If this happens, however, in such a manner that the second amino group is also coordinated as in IIa, the amide nitrogen would be directed away from the position to which it eventually becomes coordinated. Thus IIa is the more stable intermediate that must rearrange to IIb before the next deprotonation and coordination change to negative amide nitrogen can occur. In spite of these complications, the step II to III is faster than I to II.

It is interesting that none of the more stable intermediates IIa and IIb resembles the planar structure indicated by III. A tetragonal structure, with two water molecules spaced above and below the plane somewhat farther away than the other four donors, is also possible. The fact that the second step is faster than the first is probably the result of the fact that the negative amide nitrogen atom that is first to be deprotonated holds the remaining donor groups of the ligand in a position that allows a fairly close average approach to the coordination sphere of the metal ion. Thus it is seen that the steric arrangement of the first two strongly coordinated groups in $NiH_{-1}L^+$ increases the probability of the formation of the conformer IIc, which may be considered the immediate precursor for the second deprotonation step. This is not the situation in the conversion of I to II, however, since the carbonyl oxygen is coordinated in a five-membered ring that includes a strongly coordinated partner. Thus it seems that the relative rates of the successive deprotonation reactions may be logically related to the probable structures of the complexes present in solution, and the more rapid rate of the second deprotonation reaction seems quite reasonable.

Finally, it is seen that the rate of the second deprotonation of the 2:1 complex NiL_2^{2+} to give $NiH_{-2}L$ would not be as rapid as for the 1:1 complex, since dissociation of the second ligand would be necessary before IIc could be formed. On this basis, therefore, one might expect higher concentrations of intermediates such as $Ni(H_{-1}L)L^+$ in both equilibrium and kinetic systems containing amide (and peptide) donor groups. In the presence of excess ligand, therefore, the conversion to III may easily occur in two steps, with partially deprotonated 2:1 complexes as intermediates.

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A New Synthetic Route to Macrocyclic Nickel(II) Complexes with Uninegative, Schiff-Base Ligands

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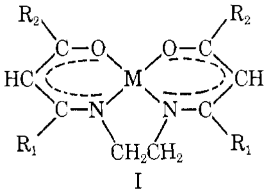
Two series of nickel(II) complexes containing uninegative, macrocyclic Schiff-base ligands have been prepared *via* simple condensation reactions. Characterization of the new compounds Ni(AT)X and Ni(TAT)X, where AT is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene, TAT is 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene, and X^- is Br^-, I^-, SCN^-, NO_3^-, BF_4^-, or PF_6^-, is discussed. Derivatives of Ni(AT)X and Ni(TAT)X are the first macrocyclic metal complexes to be synthesized by reaction of both oxygen atoms of a β-diketone (enol form) with both terminal $-NH_2$ groups of a polyamine. The cyclization reaction is predominant, even in the preparation of Ni(TAT)X complexes, where it requires condensation at a carbonyl oxygen atom adjacent to a normally deactivating trifluoromethyl group.

Introduction

The condensation of amines with β-diketones and β-keto aldehydes to form β-keto amines and the use of β-keto amines as ligands in the preparation of metal complexes are well known. A review[2] of work in this area shows that many investigations have been concerned with the formation and structure of tetradentate metal complexes (I) derived from various diamines and β-diketones.



I

The effect of trifluoromethyl groups at positions R_1 and R_2 on directing the course of the Schiff-base condensation and the normal bis(keto amine) stoichiometry of the ligands should be mentioned, as they are particularly relevant to the work presented here.

Dipole moment studies on the condensation products of trifluoroacetylacetone with diamines[3,4] and the resulting metal complexes[5,6] have shown that condensa-

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[1] Author to whom inquiries should be addressed at the Department of Chemistry, Wright State University, Dayton, Ohio 45431.

[2] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

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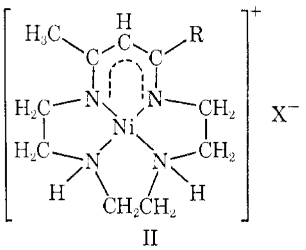
[6] P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 3106 (1956).

tion occurs exclusively at the carbonyl oxygen adjacent to the $-CH_3$ group. This apparent decrease in reactivity of carbonyl oxygen atoms adjacent to $-CF_3$ groups has been noted by other workers[7,8] whose attempts to effect Schiff-base condensations with hexafluoroacetylacetone and diamines under normal conditions have failed. Success in this area has now been achieved in our laboratory and will be reported here and in forthcoming papers.[9,10]

The stoichiometry of the tetradentate β-keto amines commonly synthesized involves a 2:1 ratio of diketone condensed with diamine. Complexes with tetradentate ligands of reverse stoichiometry, *i.e.*, derived from 2 equiv of diamine and 1 equiv of β-diketone by condensation at both carbonyl oxygen atoms, are quite rare. Indeed, the first report of a metal complex containing such a ligand appeared only recently. The ligand, abbreviated mena, was formed by condensation of 2 equiv of N-methylethylenediamine with 1 equiv of acetylacetone in the presence of nickel(II) ions and was isolated as the nickel(II) complex, Ni(mena)-ClO_4. The preparation of a similar complex with ethylenediamine was also mentioned; however, characterization of the complexes was not discussed.[11] Bidentate nitrogen ligands prepared by condensation of a β-diketone with 2 equiv of various monofunctional amines were reported somewhat earlier.[12]

In this paper, we report the synthesis and characterization of new nickel(II) complexes containing macrocyclic, uninegative Schiff-base ligands formed by condensation of 1 equiv of β-diketone with 1 equiv of triethylenetetramine (trien). Two ligands, 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene (TAT) and 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene (AT), have been derived from trien and trifluoroacetylacetone and trien and acetylacetone, respectively.[13] The general structure of the complexes is



II

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

Experimental Section

Materials.—Triethylenetetramine was purchased from Aldrich Chemical Co. and used as received. Acetylacetone and trifluoroacetylacetone were obtained from Fisher Chemical Co. and Pierce Chemical Co., respectively. Both were freshly distilled before use. All other chemicals were reagent grade or equivalent.

Measurements.—Infrared spectra were determined on Perkin-Elmer Model 137-B and Model 521 spectrophotometers using the Nujol and Fluorolube mull techniques. Visible and ultraviolet spectra were obtained using a Cary 14 recording spectrophotometer. All reported proton magnetic resonance spectra were determined using a Varian A-60 nmr spectrometer. Chemical shifts were measured using TMS as an internal reference.

Magnetic susceptibilities were determined utilizing the Faraday technique. Conductances were obtained for 10^{-3} *M* aqueous and methanolic solutions using an Industrial Instruments Model RC-16B conductivity bridge. Mass spectra were obtained with an LKB 9000 mass spectrometer. We are indebted to G. Nicholson, Tuebingen University, Tuebingen, Germany, for the latter measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparations.—Synthesis of 11-Methyl-13-(-trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Iodide, Ni(TAT)I. Method A.—The linear, potentially sexadentate, Schiff-base ligand, bis(trifluoroacetylacetone)triethylenetetramine, abbreviated H_2(BTAT), was first prepared. A 30-g sample of trien was diluted with 100 ml of ethanol and chilled to 10°. To this was slowly added, with stirring, a solution of 61.6 g of trifluoroacetylacetone in 50 ml of ethanol. The pale yellow solution which resulted was diluted with 1 l. of water. Subsequent concentration of the cloudy solution under an air stream caused precipitation of about 50 g of H_2(BTAT) as a white, crystalline material.[10] The crystals were dried, *in vacuo*, at room temperature for 6 hr. *Anal.* Calcd for $C_{16}H_{24}N_4O_2F_6$: C, 45.92; H, 5.79; N, 13.39; F, 27.24; O, 7.65. Found: C, 45.76; H, 5.70; N, 13.20; F, 27.23; O, 8.11 (by difference). Mol wt: calcd, 418.44; found, 430 ($CHCl_3$).

A 7.8-g sample of H_2(BTAT) was dissolved in 50 ml of water which had been adjusted to pH 5 with acetic acid. After the ligand solution had begun to reflux, 7.0 g of $Ni(OAc)_2 \cdot 4H_2O$ which had been dissolved in 50 ml of water was added. The resulting solution was refluxed for 3–6 hr, during which time the color changed from orange to deep red. The hot reaction mixture was filtered into a concentrated solution of NaI, and the pH was adjusted to 10 with 6 *N* NaOH. Chilling and concentrating of the solution resulted in precipitation of 2.5 g of a mixture of hydrated nickel(II) trifluoroacetylacetonate and Ni(TAT)I. This mixture was taken up in hot water and the insoluble nickel trifluoroacetylacetonate was removed by filtration. Red-orange crystals of Ni(TAT)I, which formed upon concentration of the filtrate, were collected and dried, *in vacuo*, at 100°; yield, 2.1 g. Analyses are reported in Table I.

Method B.—A 1.2-g sample of Ni(BTAT), prepared by a method described elsewhere,[10] was dissolved in 100 ml of water which had been adjusted to pH 5 with acetic acid. The resulting solution was refluxed for 6 hr and the color changed from yellow-brown to cherry red. The hot solution was filtered into a concentrated solution of NaI, and the pH was adjusted to 10 with 6 *N* NaOH. Concentration of the solution produced red-orange crystals of Ni(TAT)I, identical with those prepared by method A. The yield for this reaction is essentially quantitative.

Method C.—Ni(TAT)I was also prepared by the *in situ* reaction of 2.5 g of $Ni(OAc)_2 \cdot 4H_2O$, 1.5 g of trien, and 3.1 g of trifluoroacetylacetone. The β-diketone was added to an aqueous solution containing the first two reactants, after the pH of the solution had been adjusted to 5 with acetic acid. The mixture was refluxed for 6 hr. Ni(TAT)I was recovered by treatment with NaI and NaOH as outlined in method A. Yields using this procedure were slightly lower than those obtained with the other two methods.

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[8] E. J. Olszewski and D. F. Martin, *ibid.*, **27**, 1043 (1965).

[9] M. F. Richardson and R. E. Sievers, *ibid.*, in press.

[10] S. C. Cummings and R. E. Sievers, to be submitted for publication.

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TABLE I

ANALYTICAL DATA FOR Ni(TAT)X AND Ni(AT)X COMPLEXES

	% calcd						% found					
Compound	C	H	N	F	Ni	Other	C	H	N	F	Ni	Other
Ni(TAT)I	29.42	4.04	12.48	12.69	13.07	28.26 I	29.50	3.93	12.45	12.61	13.09	28.67, I
Ni(TAT)Br	32.86	4.52	13.94	14.18	14.60	19.88, Br	32.87	4.54	13.86	14.15	14.08	20.19, Br
Ni(TAT)SCN	37.91	4.78	18.42	14.99	15.44	8.43, S	37.73	4.41	18.30	15.26	15.36	8.68, S
Ni(TAT)NO_3	34.39	4.73	18.23	14.84	15.28	...	34.37	4.81	18.07	14.69	15.69	...
Ni(TAT)BF_4	32.31	4.44	13.70	32.53	14.35	...	32.03	4.24	13.89	30.09	14.36	...
Ni(TAT)PF_6	28.28	3.89	11.99	36.61	12.57	6.63, P	28.53	3.07	12.05	37.08	12.94	6.64, P
Ni(AT)I	33.44	5.37	14.18	...	14.86	32.12, I	33.51	4.95	14.10	...	15.06	32.47, I
Ni(AT)Br·0.5H_2O[a]	37.00	6.22	15.69	...	16.44	22.38, Br	37.36	5.93	15.48	...	16.66	22.70, Br
Ni(AT)Br·0.5H_2O[b]			Same				36.74	5.52	15.50	...	16.31	22.17, Br
Ni(AT)SCN	44.18	6.50	21.47	...	18.00	9.82, S	44.16	6.20	21.07	...	17.78	10.06, S
Ni(AT)NO_3·0.5H_2O	38.96	6.55	20.65	...	17.31	...	39.29	6.17	20.40	...	18.75	...
Ni(AT)BF_4	37.22	5.97	15.79	21.41	16.54	...	37.51	5.95	15.64	20.16	15.63	...
Ni(AT)PF_6	31.98	5.13	13.56	27.60	14.21	7.49, P	32.12	5.21	13.65	27.32	14.51	7.88, P
Ni(AT)ClO_4	35.94	5.77	15.24	...	15.97	9.64, Cl	36.02	5.72	15.12	...	16.35	9.60, Cl

[a] Yellow-orange crystals. [b] Red crystals.

Synthesis of Other Derivatives of Ni(TAT)$^+$.—The Br^-, SCN^-, NO_3^-, BF_4^-, and PF_6^- derivatives were prepared either by substituting the appropriate sodium salt for NaI in methods A and B or by metathesis of Ni(TAT)I using a stoichiometric amount of $AgNO_3$ and the required sodium salt. Analyses for all derivatives are reported in Table I. Yields by metatheses varied from 70 to 90%.

Synthesis of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Iodide, Ni(AT)I. Method A.—The linear, potentially sexadentate, Schiff-base ligand bis(acetylacetone)triethylenetetramine, abbreviated H_2(BAT), was prepared first. A 36.8-g sample of trien was diluted with 100 ml of benzene and chilled in an ice bath. To this was slowly added, with stirring, a solution of 40 g of acetylacetone which had been dissolved in 100 ml of benzene. The solution was chilled overnight and white crystals of H_2(BAT) precipitated from solution. The product was removed by filtration. Evaporation of the solvent, followed by addition of an ethanol–water mixture, produced additional white, needle like crystals;[10] total yield, ~25 g. *Anal.* Calcd for $C_{16}H_{30}N_4O_2 \cdot H_2O$: C, 58.49; H, 9.84; N, 17.06; O, 14.61. Found: C, 58.17; H, 9.23; N, 17.18; O, 15.42 (by difference). Mol wt: calcd, 328.52; found, 314 ($CHCl_3$).

A 2.1-g sample of H_2(BAT) was dissolved in 25 ml of water and the pH was adjusted to 5 with acetic acid. The ligand solution was brought under reflux and a solution of 2.5 g of $Ni(OAc)_2 \cdot 4H_2O$ which had been dissolved in 50 ml of water was added. The resulting solution was refluxed for 6 hr during which time the color changed to red-brown. The hot solution was filtered into a concentrated aqueous solution of NaI and the pH was adjusted to 10 with 6 *N* NaOH. Concentration and chilling of the solution caused precipitation of Ni(AT)I as dark red needles. The crystals were collected and dried, *in vacuo*, at 100°; yield, ~1 g. Analyses are reported in Table I.

Method B.—The procedure involves the *in situ* reaction of 2.5 g of $Ni(OAc)_2 \cdot 4H_2O$, 1.5 g of trien, and 2.0 g of acetylacetone. The method used was the same as that described in part C for the TAT complexes.

Synthesis of Other Derivatives of Ni(AT)$^+$.—The Br^-, SCN^-, NO_3^-, BF_4^-, ClO_4^- and PF_6^- derivatives were prepared directly from the reaction mixture by substituting the required sodium salt for NaI in the procedures given in methods A and B. The PF_6^- complex precipitated immediately from solution. All other compounds crystallized slowly from chilled solutions. Two crystalline forms were isolated for Ni(AT)Br. A yellow-orange fibrous material crystallized from the cold, aqueous solution containing NaBr. This material could only be isolated by rapid filtration followed by drying, *in vacuo*, at 100°. When the filtration was not performed rapidly and air was drawn through the matted fibers or when the partially dried yellow-orange fibers were allowed to stand in the open air, total conversion to red needles occurred. Recrystallization of the red needles from aqueous solutions yielded the aforementioned yellow-orange crystals. Analyses for all of the derivatives are reported in Table I.

Attempts to Prepare the Macrocyclic Ligands in the Absence of Nickel(II) Ions.—A 1.0-g sample of acetylacetone was added slowly to a warm solution of 1.5 g of trien which had been dissolved in ethanol and acetic acid according to the method of Barltrop, *et al.*[14] The solution was refluxed for 30 min and then concentrated sulfuric acid was added. Elemental analyses of the resulting precipitate corresponded to the amine salt. Modifying the procedure by using water as the solvent, followed by addition of perchloric acid, gave no immediate precipitate. Concentration of the solution eventually resulted in precipitation of the amine salt in 70% yield. Substituting trifluoroacetylacetone in the above procedures led to similar results.

Results and Discussion

Two series of nickel(II) complexes, Ni(TAT)X and Ni(AT)X, where the ligands are uninegative, macrocyclic, Schiff bases derived from triethylenetetramine and trifluoroacetylacetone (TAT) and from triethylenetetramine and acetylacetone (AT) and X^- is Br^-, I^-, SCN^-, NO_3^-, BF_4^-, ClO_4^-, or PF_6^-, have been prepared. The general structure of the derivatives, shown in II, has been deduced from elemental analyses, conductivities, magnetic susceptibility measurements, and infrared, nmr, and mass spectra.

Analytical data are presented in Table I. These data suggest that the ligands have resulted from total condensation of 1 mol of trien with only 1 mol of the β-diketone, since all but three of the complexes have been isolated in the anhydrous form.

All of the macrocyclic complexes reported here are obtained as red or yellow-orange crystalline solids which are diamagnetic in the solid state ($\mu_{eff} \leq 0.5$ BM) and in solution. The derivatives are soluble in most polar solvents and are 1:1 electrolytes in water and methanol, exhibiting molar conductances (Λ_M) of 89–103 and 82–110 mhos/cm, respectively.

The visible and ultraviolet spectra of Ni(TAT)BF_4 and Ni(AT)BF_4 in aqueous solution are typical of the spectra of members of the two series. Ni(TAT)$^+$ exhibits absorption bands at 474 (ε 153), 396 (ε

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(14) J. A. Barltrop, C. G. Richards, D. M. Russel, and G. Ryback, *J. Chem. Soc.*, 1132 (1959).

1940), and 370 mμ (ε 3950); while Ni(AT)$^+$ exhibits bands at 485 (ε 128) and 358 mμ (ε 1640). The first band observed in each spectrum has been assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition which is consistent with the presence of square-planar nickel(II).[15] The higher energy bands are attributed to transitions within the ligands.

The cyclic nature of the ligands has been demonstrated most convincingly by measurement and interpretation of the infrared, nmr and mass spectra of the Ni(TAT)X and Ni(AT)X complexes.

The infrared spectra of Ni(TAT)I and Ni(AT)I are listed in Table II. These examples were chosen because the spectra are typical of the two series and are not complicated by absorptions due to the anion. It should be pointed out, however, that bands attributable to SCN$^-$, NO$_3^-$, BF$_4^-$, ClO$_4^-$, and PF$_6^-$, in both the TAT and AT derivatives, indicate that these anions are not coordinated.[16-18] In general, spectra of Ni(TAT)I and Ni(AT)I are quite similar. The main differences occur in the 1200–1100-cm^{-1} region of the spectrum where the TAT derivatives exhibit very strong absorptions due to the stretching modes of the –CF$_3$ group. A comparison of other regions shows that both contain (1) a strong, slightly broad band in the 3100–3000-cm^{-1} region, which has been assigned to the –NH stretching vibration, and (2) medium or strong bands in the 1570–1520-cm^{-1} region due to C=N and/or C=C stretching modes. The presence of these bands, coupled with the absence of any absorptions attributable to –NH$_2$ groups or free >C=O groups, provides strong evidence that both terminal –NH$_2$ groups of trien have undergone Schiff-base condensation with both oxygen atoms of the β-diketone.

TABLE II
INFRARED SPECTRA[a] OF REPRESENTATIVE COMPOUNDS Ni(TAT)X AND Ni(AT)X (CM^{-1})

Ni(TAT)I[b]		Ni(AT)I[b]	
3053	s, b[d]	3073	s, b[d]
2920[c]	m[e]	2928[c]	m[e]
2850[c]	m[e]	2870[c]	m[e]
1559	m, sh[f]	1564	s, b[f]
1545	m, sh[f]	. . .	
1525	s[f]	1520	vw[f]
1471[c]	s	1475[c]	vs
1447[c]	m	1460[c]	vs
1435[c]	s	1440[c]	vs
1398	vs	1373	s
1350	w	1360	s
1336	s	1344	s
. . .		1333	m, sh
1310	m	1303	vs
1281	m	1288	s
. . .		1270	m
1254	m	1254	s
1232	w	1237	w
. . .		1187	vs[g]
1163	m	1169	s[g]
. . .		1145	vs[g]
. . .		1092	vs[g]
1084	s	1071	vs, sh[g]
1051	m	1052	m
1031	m	1030	m
1014	m	. . .	
1001	m	. . .	
942	w	956	w
860	w	877	w
770	m	785	m
549	vw	604	vw
523	w	513	m

[a] Obtained on a Perkin-Elmer Model 521 infrared spectrophotometer. [b] Abbreviations used: b, broad; m, medium; s, strong; w, weak; vw, very weak; vs, very strong; sh, shoulder. [c] Values taken using Fluorolube mulls rather than Nujol. [d] NH stretch. [e] CH stretch. [f] C=N and/or C=C. [g] CF$_3$ stretch.

An interesting trend in the shape and position of the –NH absorption band is observed as the anion is changed. This band becomes sharper and moves to higher energy as the extraplanar anion is changed from Br$^-$ to I$^-$ to SCN$^-$ to NO$_3^-$ to BF$_4^-$ to PF$_6^-$ (–NH band at 3283 cm^{-1} for both PF$_6^-$ derivatives). This shift, of about 220 cm^{-1}, is taken as evidence for hydrogen bonding between the -NH protons and the more electronegative anions.[19,20] Evidence for hydrogen bonding is also found in the nmr spectra of the complexes (*vide infra*).

The proton nmr spectra of Ni(TAT)NO$_3$ and Ni(AT)NO$_3$ in CDCl$_3$ are reproduced in Figure 1 and are typical of all derivatives. The spectra consist of four distinct regions with resonances attributable to -NH (broad singlet), =CH– (singlet), –CH$_2$– (multiplet), and –CH$_3$ (singlet). The relative areas are 2:1:13:3 for Ni(TAT)NO$_3$ and 2.3:1:13:6 for Ni(AT)NO$_3$. The absence of any bands due to –NH$_2$ or diketo –CH$_2$– groups is consistent with the infrared data and helps to confirm the cyclic structure of the ligands. Chemical shifts of Ni(TAT)NO$_3$ and Ni(AT)NO$_3$ and several other derivatives, measured in various solvents, are listed in Table III. A marked decrease in the line width of the –CH$_2$– nmr spectrum was observed upon deuteration of the –NH protons.

TABLE III
PROTON MAGNETIC RESONANCE SPECTRA[a] OF Ni(TAT)$^+$ AND Ni(AT)$^+$ COMPOUNDS

		Assignments			
Compound	Solvent	–CH$_3$	–CH$_2$–[b]	=CH–	–NH–
Ni(TAT)NO$_3$	CDCl$_3$	1.93	3.50, 2.73	5.20	6.23
Ni(TAT)I[c]	CD$_3$OD	2.02	3.53, 2.77	5.28	. . .
Ni(AT)NO$_3$	CDCl$_3$	1.87	3.46, 2.79	4.70	5.88
Ni(AT)SCN	CDCl$_3$	1.92	3.45, 2.88	4.75	5.48
Ni(AT)SCN[d]	CDCl$_3$	1.90	3.45, 2.85	. . .	. . .

[a] Chemical shifts in ppm downfield from an internal TMS standard at 60 MHz. [b] Centers of gravity for overlapping multiplets. [c] Amine protons have been replaced by deuterium. [d] Amine and vinyl protons have been replaced by deuterium by recrystallization of the complex from hot, neutral D$_2$O.

An upfield shift of the –NH resonance from 5.88 ppm in Ni(AT)NO$_3$ to 5.48 ppm in Ni(AT)SCN in-

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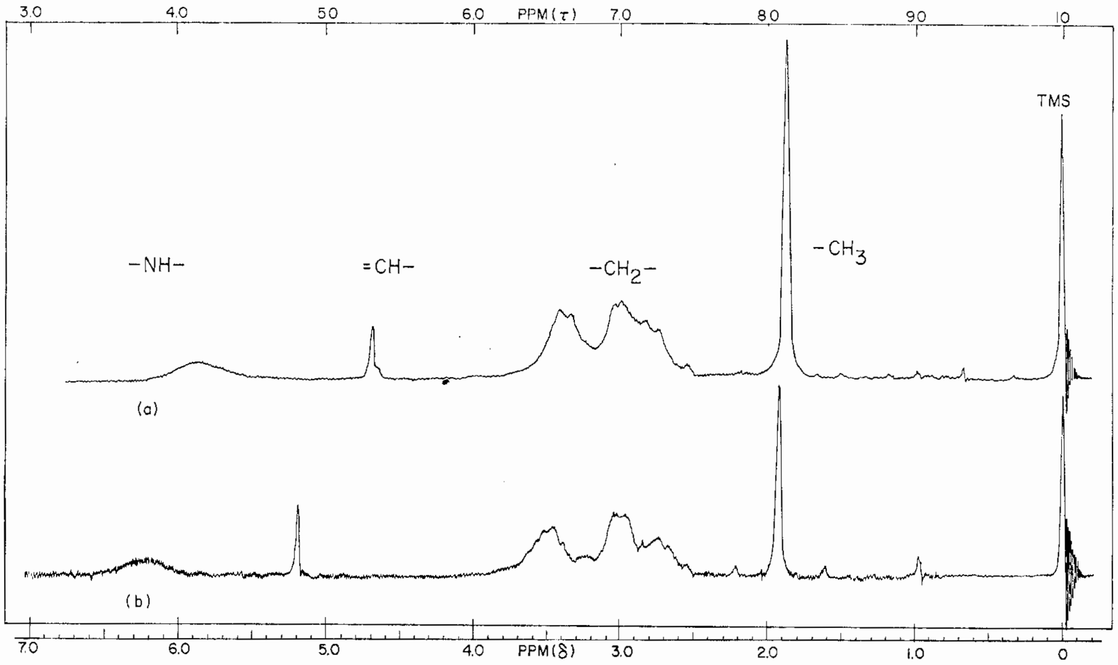
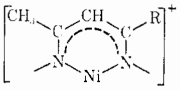


Figure 1.—The 60-MHz pmr spectra of (a) $Ni(AT)NO_3$ and (b) $Ni(TAT)NO_3$ in $CDCl_3$.

dicates increased shielding of the –NH protons in the latter complex. This has been attributed to the ability of SCN^- to hydrogen bond more strongly than NO_3^- to these protons and is consistent with the trend observed in the infrared spectra. The positions of the vinyl proton resonance in the TAT and AT derivatives are not dependent upon the anion; however, they do change with the ligand. Thus, the =CH– singlet in the TAT complexes is shifted to lower fields due to the electron-withdrawing effect of the fluorine atoms in the trifluoromethyl group located at position R in structure II. Similar shifts have been reported for fluorinated β-diketone metal complexes,[21] and it may be inferred from this that the six-membered chelate ring within the macrocyclic TAT and AT complexes is partially delocalized. Certainly some degree of Hückel aromaticity is anticipated since the number of π electrons in the ring (six) satisfies the $4n + 2$ rule.

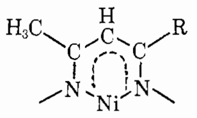
TABLE IV

MASS SPECTRA OF Ni(TAT)Br AND Ni(AT)Br

Ni(TAT)Br[a] *m/e*	Ni(TAT)Br[a] Rel abund	Ni(AT)Br[b] *m/e*	Ni(AT)Br[b] Rel abund	Assignments[c]
320	100	266	100	$(P - HBr)^+$ (≡M)
292	13	238	8	$[M - (CH_2CH_2)]^+$
277	7	223	8	$[M - (CH_2CH_2NH)]^+$
263	15	209	14	$[M - (CH_2CH_2NHCH_2)]^+$
249	7	195	8	$[M - (CH_2CH_2NHCH_2CH_2)]^+$
234	4	180	12	$[M - (CH_2CH_2NHCH_2CH_2NH)]^+$
220	3	166	9	$[M - (CH_2CH_2NHCH_2CH_2NHCH_2)]^+$
207	4	153	12	 (≡Q)
193	4	139	11	$(Q - N)^+$
160	15	133	14	$(P - HBr)^{2+}$
128	8	128	12	$(CH_2CH_2NHCH_2CH_2NHCH_2CH_2N)^+$
114	8	114	5	$(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)^+$
100	7	100	7	$(CH_2CH_2NHCH_2CH_2NHCH_2)^+$
80	35	80	42	$(HBr)^+$
71	8	71	4	$(CH_2CH_2NHCH_2CH_2)^+$
69	11	. . .	. . .	$(CF_3)^+$
57	14	57	8	$(CH_2CH_2NHCH_2)^+$
42	22	42	15	$(CH_2CH_2N)^+$

[a] Direct injection at 250° and 70 eV. [b] Direct injection at 290° and 70 eV. [c] Other very strong peaks at $m/e \pm 2$ were observed due to ^{60}Ni and ^{81}Br. Peaks at $m/e \pm 1$ corresponding to gain or loss of a hydrogen atom or presence of ^{13}C were also seen. Appropriate isotopic distributions were sometimes obscured when peaks due to these species coincided.

Finally, the data from the mass spectral analysis of Ni(TAT)Br and Ni(AT)Br are consistent with the proposed structure. The most intense *m/e* peaks are listed in Table IV. In each case, the highest mass peaks which are observed are those for the (parent − $HBr)^+$. Peaks for the doubly charged species (parent − $HBr)^{2+}$ are also evident. Of particular interest is the fragmentation pattern involving sequential loss of the elements of the trien backbone, until a fragment containing only the nickel(II) ion coordinated to the six-membered chelate ring remains, structure III. The unusual stability of this fragment in the mass spectrometer may be related to the partially delocalized nature of the ring.



III

On the basis of the evidence just presented, derivatives of Ni(TAT)X and Ni(AT)X have been identified as macrocyclic nickel(II) complexes, structure II, containing uninegative, cyclic, Schiff-base ligands formed by condensation of both oxygen atoms of the required β-diketone with the terminal $-NH_2$ groups of triethylenetetramine.

It should be noted that two diastereoisomers can be envisaged for these nickel(II) complexes, depending

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[21] R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).

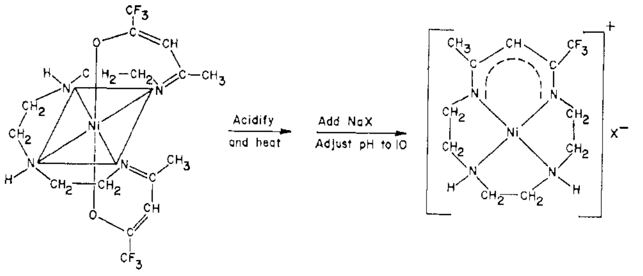

Figure 2.—Rearrangement of Ni(BTAT) to Ni(TAT)X. (The *trans* isomer of Ni(BTAT) has been shown arbitrarily.)

upon the asymmetry of the coordinated secondary amines. We have not pursued this aspect of the problem other than to note that two forms of Ni(AT)Br, one yellow and one red, could be isolated. These may be isomers or simply different hydrates. A thorough study of the isomer possibilities is now underway.[22]

Attempts to prepare the cyclic ligands in the absence of nickel(II) ions have so far been unsuccessful. It is therefore inferred that the condensation is controlled by metal ion template effects. This seems particularly reasonable in the synthesis of Ni(TAT)X complexes *via* rearrangement of Ni(BTAT). In this reaction, shown in Figure 2, the nickel(II) ion may be required to hold the ligand in a position such that acid-catalyzed self-condensation of the sexadentate Schiff base can occur with loss of 1 mol of trifluoroacetylacetone. Regardless of which of the three reported methods is used, cyclization seems to be favored, even when it requires condensation at a carbonyl oxygen adjacent to a normally deactivating $-CF_3$ group.

In view of the foregoing discussion, the new compounds are unique in two ways: (1) the Ni(TAT)X derivatives provide the first examples of chelate formation involving condensation at a carbonyl oxygen adjacent to a trifluoromethyl group; and (2) members of the Ni(TAT)X and Ni(AT)X series are the first macrocyclic metal complexes to be synthesized by condensation of both oxygen atoms of a β-diketone with a polyamine.

In addition, the uninegative nature of the two ligands, resulting in partial delocalization of the six-membered chelate ring within the macrocycles, is most important and serves to distinguish these complexes from the tetraazadienes of Curtis[23] (neutral ligands), and the tetraazaannulens of Jäger[24] (ligands of double negative charge) which are models of the well known phthalocyanines and porphyrins. The cyclization reaction reported here may ultimately provide the first simple route to metal complexes containing macrocyclic ligands of uninegative charge, which should serve as models for the corrin ring. The scope and general applicability of these reactions are currently being investigated.

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(22) W. Elfring and N. J. Rose, private communication, University of Washington, 1969.

(23) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(24) E. G. Jäger, *Z. Anorg. Allgem. Chem.*, **364**, 177 (1969), and references therein.

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Iodonium Salts of Complex Anions. II.[1] Pyrolytic Autoarylation Reactions of Diphenyliodonium Bis(N-cyanodithiocarbimato)nickel(II)

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Diphenyliodonium bis(N-cyanodithiocarbimato)nickel(II) has been prepared and its solid-state thermal autoarylation studied. The diphenyliodonium cation phenylates the complex anion; attack occurs on the two sulfur atoms of the same ligand. This has been verified by the isolation and identification of N-cyanodiphenyldithiocarbimate, $(C_6H_5S)_2C{=}NC{\equiv}N$. As a result of the phenylation the configuration about nickel changes from planar to octahedral, giving a polymeric species.

Introduction

The usefulness of the diphenyliodonium cation (dpi) for precipitating complex anions in pure form and good yield from aqueous solution has been demonstrated. Isolation and reactions of dpi salts of the binegative anions tetrachloroplatinate(II)[2] and bis(dithiooxalato)platinate(II) and -palladate(II)[1] have been reported. As part of our investigation on ligand reactions of dpi salts of complex anions, we have conducted studies employing the diprotic ligand N-cyanodithiocarbimate (cdc). The preparation and characterization of tetramethylammonium[3] and tetrapropylammonium[4] salts of the anion bis(N-cyanodithiocarbimato)nickel(II) have been reported recently.

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