-$ ions at room temperature giving $Ir(CO)_2X_3(CH_3CO)^-$ ions. This is in marked contrast with the analogous rhodium system where acyl halides could not be added.

Reactions of Olefins.—Simple olefins do not react with $Ir(CO)_2X_2^-$ ions at temperatures in the range 20–100°. However, tetracyanoethylene reacts essentially immediately with $Ir(CO)_2X_2^-$ ions at 25° giving new species which we have not been able to isolate as solids but appear to be $Ir(CO)_2X_2(TCNE)^-$. These species exhibit two CO stretching frequencies in positions regarded as that of Ir(III) (see Table I). Again, a difference is observed between the corresponding iridium and rhodium systems. In reactions of TCNE with $Rh(CO)_2X_2^-$ ions, addition is accompanied by loss of a carbonyl group.[6]

Reactions with Mercuric Halides.—Mercuric halides react essentially instantaneously with $Ir(CO)_2X_2^-$ ions at room temperature giving $Ir(CO)_2X_3(HgX)^-$ ions.

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Copper(II) Complexes with 13-Membered Macrocyclic Ligands Derived from Triethylenetetramine and Acetylacetone

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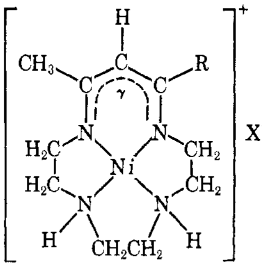
Seven new macrocyclic copper(II) complexes Cu(AT)X, where X^- is NO_3^-, I^-, Br^-, SCN^-, and PF_6^-, and $Cu(ATH)X_2$, where X^- is I^- and PF_6^-, have been prepared and characterized. These compounds contain the uninegative ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene (AT) and the neutral ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene (ATH) which are formed in the presence of copper(II) ions. The Cu(AT)X and $Cu(ATH)X_2$ complexes can be interconverted in solution by reversible protonation of the coordinated ligand ($K_a = 10^{-9}$). The relative acidity of the coordinated ligand in $Cu(ATH)X_2$ is 1000-fold less than in the analogous nickel(II) complex.

Introduction

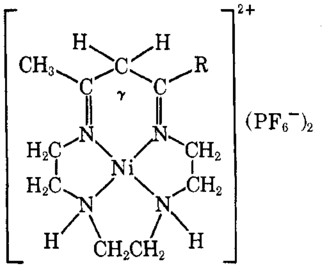
Recently we reported the synthesis of macrocyclic nickel(II) complexes (I), abbreviated Ni(AT)X and Ni(TAT)X,[1] *via* condensation of triethylenetetramine (trien) and the required β-diketone in the presence of the metal ion.[2] The identity of the 13-membered macrocyclic ligand, which contains a partially delocalized planar six-membered chelate ring, has since been confirmed by a single-crystal X-ray structure determination on $Ni(AT)ClO_4$.[3]



I

TAT, R = CF_3
AT, R = CH_3
$X^- = I^-, Br^-, SCN^-, NO_3^-, PF_6^-, BF_4^-,$ and ClO_4^-

Further investigations of the $Ni(AT)^+$ system have shown that, in acidic solutions, protonation of the coordinated ligand occurs at the methine (γ) carbon atom in I, and a nickel(II) complex (II) containing the neu-



$Ni(ATH)(PF_6)_2$
II

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(1) TAT is 11-methyl-13-trifluoromethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene, and AT is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene.

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TABLE I

ANALYTICAL DATA FOR Cu(AT)X AND $Cu(ATH)X_2$ COMPLEXES

Compound	% calcd C	H	N	F	Cu	Other	% found C	H	N	F	Cu	Other
$Cu(AT)NO_3 \cdot H_2O$	37.43	6.58	19.85	...	18.00	18.13, O	37.74	6.00	20.12	...	17.93	18.21, O
$Cu(AT)Br \cdot H_2O$	33.97	5.78	14.41	...	16.34	20.55, Br	33.69	5.43	14.06	...	15.70	20.85, Br
$Cu(AT)I \cdot H_2O$	31.62	5.56	13.41	...	15.21	30.37, I	31.43	5.09	13.13	...	14.91	30.29, I
$Cu(AT)SCN \cdot H_2O$	41.30	6.66	20.07	...	18.21	9.19, S	41.82	6.11	20.41	...	18.41	9.45, S
$Cu(AT)PF_6$	31.62	5.08	13.41	27.28	15.20	...	31.56	5.16	13.16	27.32	14.94	...
$Cu(ATH)(PF_6)_2$	23.43	3.94	9.94	40.44	11.27	10.99, P	23.53	4.43	10.10	40.54	11.08	10.93, P
$Cu(ATH)I_2$	25.03	4.21	10.62	...	12.04	48.66, I	24.83	4.18	10.69	...	11.95	48.22, I

tral macrocyclic β-diimine ligand 11,13-dimethyl-1,4,-7,10-tetraazacyclotrideca-10,13-diene, hereafter abbreviated ATH, has been isolated and characterized as the PF_6^- salt.[4]

In our laboratory we have been studying the scope of the macrocyclization reaction; in particular, its extension to complexes containing different metal ions and different-sized macrocyclic rings. We now report the successful extension of the parent condensation reaction between acetylacetone and trien to copper(II) ions. Several complexes of general formulas Cu(AT)X and $Cu(ATH)X_2$ have been prepared and characterized. The new compounds are similar to their nickel(II) analogs except for a remarkable 1000-fold decrease in the relative acidity of the protons on the γ carbon of the ATH ligand when coordinated to copper(II).

Experimental Section

Materials.—Triethylenetetramine (trien) was purchased from Aldrich Chemical Co. and acetylacetone (acac) was obtained from Matheson Coleman and Bell, Inc. Both chemicals were used as received. All other chemicals were reagent grade or equivalent.

Measurements.—Infrared spectra were recorded on a Perkin-Elmer Model 621 or Model 457 spectrophotometer using Nujol mulls or KBr disks. Visible spectra were measured using a Cary 14 recording spectrophotometer. Magnetic susceptibility measurements were obtained utilizing the Faraday technique. Conductivities were calculated from electrical resistances of $\sim 10^{-3}$ *M* aqueous and/or methanolic solutions using an Industrial Instruments Model RC-16B conductivity bridge. Acid and base constants were obtained by titrating ~0.0300 *M* solutions of the AT complexes with 0.1000 *M* HCl. Back-titration with 0.1000 *M* NaOH showed that all titrations were completely reversible. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Preparation of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatocopper(II) Nitrate, $Cu(AT)NO_3$.—A 20.0-g sample of $Cu(OAc)_2 \cdot 4H_2O$ (0.1 mol) was dissolved in 250 ml of water. To this were added in rapid succession 15.0 g (0.1 mol) of trien in 200 ml of water, 10 ml of glacial acetic acid, and 10.0 g (0.1 mol) of acetylacetone. The solution turned purple upon addition of the tetramine and crystals of copper acetylacetonate precipitated upon addition of the β-diketone. The mixture was refluxed for 6 hr and the color of the reaction solution changed from purple to blue. The resulting mixture was chilled and the undissolved $Cu(acac)_2$ was removed by filtration. The pH of the resulting solution was adjusted to 10 with NaOH and it was then filtered into a concentrated soluton containing a twofold excess of $NaNO_3$. Concentration and chilling of the resulting blue-green solution caused green crystals of $Cu(AT)NO_3$ to form. The crystals were isolated by filtration, washed with ice water, sucked dry in air, and then dried *in vacuo* at 80° for several hours; yield 6–8 g. The product was recrystallized twice from basic aqueous solution containing a small amount of $NaNO_3$. Analytical data are reported in Table I.

Synthesis of Other Derivatives of $Cu(AT)^+$.—The Br^-, I^-, SCN^-, and PF_6^- derivatives were prepared *via* metathetical reactions of $Cu(AT)NO_3$ in aqueous solutions containing an excess of the required sodium or ammonium salt. During each metathesis it was necessary to maintain the pH at 10 in order to prevent formation of complexes containing the neutral ligand which would contaminate the product. All of the complexes were isolated as dark green platelets which formed upon chilling the respective solutions. Each derivative was recrystallized twice from hot aqueous solutions at pH 10. The yields varied from 50 to 90%. Analytical data for these complexes appear in Table I.

Preparation of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienecopper(II) Hexafluorophosphate, $Cu(ATH)(PF_6)_2$.—A 20.0-g sample of $Cu(OAc)_2 \cdot 4H_2O$ was allowed to react with trien and acac as outlined above in the synthesis of $Cu(AT)NO_3$. However, instead of making the reaction solution basic after removal of the undissolved $Cu(acac)_2$, the filtered solution was added to a concentrated aqueous solution containing an excess of NH_4PF_6. Concentration of this solution resulted in the formation of large purple crystals of hydrated $Cu(ATH)(PF_6)_2$; yield ~12 g. The water of hydration could be removed by drying the crystals *in vacuo* at 100° for several hours. The resulting brown crystals of $Cu(ATH)(PF_6)_2$ were extremely hygroscopic and quickly reverted to the hydrated species on exposure to air. Analytical data for the anhydrous sample appear in Table I.

Synthesis of Other Derivatives of $Cu(ATH)^{2+}$.—Attempts to prepare other derivatives from the PF_6^- complex *via* metathetical reactions met with little success due to the relatively low solubility of the PF_6^- derivative. However, $Cu(ATH)I_2$ was prepared by strongly acidifying an aqueous solution containing Cu(AT)I and NaI with acetic acid. Concentration of this solution yielded dark blue crystals of $Cu(ATH)I_2$.

Results and Discussion

Synthesis.—The reaction of equimolar amounts of trien and acac in the presence of copper(II) ions and acetic acid leads to the formation of macrocyclic copper(II) complexes. Compounds of stoichiometry Cu(AT)X and $Cu(ATH)X_2$ have been isolated, where X^- is NO_3^-, I^-, Br^-, SCN^-, and/or PF_6^- and AT and ATH are the closely related 13-membered macrocyclic ligands shown in I and II, respectively.

The general method of synthesis of the copper(II) complexes is shown in Figure 1. The form in which the complexes are isolated depends upon the pH of the solution since the coordinated ligand can undergo reversible protonation of the γ carbon. All derivatives of Cu(AT)X, *i.e.*, Br^-, I^-, NO_3^-, SCN^-, and PF_6^-, can be prepared directly from the filtered reaction solution if it is first made strongly basic with NaOH before addition of the required anion. In addition, the Br^-, I^-, SCN^-, and PF_6^- complexes have been prepared by metathesis from the very soluble and easily purified $Cu(AT)NO_3$. This latter method proved more convenient and is recommended.

Only two derivatives containing the neutral ligand have been isolated. The relatively insoluble $Cu(ATH)(PF_6)_2$ can be obtained directly from the reaction solution by addition of HOAc and NH_4PF_6. Conversion of Cu(AT)X to $Cu(ATH)X_2$ by addition of acid (Figure 1) has also been used to prepare $Cu(ATH)(PF_6)_2$ and serves as the best synthetic method for $Cu(ATH)I_2$.

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[4] W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

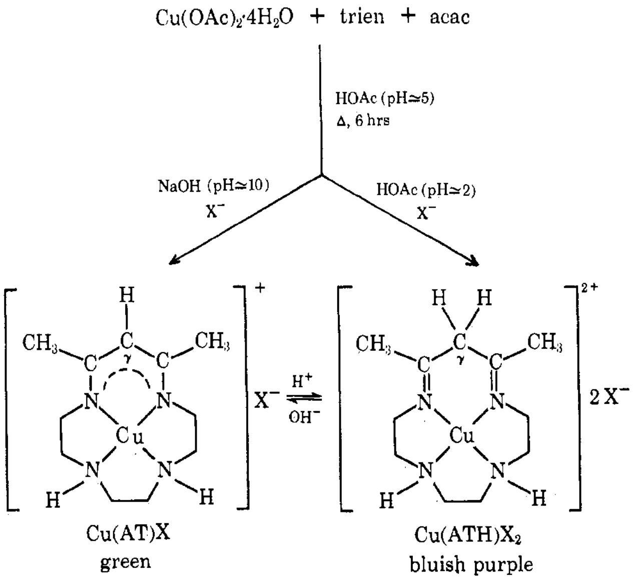

Figure 1.—General method of synthesis of Cu(AT)X and Cu(ATH)X_2.

Although acidification of the NO_3^-, Br^-, and SCN^- derivatives of Cu(AT)X produced a color change from green to bluish purple typical of formation of complexes containing the protonated ligand, the desired Cu(ATH)X_2 species could not be recovered from solution, presumably due to their high solubilities.

Characterization.—Characterization of the macrocyclic copper(II) complexes is based on elemental analyses, conductivity and magnetic susceptibility measurements, and infrared and electronic spectra of the seven compounds mentioned above.

Analytical data for all the complexes are presented in Table I and indicate the presence of one or two anions depending upon the nature of the macrocyclic ligand. Compounds which required the inclusion of H_2O in their formula to provide a best fit with the analytical results always showed bands in the infrared spectrum attributable to H_2O; however, no effort has been made to determine the exact degree of hydration.

All of the macrocyclic AT complexes have been obtained as green crystalline solids which are soluble in polar solvents. The derivatives are 1:1 electrolytes, exhibiting molar conductances (Λ_M) of ~120 (H_2O) and ~95 (MeOH) mhos/cm. In contrast, Cu(ATH)$(PF_6)_2$ and Cu(ATH)I_2 have been isolated as dark bluish purple crystals which are 2:1 electrolytes in solution, exhibiting molar conductances (Λ_M) of ~190 (H_2O) and ~160 (MeOH) mhos/cm. Magnetic susceptibility measurements (Table II) indicate one unpaired electron and confirm the presence of divalent copper in all of the complexes.

TABLE II

MAGNETIC SUSCEPTIBILITIES[a] OF THE COPPER(II) COMPLEXES

Compound	$10^6\chi_M$, cgsu		μ_{eff}, BM
	Uncor	Cor[b]	
Cu(AT)$NO_3 \cdot H_2O$	1238	1419	1.84
Cu(AT)$Br \cdot H_2O$	1168	1365	1.81
Cu(AT)$I \cdot H_2O$	1160	1373	1.83
Cu(AT)$SCN \cdot H_2O$	1128	1321	1.78
Cu(AT)PF_6	1262	1478	1.88
Cu(ATH)$(PF_6)_2 \cdot H_2O$	1138	1434	1.85
Cu(ATH)I_2	1207	1457	1.86

[a] All measurements were carried out at 298°. [b] Diamagnetic corrections for the ligands were calculated from Pascal's constants.

Structures of the new macrocyclic copper(II) compounds have been inferred from measurements of the infrared and visible spectra. Infrared spectra of Cu(AT)PF_6 and hydrated Cu(ATH)$(PF_6)_2$ are typical of the two series of compounds and are reported in Table III.[5] Spectra of both types of complexes are characterized by the absence of bands due to free or coordinated $-NH_2$ and $>C{=}O$ groups, which suggests the presence of a completely condensed, macrocyclic organic ligand.

TABLE III

INFRARED SPECTRA[a] OF Cu(AT)PF_6 AND Cu(ATH)$(PF_6)_2$ (CM^{-1})

Cu(AT)PF_6[b]		Cu(ATH)$(PF_6)_2 \cdot H_2O$[b]	
...	1238 m	3640 m[d]	...
...	...	3560 m[d]	1225 w
3300 s[e]	...	3317, 3299	1192 m
3215 m	1175 m	s, d[e]	...
2930[c] m, b[f]	...	2930[c] m, b[f]	1100 m
2850[c] m, sh[f]	1075 m	2830[c] m, sh[f]	1082 s
...	1035 s	1695 s, sp[g]	1040 s
...	970 m	1620 w[d]	975 s
1550 s, b[h]	945 m	...	963 m
1520 m, sh[h]	918 w	...	930 s
1450[c] vs, b	835 vs, b[i]	1468[c] m, sh	835 vs, b[i]
1400[c] vs	738 m	1429[c] s	739 w
1368[c] m	720 w	1387[c] s	...
1335 vs	690 w	1340 m, sh	...
1315 vs	560 vs[i]	...	560 vs[i]
1290 m	530 w, sh	1300 w	505 w
...	477 m	1282 w	479 w
1262 s	430 w	1262 vw	400 w

[a] Obtained on a Perkin-Elmer Model 457 IR as Nujol mulls. [b] Abbreviations used: b, broad; sp, sharp; sh, shoulder; d, doublet; m, medium; s, strong; w, weak; vw, very weak; vs, very strong. [c] Values taken using KBr disks rather than Nujol. [d] H_2O. [e] NH stretch. [f] CH stretch. [g] $C{=}N$. [h] $>C\overset{\cdots}{=}N$ and/or $>C\overset{\cdots}{=}C<$. [i] PF_6^-.

In addition, spectra of the Cu(AT)X derivatives show new bands attributable to –NH, –CH, and $>C\overset{\cdots}{=}N$ and/or $>C\overset{\cdots}{=}C<$ stretching modes (Table III). These assignments plus the striking similarity between these spectra and those of the corresponding, fully characterized Ni(AT)X derivatives[1-3] help to confirm the presence of the 13-membered uninegative macrocyclic ligand in these copper(II) complexes.

As can be seen from Table III, spectra of the Cu(ATH)X_2 derivatives are different in several respects from their nonprotonated Cu(AT)X analogs. The major difference occurs in the 1700–1500-cm^{-1} region. The rather broad absorption band attributed to the $>C\overset{\cdots}{=}N$ and/or $>C\overset{\cdots}{=}C<$ stretching modes of the partially delocalized ring in Cu(AT)X is not observed in spectra of the Cu(ATH)X_2 species. Instead, a new band which is both strong and sharp appears at 1695–1670 cm^{-1}. This is attributed to the stretching vibration of the two equivalent and localized β-diimine linkages present in the protonated form of the ligand, Figure 1. The appearance of a single higher energy band due to the imines is also characteristic of the spectrum of Ni(ATH)$(PF_6)_2$[4] and indicates the similar nature of the ligand in both the nickel(II) and copper(II) complexes.

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(5) The infrared spectra reported in Table III were obtained almost entirely from Nujol mulls because anion exchange is found to occur when samples of the various derivatives are ground in KBr. For example, when Cu(ATH)$(PF_6)_2$ is ground with KBr, the spectrum of the KBr disk shows not only a sharp but somewhat weakened –NH absorption (~3300 cm^{-1}) typical of the PF_6^- derivative but also a broadened –NH band at lower energy (~3160 cm^{-1}) due to –NH hydrogen bonded with the Br^- ion.

TABLE IV

ELECTRONIC ABSORPTION SPECTRA (CM^{-1}) OF THE COPPER(II) COMPLEXES

Compound	Medium	$\nu_1{}^a$	$\nu_2{}^a$	$\nu_3{}^a$	$\nu_4{}^a$
$Cu(AT)NO_3$	H_2O	17,700 (125)	23,350 (192)	30,300 (4400)	40,500 (8000)
	Nujol	17,800	22,700	29,200	41,700
Cu(AT)Br	H_2O	17,700 (129)	23,050 (228)	39,200 (5200)	43,800 (12,300)
	MeOH	16,950 (225)	22,800 (371)	29,900 (14,600)	45,400 (24,900)
	CH_3NO_2	16,850 (189)	23,350 (325)	27,000 (3290)	. . .
	Nujol	18,900	23,200	32,200	40,500
Cu(AT)I	MeOH	16,750 (269)	23,000 (392)	29,700 (11,000)	45,600 (32,000)
	Nujol	16,400	22,900	29,200	40,500
Cu(AT)SCN	MeOH	16,750 (201)	23,100 (310)	29,650 (14,700)	46,500 (19,200)
	CH_3NO_2	16,700 (189)	22,950 (280)	27,200 (2450)	. . .
	Nujol	17,000	23,200	28,600	38,800
$Cu(AT)PF_6$	MeOH	17,650 (84)	22,700 (82)	29,600 (12,700)	46,100 (26,000)
	Nujol	16,800	22,900	30,300	39,400
$Cu(ATH)(PF_6)_2$	H_2O	18,900 (175)	. . .	30,400 (428)	39,100 (5800)
	MeOH	18,800 (164)	. . .	28,800 (1430)	40,800 (7370)
	Nujol	18,900		31,200	39,000
$Cu(ATH)I_2$	H_2O	17,800 (328)	. . .	. . .	37,900 (7230)
	Nujol	16,100	. . .	29,400	38,800

[a] Values of molar absorptivitirs (ϵ) are given in parentheses.

As was observed in Ni(AT)X and Ni(TAT)X,[1,2] the peak due to the –NH stretching vibration in Cu(ATH)X_2 broadens and shifts to lower energies as the electronegativity and hence hydrogen-bonding ability of the anion increases.[6,7] The overall energy shift is about 200 cm^{-1} with the highest energy band found for the PF_6^- derivatives and the lowest energy band found for the Br^- and I^- derivatives. Hydrogen bonding also contributes to the doublet character of the –NH band which is observed in the Nujol spectrum of hydrated $Cu(ATH)(PF_6)_2$ (Table III). The splitting of the –NH absorption and the H_2O bands at 3640 (asym str), 3560 (sym str), and 1620 (sym bend) cm^{-1} are not observed in the Nujol spectrum of anhydrous $Cu(ATH)(PF_6)_2$. When the mull is opened to the air, the doublet character of the –NH band and the bands due to H_2O reappear simultaneously. This splitting may involve hydrogen bonding to the H_2O molecules or may be the result of a change in crystal packing upon hydration.

The infrared spectra also show absorptions due to NO_3^-, SCN^-, and PF_6^- which indicate that these anions are not coordinated to the copper(II) ion.[8-11] This suggests the presence of square-planar copper(II) which is consistent with interpretation of the electronic spectra (*vide infra*).

The visible and ultraviolet spectra of the copper(II) complexes are reported in Table IV. The spectra have been measured in three solvents and in the solid state by the diffuse transmittance technique.[12] As expected, the spectra of the Cu(AT)X derivatives are quite similar to one another and exhibit four absorption bands except in CH_3NO_2 where the highest energy band is obscured by solvent. The bands at ~17,000 cm^{-1} (ϵ ~150) and ~23,000 cm^{-1} (ϵ ~300) are attributed to d–d transitions on the metal and have been tentatively assigned as the $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ transitions of square-planar copper(II).[13] The higher energy bands at ~30,000 (ϵ ~10,000) and ~45,000 (ϵ ~15,000) cm^{-1} are assigned to ligand-to-metal charge-transfer transitions or parity-allowed transitions of the ligand involving the >C⩵N and >C⩵C< chromophores. Spectra of the $Cu(ATH)^{2+}$ derivatives exhibit only three electronic absorption bands. A broad absorption in the visible region centered at 18,000 cm^{-1} (ϵ ~250) probably contains both d–d transitions mentioned earlier. Indeed, the appearance of only one broad band in the visible spectra of square-planar copper(II) complexes containing neutral macrocyclic diimine ligands is well documented.[14] The absorptions in the ultraviolet region, ~30,000 cm^{-1} (ϵ ~1000) and 38,000 cm^{-1} (ϵ ~7000), are attributed to charge-transfer or intraligand transitions.

The electronic spectrum of Cu(AT)SCN has also been measured in the presence of excess SCN^- to determine if there is any tendency for the copper(II) ion to form five- or six-coordinate species in solution. Only those bands reported in Table IV which have been correlated with square-planar copper(II) were observed. This is consistent with the infrared spectral data (*vide infra*) and suggests the presence of only four-coordinate, square-planar copper(II) both in the solid state and in solution. These interpretations plus the strong similarities between the copper(II) complexes and their nickel(II) analogs leave little doubt that the structures of Cu(AT)X and Cu(ATH)X_2 are those shown in Figure 1.

While this paper has stressed the numerous similarities between the copper(II) complexes and their nickel(II) counterparts, there exists one most striking difference, namely, the relative acidity of the protons on the γ carbon of the coordinated ATH ligand. Elfring and Rose[4] have reported a K_a of 10^{-6} for $Ni(ATH)(PF_6)_2$. We have repeated this measurement on $Ni(AT)BF_4 \leftrightarrows Ni(ATH)(BF_4)_2$ and have confirmed the above result. A similar study of $Cu(AT)I \leftrightarrows Cu(ATH)I_2$ yielded a K_a of 10^{-9}, which represents a 1000-fold decrease in the relative acidity of the coordinated

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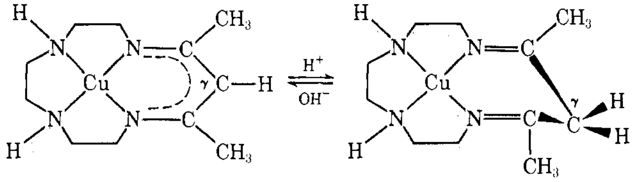
ATH ligand. This large difference is believed to be related to steric strain introduced into the six-membered chelate ring by coordination to the slightly larger copper(II) ion. The strain is expected to be greater in AT complexes since this form of the ligand contains a rigid planar six-membered ring.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



III

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

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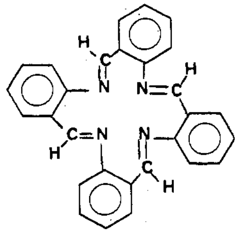
Nickel(II) and copper(II) complexes containing a cyclotetrameric Schiff base ligand, TAAB, may be chemically reduced by hydrogen at relatively low pressures to yield very different materials, depending on the metal ion. The azomethine linkages are hydrogenated in the case of the nickel complex and the product has been formulated as $Ni(H_8TAAB)X_2 \cdot nH_2O$, where $X^- = ClO_4^-, BF_4^-, PF_6^-, NO_2^-, NO_3^-, NCS^-, Cl^-, Br^-$, 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 $[Cu^{III}(TAAB^{2-})](HgCl_3) \cdot 3H_2O$. 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.

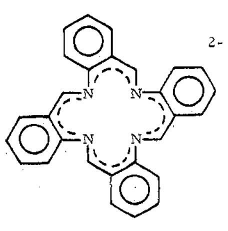
Introduction

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 nonaromatic; it is a 16-annulene. We have indicated in an earlier communication that electrochemical reduction[2] 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-

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(1) (a) On leave from the University and Institute "R. Bosković," Zagreb, Croatia, Yugoslavia. (b) The Ohio State University.

(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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