the energy gap between these states is less than or comparable to β. This study shows that the largest solvent effects on the lifetimes are actually found for $[IrCl_2(5,6\text{-}Mephen)_2]Cl$ where the energy of the charge-transfer state is substantially above that of the ligand-localized state.

In conclusion, we wish to point out that this is, to the best of our knowledge, the first quantitative estimate of the validity of the widely used model to label states as charge transfer or ligand localized in these kinds of complexes. At present we have no way of deducing whether our determination of β for the species studied here will provide a rough estimate of such interactions for other complexes. If β is determined primarily by electron repulsion terms rather than spin-orbit-coupling terms, as we have suggested, it is probably reasonable to assume that similar values of β will apply to complexes of similar ligands with different metals. The values of β might be quite sensitive, however, to large alterations of the ligands. Our study provides no means of estimating the magnitude of the interactions of crystal field (d-d) with either ligand-localized or charge-transfer states. If, in the future, the magnitude of such interactions can be deduced, a complete analysis of the range of validity of pure configuration labeling will be possible.

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Pseudooctahedral Cobalt(III), Nickel(II), and Cadmium(II) Complexes of Linear, Sexadentate, Fluorinated Schiff Base Ligands

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New pseudooctahedral complexes, Ni(BTAT), Ni(BHAT), Cd(BTAT), Co(BTAT)X, and $[Co(BTAT)]_2CoY_4$ where $X^- = Br^-, I^-, NO_3^-$, and ClO_4^- and $Y^- = Cl^-$ and SCN^-, have been prepared from the linear Schiff base ligands bis(trifluoroacetylacetone)triethylenetetramine, abbreviated H_2BTAT, and bis(hexafluoroacetylacetone)triethylenetetramine, abbreviated H_2BHAT. Characterization of the complexes by elemental analyses, molecular weight, magnetic susceptibility, and conductivity measurements and by nmr, infrared, visible, and mass spectral data has shown that the reactions proceed stereospecifically with formation of only the s-cis isomer.

Introduction

Studies on volatile metal chelates containing β-diketonate ligands have shown that maximum volatility results when the ligands are highly fluorinated and simultaneously satisfy the charge and coordination number of the metal ion.[1-3] We have used these criteria as guidelines in the synthesis of some potentially volatile transition metal complexes containing divalent metal ions and fluorinated Schiff base ligands.

The usual octahedral geometry of the dipositive transition metals dictates that if inner complexes are to result, the Schiff base ligands should be sexadentates and capable of coordinating to the metal as dinegative ions. While numerous metal complexes containing sexadentate Schiff base ligands have been prepared by Lions, *et al.*,[4] most of these were prepared from linear tetradentate ligands containing terminal NH_2 groups with two bridging sulfur atoms in the backbone and various aldehydes or, in a few cases, acetylacetone. For purposes of this study, ligands derived solely from linear tetramines and fluorinated β-diketones were used. Specifically, the sexadentate ligand obtained by condensation of 2 equiv of trifluoroacetylacetone with 1 equiv of triethylenetetramine (trien), abbreviated H_2BTAT, and that obtained from 2 equiv of hexafluoroacetylacetone and 1 equiv of trien, abbreviated H_2BHAT, have been prepared and used to synthesize complexes abbreviated Ni(BTAT), Ni(BHAT), Cd(BTAT), [Co(BTAT)]X, and $[Co(BTAT)]_2CoY_4$, where $X^- = Br^-, I^-, NO_3^-$, and ClO_4^- and $Y^- = Cl^-$ and SCN^-.[5]

While none of the neutral complexes possess the desired high volatility, Ni(BHAT) provides a new example of a Schiff base compound obtained by condensation of a carbonyl oxygen atom adjacent to a presumably deactivating CF_3 group.[6,7] To date only one other metal complex of this type is known. It is the macrocyclic Ni(II) complex Ni(TAT)X, where TAT is the uninegative, fluorinated tetramine ligand 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene, which can be prepared in several ways including rearrangement of the Ni(BTAT) complex characterized in this paper.[8] Although four geometrical isomers are possible for the sexadentate complexes, studies suggest that the syntheses are stereospecific.

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TABLE I

ANALYTICAL DATA FOR COBALT(III), NICKEL(II), AND CADMIUM(II) COMPLEXES

	% calcd						% found					
Complex	C	H	N	F	Metal	Other	C	H	N	F	M	Other
$[Co(BTAT)]_2CoCl_4 \cdot 2DMF$	35.17	4.52	10.80	17.57	13.62	10.93, Cl	35.40	4.48	10.89	17.62	13.76	11.51, Cl
$[Co(BTAT)]_2[Co(SCN)_4]$	34.82	3.58	13.54	18.36	14.24	10.33, S	34.76	3.49	13.67	18.69	13.17	10.68, S
Co(BTAT)I	31.91	3.68	9.31	18.93	9.79	21.07, I	31.91	3.75	9.25	18.62	9.86	21.90, I
Co(BTAT)Br	34.61	3.99	10.09	20.53	10.62	14.39, Br	34.15	4.09	10.11	20.41	10.94	14.32, Br
$Co(BTAT)NO_3$	35.63	4.49	12.99	21.14	10.93	14.83, O	36.06	4.17	13.27	20.93	11.00	14.57, O[a]
$Co(BTAT)ClO_4$	33.43	3.86	9.75	19.83	10.25	6.17, Cl	33.60	3.95	9.87	19.73	10.10	6.32, Cl
Ni(BTAT)	40.44	4.68	11.79	23.99	12.36		40.38	4.82	11.78	23.75	12.94	
Ni(BHAT)	32.96	2.71	9.61	39.10	10.07		33.22	2.80	9.56	38.52	11.42	
Cd(BTAT)	36.34	4.20	10.60	21.56	21.25		36.43	4.15	10.55	20.90	20.37	

[a] Obtained by difference.

Experimental Section

Materials.—Triethylenetetramine was purchased from Aldrich Chemical Co. and used as received. Trifluoroacetylacetone and hexafluoroacetylacetone were obtained from Pierce Chemical Co. and were freshly distilled before use. All other chemicals were reagent grade or equivalent.

Measurements.—Infrared spectra were determined on a Perkin-Elmer Model 137-B spectrophotometer using the Nujol mull technique. Visible and ultraviolet spectra were obtained using a Cary 14 recording spectrophotometer. All reported nuclear magnetic resonance spectra were determined using a Varian A-60 nmr spectrometer. Chemical Shifts for pmr spectra were measured using TMS as an internal standard. Chemical shifts for ^{19}F nmr spectra were measured with trichlorofluoromethane as an internal standard.

Magnetic susceptibilities were determined utilizing the Faraday technique. Conductances were obtained for 10^{-3} *M* aqueous or methanolic solutions using an Industrial Instruments Model RC-16B conductivity bridge. Mass spectra were obtained with an LKB 9000 or MS-9 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Ligand Preparations. Bis(trifluoroacetylacetone)triethylenetetramine, H_2BTAT.—An 18.4-g sample (0.13 mol) of trien was diluted with 100 ml of absolute ethanol and the solution was chilled in an ice bath to 20°. To this was added slowly, with stirring, a 30.8-g sample (0.20 mol) of freshly distilled trifluoroacetylacetone which had been diluted with 100 ml of ethanol. During the addition of the β-diketone to the amine, heat was evolved and the solution turned pale yellow. The solution was warmed and stirred for 0.5 hr. A large volume of H_2O (750 ml) was then added and the resulting cloudy solution was concentrated under an air stream for 18 hr. The white, needlelike crystals which formed were collected, washed with water, and dried overnight, *in vacuo*, at room temperature; yield 12–15 g. *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). Molecular weight: calcd, 418.44; found, 430 ($CHCl_3$). Nmr spectrum in $CDCl_3$: CH_3 singlet, 2.08 ppm; $=CH-$ singlet, 5.30 ppm; $-CH_2-$ multiplets, 2.4–3.5 ppm; $-NH-$ broad singlet, 11.12 ppm.

Bis(hexafluoroacetylacetone)triethylenetetramine, H_2BHAT.—When a procedure analogous to that just described for synthesis of H_2BTAT was used, addition of the β-diketone to the amine solution (or *vice versa*) resulted in precipitation of the salt trien·2hfa. Removal of the salt, followed by concentration of the filtrate, produced an oil which could not be induced to crystallize. This oil was used in the preparation of Ni(BHAT).

Synthesis of Cobalt(III) Complexes. $[Co(BTAT)]_2CoCl_4 \cdot 2DMF$.—A 4.76-g sample (0.02 mol) of $CoCl_2 \cdot 6H_2O$ was dissolved in 100 ml of DMF. This was added to 50 ml of a DMF solution containing 8.4 g (0.02 mol) of H_2BTAT. During the addition, the color of the solution changed from red to dark green. About 100 ml of methanol was added, and air was bubbled through the solution. After 3 hr, maroon needles began to form. Air oxidation was continued for 8 hr. The mixture was then chilled and the crystals were collected, washed with acetone and ether, and dried, *in vacuo*, at room temperature; yield 4.4 g.

$[Co(BTAT)]_2Co(SCN)_4$.—A 1.16-g sample of $[Co(BTAT)]_2CoCl_4 \cdot 2DMF$ was dissolved in 75 ml of a 1:1 methanol–water solution. A silver nitrate solution was added dropwise until precipitation of AgCl appeared complete. The AgCl was removed by filtration and the filtrate was added to a saturated solution containing a large excess of KSCN. The AgSCN which precipitated was removed. Slow evaporation of the resulting blue-green solution resulted in the formation of large, dark blue-green crystals which were collected, washed with ether, and dried, *in vacuo*, at room temperature; yield 0.90 g.

$[Co(BTAT)]X$ ($X^- = Br^-, I^-, NO_3^-, ClO_4^-$).—The synthesis of these derivatives was achieved *via* metathetical reactions on the tetrachlorocobaltate derivative. A typical metathesis involved the dissolution of 2.0 g of $[Co(BTAT)]_2CoCl_4 \cdot 2DMF$ in 75 ml of a 1:1 methanol–water solution and the precipitation of Cl^- with silver nitrate solution. After removal of the AgCl by filtration the filtrate was added to a saturated solution containing an excess of the appropriate sodium salt. Any silver salt which precipitated was removed. Concentration of the resulting solution caused maroon crystals of the desired products to form. The crystals were collected, washed with ether, and dried, *in vacuo*, at room temperature. Yields varied from 30% for the very soluble NO_3^- derivative to ~100% for the relatively insoluble ClO_4^- derivative.

Analytical data for the six new cobalt(III) complexes are presented in Table I. Small quantities of [Co(BTAT)]Cl and [Co(BTAT)]SCN were prepared by metathesis of the nitrate complex and the required sodium or potassium salt; however, these complexes were not characterized except *via* their ir spectra.

Synthesis of Nickel(II) Complexes. Ni(BTAT).—A 4.18-g sample of H_2BTAT was dissolved in 100 ml of DMF. To this was added 2.38 g of $NiCl_2 \cdot 6H_2O$ which had been dissolved in 50 ml of DMF. The solution turned dark green. A large volume of acetone was added, causing the solution to become cloudy. The green powder, $Ni(H_2BTAT)Cl_2$, which precipitated from solution after several hours was collected and dissolved with some difficulty in boiling water. When the resulting orange solution was made basic with concentrated NaOH solution, the neutral complex Ni(BTAT) precipitated. The product was recrystallized from methanol; yield ~20%. When a 1.2-g sample of Ni(BTAT) was refluxed in 100 ml of H_2O which had been adjusted to pH 5 with acetic acid, the color of the solution changed from brown to red. Addition of NaI and NaOH (pH 10) yielded crystals of Ni(TAT)I, a macrocyclic complex which has been described elsewhere.[8]

Ni(BHAT).—The oil obtained from the H_2BHAT ligand preparation was dissolved in hot water by adjusting the pH to 5 with acetic acid. A 1.0-g sample of $Ni(OAc)_2 \cdot 4H_2O$ was dissolved in hot water and was added to the refluxing ligand solution. An immediate color change from green to brown occurred, and a pale brown precipitate formed. After 3 hr of refluxing, the precipitate was removed by filtration and dried, *in vacuo*, at room temperature; yield 0.3 g. The product was recrystallized from methanol–water solution. Analytical data for the two new Ni(II) complexes are reported in Table I.

Synthesis of Cd(BTAT).—A 12.54-g sample of H_2BTAT was dissolved in 50 ml of methanol. To this was added with stirring 0.88 g of $CdCl_2$ which had been dissolved in 50 ml of a methanol–water solution. A white powder precipitated immediately. The reaction mixture was stirred and warmed for ~0.5 hr, and more product formed. After chilling the mixture, the white powder was collected, washed with acetone, and dried over $CaCl_2$; yield 9.9 g. A 6.0-g sample of the dried product was ground in a mortar and pestle with a stoichiometric amount of washed Ag_2O which had been freshly prepared by addition of NaOH solution to 3.4 g of silver nitrate. The slurry was taken up in methanol and the AgCl was removed by filtration. Concentration of the filtrate, to which a few drops of NaOH had been added, gave white crystals of Cd(BTAT), which were collected and dried, *in vacuo*, at 105°; yield 3.3 g. Analytical data are presented in Table I.

Results and Discussion

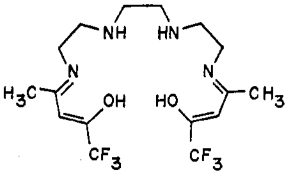
Ligands.—The sexadentate ligands bis(trifluoroacetylacetone)triethylenetetramine, H_2BTAT, and bis(hexafluoroacetylacetone)triethylenetetramine, H_2BHAT, were prepared by extension of the procedure reported by Calvin, *et al.*,[9] for the synthesis of bis(acetylacetone)ethylenediamine. H_2BTAT was isolated as a white crystalline material and was characterized on the basis of elemental analyses, molecular weight data, and nmr, infrared, and mass spectra. Analytical and molecular weight data have been reported in the Experimental Section and confirm the 2:1 keto–amine stoichiometry. The infrared spectrum of H_2BTAT, reported in column one, Table II, exhibits a sharp but weak –NH stretching vibration at 3380 cm^{-1}. A strong, sharp band at 1630 cm^{-1} has been assigned as the C—O stretching mode while a strong, broader band at 1575 cm^{-1} has been attributed to both the C=C and C=N stretching modes. Absorptions at 1252–1100 cm^{-1} are typical of the $-CF_3$ stretching vibrations.

TABLE II

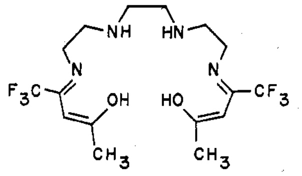
INFRARED SPECTRA[a] OF METAL COMPLEXES

H_2BTAT[b]	Co(BTAT)I[b]	Cd(BTAT)[b]	Ni(BTAT)[b]	Ni(BHAT)[b]
3380 w, sp[c]	3106 s[c]	3360 w[c]	3335 w[c]	3350 w[c]
d	*d*	*d*	*d*	*d*
1630 vs, sp[e]	1631 vs[e]	1616 vs[e]	1616 vs[e]	1614 s[e]
1575 vs, b[f]	1548 s[f]	1556 vs[f]	1540 vs[f]	1530 vs[f]
				1510 s, sh[f]
d	*d*	*d*	*d*	*d*
1340 w	1326 vw	1334 w	1334 w	1312 s
1280 m, sh	1294 vs	1272 vs	1282 vs	1270 s, sh
1252 vs[g]	1250 w	1242 m, sh	1262 s, sh[g]	1262 s[g]
				1250 s, sh[g]
	1238 w		1234 w	
	1222 vw			1222 w
	1205 w, sh	1200 vw, sh		
1195 s, sh[g]	1195 vs[g]	1178 vs[g]	1198 vw, sh[g]	1187 vs[g]
1180 vs[g]	1149 vs[g]	1163 vs[g]	1155 vs[g]	1170 vs[g]
1130 vs, b[g]	1131 vs[g]	1138 vs[g]	1140 vs[g]	1150 s, sh[g]
1110 vs, sh[g]		1120 vs[g]	1111 vs[g]	1115 s, sh[g]
	1094 m[g]	1101 vs[g]		1092 s[g]
	1078 m[g]	1080 vs[g]	1088 s, sh[g]	1075 m[g]
1048 w	1053 vw	1038 vw	1026 vw	1042 w
1018 w	1012 w	1010 vw	1015 vw	1008 vw
955 vw	952 vw	952 w	946 vw	956 w
935 vw	922 vw	917 w	914 m	918 m
897 w	882 m	902 w	897 w	909 m
870 s		864 m	881 s	877 m
768 m	765 s	755 s	764 s	772 s
737 m	735 m	734 vw	747 s	736 w
723 s	725 s	719 s	722 s	717 vw

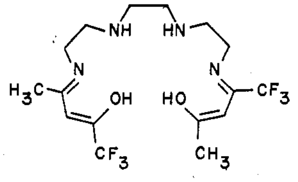
[a] Obtained on a Perkin-Elmer Model 137-B spectrophotometer and reported in cm^{-1}. [b] Abbreviations used: b, broad; sp, sharp; sh, shoulder; vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [c] NH stretching mode. [d] CH stretching and bending regions obscured by Nujol peaks. [e] $C\overset{\cdots}{-}O$ stretching vibration. [f] $C\overset{\cdots}{-}N$ and/or $C\overset{\cdots}{-}C$ stretching modes. [g] CF_3 stretching modes.



I



II



III

Three possible isomers can be envisaged for the H_2BTAT ligand, structures I–III, depending upon which "end" of the trifluoroacetylacetone moiety has condensed with the terminal NH_2 groups of the amine. Analysis of nmr and mass spectral data for H_2BTAT has been most useful in distinguishing among these possibilities. The nmr spectrum shows two sharp singlets at 2.08 and 5.30 ppm with relative intensities of 3:1 which have been assigned to the $-CH_3$ and $=CH-$ resonances, respectively. A broad singlet at 11.12 ppm has been attributed to the –NH of the trien backbone. Resonances due to the bridging CH_2 groups were observed from 2.3–3.9 ppm. A low-field quartet centered at 3.5 ppm has been assigned to the bridging CH_2CH_2 group between the secondary nitrogen atoms, while a more complex pattern, centered at 2.6 ppm, has been attributed to the more highly shielded CH_2CH_2 groups between the secondary nitrogen atoms and imine functional groups. Both the methyl and methine proton resonances maintain their sharp singlet character when the spectrum is expanded. Barring any accidental degeneracies, this eliminates III and indicates the presence of either pure I or pure II. The position of the methyl singlet in the spectrum of H_2BTAT agrees closely with that reported for bis(trifluoroacetylacetone)propylenediamine which occurs as a doublet centered at 2.05 ppm.[10] Dipole moment measurements on metal chelates of Schiff bases formed from trifluoroacetylacetone and propylenediamine and ethylenediamine have shown that the methyl groups are adjacent to the diimine bridge.[11,12] A comparison of resonance positions for the inside and outside methyl groups of bis(acetylacetone)triethylenetetramine with that of H_2BTAT is also somewhat helpful in differentiating the type of methyl groups in the fluorinated ligand; however, the presence of the strongly electron-withdrawing CF_3 groups causes the methyl resonance in H_2BTAT to be shifted downfield from where it occurs in the spectrum of the nonfluorinated Schiff base. If one assumes a downfield shift of 0.15 ppm as reported in the case of bis(trifluoroacetylacetone)propylenediamine,[10] then the methyl signal of H_2BTAT agrees most closely with the inside methyl of the nonfluorinated Schiff base which occurs at 1.92 ppm. Both of the comparisons just cited suggest that the methyl groups in H_2BTAT are adjacent to the diimine bridge.

Further evidence that H_2BTAT has structure I has been obtained from the mass spectrum of the ligand which is reported in Table III. The spectrum does not contain a peak which can be assigned to the parent ion but is characterized by the regularity of the fragmentation pattern. This pattern shows the presence of fragments resulting from loss of a CF_3 group and

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TABLE III

MASS SPECTRUM[a] OF H_2BTAT

m/e	Rel abund	Assignments[b]
348	8	$[P - (CF_3, H)]^+$
306	5	$[P - (CF_3C(OH){=}CH, H)]^+$
290	10	$[P - (CF_3C(OH){=}CH, CH_3, 2H)]^+$
278	11	$[P - (CF_3C(OH){=}CHC(CH_3)\text{–}, 2H)]^+$
265	5	$[P - (CF_3C(OH){=}CHC(CH_3){=}N\text{–}, H)]^+$
252	100	$[P - (CF_3C(OH){=}CHC(CH_3){=}NCH_2\text{–})]^+$
223	9	$[P - (CF_3C(OH){=}CHC(CH_3){=}NCH_2CH_2N(H)\text{–})]^+$
209	100	$[P/2]^+$
192	8	$[CF_3C(OH){=}CHC(CH_3){=}NCH_2CH_2N, -2H]^+$
180	32	$[CF_3C(OH){=}CHC(CH_3){=}NCH_2CH_2\text{–}]^+$
166	29	$[CF_3C(OH){=}CHC(CH_3){=}NCH_2\text{–}]^+$
153	14	$[CF_3C(OH){=}CHC(CH_3){=}N, +H]^+$
138	10	$[CF_3C(OH){=}CHC(CH_3)\text{–}]^+$
127	100	$[CF_3C(OH){=}CH\text{–}, +CH_3, +H]^+$
111	11	$[CF_3C(OH){=}CH\text{–}]^+$
98	60	$[CF_3C(OH)\text{–}]^+$
81	18	$[CF_3C\text{–}]^+$
69	98	$[CF_3\text{–}]^+$
57	90	$F_3{}^+$
56	99	$[\text{–}NCH_2CH_2N\text{–}]^+$
43	100	$[\text{–}NHCH_2CH_2\text{–}]^+$

[a] Direct introduction at 200° and 70 eV. [b] Peaks at *m/e* ± 1 corresponding to gain or loss of a hydrogen atom and/or presence of ^{13}C were also seen.

successively larger groups until the most intense peak at mass number 209 equal to half the ligand mass is observed. Most important is the presence of mass peak 306 assigned as $[P - (CF_3C(OH){=}CH, H)]^+$ and the absence of a peak at mass number 361 attributable to $[P - (CH_3C(OH){=}CH)]^+$ which indicates that the CH_3 groups are adjacent to the Schiff base linkages. If any of the other isomers are present, they must exist in very small amounts which cannot be detected by the nmr and mass spectral techniques used. The entire fragmentation pattern for the ligand is very similar to those of the metal complexes which are discussed later (*vide infra*). While H_2BTAT was isolated as a discrete, completely characterizable compound, H_2BHAT could be obtained only as a crude oil which was not characterized.

Synthesis of Metal Complexes.—In general, synthesis of the metal complexes involved reaction of the metal salt with a stoichiometric amount of the ligand. In the synthesis of Ni(BTAT) and Co(BTAT)X, the reactions could only be performed using DMF as a solvent. A mixture of water and methanol proved to be a satisfactory solvent for formation of the Cd(II) complex. While the Co(III) complexes containing the dinegative sexadentate ligand crystallized directly from the reaction solution or could be made by metathetical reactions, isolation of the corresponding Ni(II) and Cd(II) complexes required the addition of base or metathesis with Ag_2O. Indeed, the latter two complexes were derived from isolable intermediates of stoichiometries $Ni(H_2BTAT)Cl_2$ and $Cd(H_2BTAT)Cl_2$. An investigation into the nature of these intermediates is in progress.

Synthesis of Ni(BHAT) was achieved by reaction of the crude oil containing the ligand with $Ni(OAc)_2 \cdot 4H_2O$ in aqueous solution. The crude neutral complex which precipitated from the reaction solution was purified by recrystallization.

Characterization of Metal Complexes.—All of the new compounds have been characterized on the basis of analytical data, conductivity measurements, and infrared, electronic, and mass spectra. The Co(III) complexes were further investigated by nmr measurements.

Analytical data for the complexes are presented in Table I and agree with the formulations shown. The dinegative character of the Schiff base ligands is indicated by the 1:1 stoichiometry of the simple Co(III) complexes and the absence of any uninegative anions in the Ni(II) and Cd(II) complexes.

Presence of the sexadentate ligands is further indicated by the mass spectra of Co(BTAT)Br, Ni(BTAT), and Ni(BHAT). Table IV contains ion assignments for the six most intense peaks which are observed in the spectrum of each of the complexes. While both Ni(BTAT) and Ni(BHAT) exhibit a relatively intense peak at a mass number corresponding to the parent ion, the highest *m/e* peak for Co(BTAT)Br is that due to $[P - HBr]^+$. Loss of HBr is probably induced by ionization but the possibility also exists that it is generated thermally. The spectra of the two BTAT compounds and the free ligand show very similar fragmentation patterns involving many peaks not listed. The sequential loss of elemental units of the ligand is most noticeable from the fragments generated.

The infrared spectrum of the free ligand H_2BTAT and spectra of Co(BTAT)I, Cd(BTAT), Ni(BTAT), and Ni(BHAT) are reported in Table II. Examination of the data shows that the spectra of all of the complexes are very similar. Assignments of the –NH stretching vibration (3380–3106 cm^{-1}), $C\overset{\cdots}{-}O$, $\text{–}C\overset{\cdots}{-}N\text{–}$ and/or $\text{–}C\overset{\cdots}{-}C\text{–}$ stretching modes (~1620 and 1550

TABLE IV

MASS SPECTRA[a] OF Co(BTAT)Br, Ni(BTAT) AND Ni(BHAT)

Co(BTAT)Br[b]		Ni(BTAT)[c]		Ni(BHAT)[d]		
m/e	Rel abund	*m/e*	Rel abund	*m/e*	Rel abund	Assignments[e]
		474	54	583	34	$[P]^+ = Q$
474	Off scale					$[P - HBr]^+ = Q$
308	Off scale	308	100	362	100	$[Q - CF_3C({=}O)CH_2C(R){=}NCH_2\text{–}]^+$
				349	34	$[Q - CF_3C(O){=}CHC(R){=}NCH_2CH_2\text{–}]^+$
266	Off scale	266	70	320	58	$[Q - {}^1/_2L]^+$
		209	34			$[{}^1/_2H_2L]^+$
208	100					$[{}^1/_2L]^+$
127	44					
						$[\text{–}CF_3]^+$
56	71	56	54	56	31	$[\text{–}NCH_2CH_2N\text{–}]^+$
		42	48	42	33	$[\text{–}NCH_2CH_2\text{–}]^+$

[a] Only the six most intense peaks in each spectrum are reported. Almost every ligand fragment is observed in the spectra of all of the complexes but these are among the weaker peaks. [b] Direct introduction at 145° and 70 eV. [c] Direct introduction at 250° and 70 eV. [d] Direct introduction at 60° and 70 eV. [e] Peaks at *m/e* ± 1 corresponding to gain or loss of a hydrogen atom or presence of ^{13}C were seen. In the Ni(II) complexes peaks at *m/e* ± 2 having the appropriate isotopic distribution for ^{60}Ni were observed. A peak due to ^{81}Br was observed in the spectrum of Co(BTAT)Br at mass number 472, $[P - HBr]^+$.

TABLE V

ELECTRONIC SPECTRA OF METAL COMPLEXES

		Absorption bands, nm (ϵ)				
Complex	Solvent	ν_1	ν_2	ν_3	ν_4	ν_5
$[Co(BTAT)]_2CoCl_4 \cdot 2DMF$	Refl[a]	696	634	555	483	333
		673	616			
	H_2O			550 (356)	490 (496)	332 (11,400)
$[Co(BTAT)]_2CoCl_4$	Refl[a]	698	636	550	475	341
		673	616			
$[Co(BTAT)]_2Co(SCN)_4$	Refl[a]		628	590	460	340
	H_2O			550 (349)	491 (490)	330 (11,750)
	MeOH			555 (291)	478 (471)	325 (485)
Co(BTAT)I	H_2O			550 (172)	490 (245)	330 (5500)
Co(BTAT)Br	H_2O			550 (175)	492 (246)	332 (5480)
$Co(BTAT)NO_3$	H_2O			550 (199)	491 (269)	328 (2920)
	MeOH			555 (102)	477 (157)	325 (216)
$Co(BTAT)ClO_4$	H_2O			550 (174)	490 (245)	332 (5700)
Ni(BTAT)	Refl[a]	855[b]	525	355		
	MeOH	885[b] (22)	548 (11)	313 (6100)		
Ni(BHAT)	MeOH	910[b] (23)	495 (38)	343 (6200)		

[a] Obtained using Nujol mull–diffuse transmittance technique. Asymmetric band.

cm^{-1}), and $-CF_3$ stretching modes (1195–1080 cm^{-1}) have been made. The absorption assigned to the –NH stretching vibration in Co(BTAT)I appears at lower energy than the corresponding band in the Ni(II) and Cd(II) complexes. This phenomenon has been observed in other ionic Schiff base complexes[8,13] and is attributed to hydrogen bonding between the secondary amine proton and the anion. This conclusion is supported by the observation that the –NH band in $Co(BTAT)ClO_4$, where little if any hydrogen bonding is expected, occurs at 3280 cm^{-1}, compared to 3106 cm^{-1} for the –NH absorption in Co(BTAT)I. The other Co(III) derivatives show varying amounts of hydrogen bonding in general accord with the electronegativity of the anion. Some structuring of the –NH absorption band is observed for the $Co(SCN)_4^{2-}$ and NO_3^- derivatives, suggesting a difference in the type or extent of hydrogen bonding for the two –NH groups. This may be due to differences in crystal packing or to the presence of diastereoisomers resulting from different orientations of the hydrogen atoms of the secondary amine groups. The possibility of diastereoisomerism has not yet been fully investigated.

The infrared spectrum of $[Co(BTAT)]_2CoCl_4 \cdot 2DMF$ has also been useful in providing evidence for the nature of this adduct. The presence of DMF is indicated by a new strong, sharp absorption band at $\sim$1652 cm^{-1} which has been assigned to the $>C{=}O$ stretching vibration of the DMF molecules.[14] This assignment has been confirmed in two ways. The sample has been dried under vacuum at temperatures up to 115° with no change. However, the DMF can be completely removed by heating the sample for 2 hr at 175° under dynamic vacuum. The infrared spectrum of the remaining compound is identical with that of the original except for the absence of the band at $\sim$1652 cm^{-1}. This compound can then be recrystallized unchanged from aqueous methanol; however, when DMF is added to the solution, only the adduct is isolated and the band at $\sim$1652 cm^{-1} is again observed in the infrared spectrum.

The close similarity between spectra of the Co(III) derivatives and the neutral Ni(II) and Cd(II) compounds, plus the absence of bands attributable to coordinated NO_3^- [15,16] and ClO_4^- [16] in the Co(III) derivatives, suggests that all of the metal complexes contain only the dinegative sexadentate ligands coordinated to the metal ion.

Further evidence for such structures has been obtained from the results of conductivity measurements in 10^{-3} M methanol solutions. As expected, Ni(BTAT) and Cd(BTAT) are nonelectrolytes, whereas, the Co(BTAT)X complexes, where $X^- = Br^-, I^-, ClO_4^-$, and NO_3^-, are 1:1 electrolytes with values of Λ_M = 90–120 mhos. The $CoCl_4^{2-}$ and $Co(SCN)_4^{2-}$ derivatives show more complex behavior in solution with values of $\Lambda_M \simeq 400$ mhos indicating partial dissociation of the complex anions.

The octahedral nature of the Ni(II) and Co(III) ions has been confirmed by magnetic susceptibility measurements and electronic spectral data. Ni(BTAT) and Ni(BHAT) possess magnetic moments of 3.06 and 3.20 BM which indicate the presence of octahedral Ni(II) ions containing two unpaired electrons. Electronic spectra, reported in Table V, also show three absorption bands at ν_1 855–910 nm, ν_2 495–525 nm, and ν_3 313–355 nm which are typical of pseudooctahedral Ni(II).[17] These have been assigned as follows: ν_1, $^3T_{2g} \leftarrow {}^3A_{2g}$; ν_2, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$; ν_3, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$.

The magnetic behavior of the Co(III) derivatives depends upon the nature of the noncoordinated anion. The Br^-, I^-, NO_3^-, and ClO_4^- derivatives are essentially diamagnetic, possessing magnetic moments of $\sim$0.55 BM, which is consistent with a spin-paired Co(III) configuration. The $CoCl_4^{2-}$ and $Co(SCN)_4^{2-}$ derivatives also contain spin-paired Co(III) but exhibit magnetic moments of 4.43 and 4.74 BM due to tetrahedral Co(II) in the complex anions. The presence of the $CoCl_4^{2-}$ and $Co(SCN)_4^{2-}$ anions is further confirmed by structured absorption bands at 696 and 634 nm in the visible spectra of these derivatives, Table V.[17] Since the complex tetrahedral Co(II) species dissociate in aqueous and methanolic solutions, the char-

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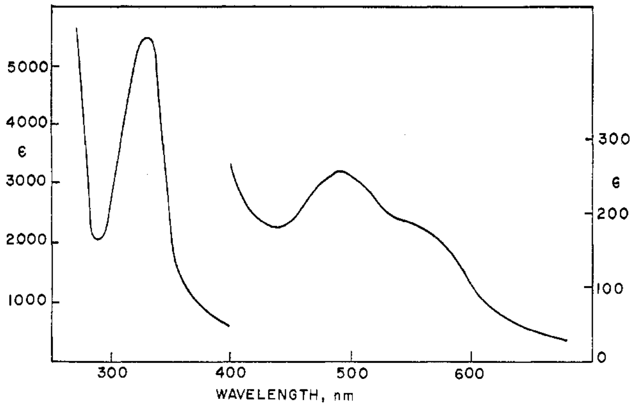
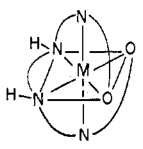


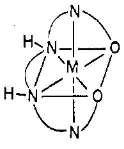
Figure 1.—Visible spectrum of [Co(BTAT)]Br in H_2O.

acteristic bands of tetrahedral Co(II) are observed only in the solid-state spectra which were obtained in Nujol mulls using the diffuse-transmittance technique.[18] As can be seen from Table V, all of the $[Co(BTAT)]^+$ complexes exhibit two major absorption bands in the 500- and 300-cm^{-1} regions which have been correlated with the $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ spin-allowed electronic transitions of low-spin octahedral Co(III).[17]

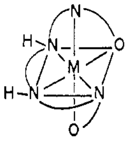
On many occasions, it has been possible to distinguish between geometrical isomers of Co(III) complexes on the basis of the number of bands in the visible region. While this is not entirely possible in the case of the Co(BTAT)X complexes, the shape of the $^1T_{1g}$ band has been useful in eliminating some of the geometrical isomers. Four geometrical isomers are possible for the octahedral BTAT complexes, structures IV–VII.



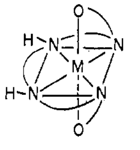
IV



V



VI



VII

Forms IV and V can be described as s-cis forms, differing principally in the NNO angle. Form VI is the uns-cis isomer and VII is the trans form, where cis and trans refer to the position of the oxygen atoms and s (symmetrical) and uns (unsymmetrical) refer to the configuration of the trien portion of the sexadentate ligand. Both s-cis forms and the trans isomer possess one unique axis of different field strength from the average of the other two. Therefore, the characteristic tetragonal splitting of the $^1T_{1g}$ state is expected. In contrast to this, the $^1T_{1g} \leftarrow {}^1A_{1g}$ band is not expected to split in the uns-cis isomer due to the fact that all three axes although different are of comparable field strengths.

The visible spectrum of Co(BTAT)Br is shown in Figure 1. It can be seen from this figure that the band attributed to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition is split into two components—a lower energy, lower intensity shoulder at 550 nm with $\epsilon \sim 175$ and a higher energy, higher intensity major band at 490 nm with $\epsilon \sim 250$. The observed tetragonal splitting in the spectra of the $[Co(BTAT)]^+$ complexes therefore suggests the presence of either the s-cis or trans forms or a mixture of isomers. The

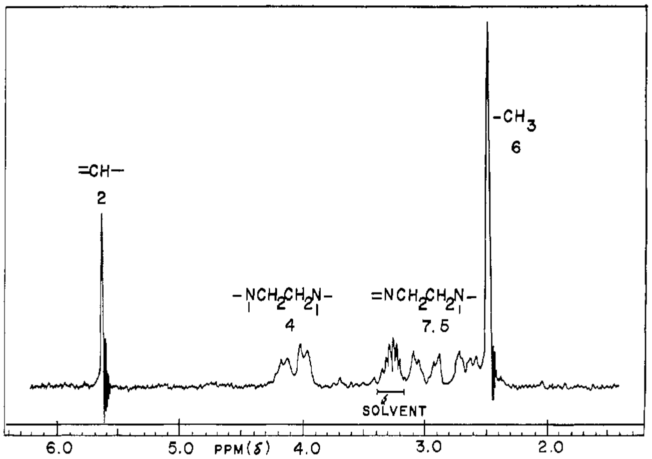
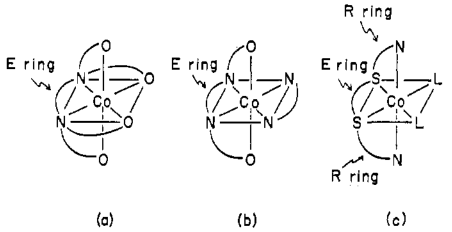


Figure 2.—The 60-MHz ^1H nmr spectrum of [Co(BTAT)]Br in methanol-d_4.



(a) (b) (c)

Figure 3.—Structures of (a) $Co(EDTA)^-$, (b) *s-cis*-Co(EDDA)-en$^+$, and (c) *s-cis*-$[Co(eee)L_2]^+$.

spectrum is not consistent with the presence of the pure uns-cis isomer. Since the relative donor strengths of the nitrogen and oxygen atoms in the sexadentate ligands are not known, the two components cannot be assigned to specific electronic transitions.

In conjunction with the electronic spectra, nmr spectra of the Co(III) complexes have provided the most information on the geometry of the Co(III) derivatives. The nmr spectrum of Co(BTAT)Br in methanol-d_4 is shown in Figure 2. Singlets at 5.64 and 2.49 ppm with relative intensities of 2:6 have been assigned to the =CH– and $-CH_3$ groups. Resonances due to the bridging methylene groups appear in two distinct regions of the spectrum. A low-field quartet centered at 4.08 ppm has been attributed to the protons of the $-CH_2CH_2-$ group in the plane containing the Co(II) ion since these protons should experience the largest amount of deshielding due to the highly electronegative nitrogen atoms of the secondary amine groups. Protons on the remaining $-CH_2CH_2-$ groups of $Co(BTAT)^+$ experience increased shielding due to the presence of the imine nitrogen atoms and consequently resonances due to these protons appear at high fields, 2.6–3 ppm. These nmr results are in accord with those reported for $Co(EDTA)^-$,[19,20] *s-cis* and *uns-cis*-Co(EDDA)en$^+$,[21] and *s-cis*-$[Co(eee)(NO_2)_2]^+$,[22] Figure 3, in which the resonances associated with the E-ring protons are observed at lower fields than those associated with the R-ring protons.

Since the high-field methylene resonance pattern cannot be assigned at this time, this region of the

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spectrum cannot be used to differentiate between geometrical isomers. However, some useful information concerning the geometry of the Co(III) complexes has been derived from the resonances in the $-\mathrm{CH_3}$ and $=\mathrm{CH}-$ regions. First the $-\mathrm{CH_3}$ and $=\mathrm{CH}-$ resonances occur as sharp singlets, even when the nmr spectrum is expanded. Since the pure *uns-cis*-[Co(BTAT)]$^+$ isomer contains two sets of nonequivalent methyl and methine protons, the nmr spectrum of this isomer, barring any accidental degeneracies, should exhibit two singlets in the methyl and methine regions, respectively. To rule out the possibility of accidental degeneracy, the ^{19}F nmr spectrum of [Co(BTAT)]Br in methanol has been obtained. A slightly broad, symmetrical singlet due to the $-\mathrm{CF_3}$ resonance was observed at −72.4 ppm. Therefore, since only one methyl and $\mathrm{CF_3}$ resonance was observed in the ^{1}H and ^{19}F nmr spectrum, the possibility that [Co(BTAT)]Br exists solely as the uns-cis isomer can be eliminated. This is supported by the interpretation of the electronic spectra (*vide infra*). A similar line of reasoning has been used to eliminate the possibility of there being a mixture of isomers present, since the chemical shifts of the $-\mathrm{CH_3}$ and $=\mathrm{CH}-$ protons should differ for each isomer. Therefore, the formation of the complex must proceed stereospecifically to yield only one of the four possible isomers. While it is impossible to distinguish between pure forms of the two s-cis isomers and the trans isomers by physical measurements other than X-ray diffraction, considerations of stereomodels of these Co(III) complexes and the corresponding Ni(II) and Cd(II) complexes show that structures V–VII are greatly strained at the imine nitrogen which leaves structure IV as the only possible isomer. This preference for formation of complexes of s-cis geometry has been well documented for other Co(III) and Ni(II) complexes.[23–27] In view of the preceding discussion it has been concluded that syntheses of Co(BTAT)X, Ni(BTAT), Ni(BHAT), and Cd(BTAT) proceed stereospecifically with formation of only the s-cis isomer.

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A New Ring-Opening Reaction of Aziridines in Nickel(II) and Copper(II) Complexes

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Reaction of the bis-salicylaldehydo complexes of nickel(II) and copper(II) with *N*-(2-aminoethyl)aziridine, AEA, and *N*-(3-aminopropyl)aziridine, APA, gives neutral complexes of the expected Schiff base condensation products, salAEA and salAPA, respectively. These complexes are characterized by their analyses, vibrational and electronic spectra, molecular weights, and magnetic moments. The reaction of nickel(II) acetate and copper(II) acetate with salicylaldehyde and AEA results in the formation of bis(salicylidene)ethylenediiminenickel(II) and bis(salicylidene)ethylenediiminecopper(II), respectively. In the presence of acetic acid, the neutral complex Ni(salAEA)$_2$ reacts to give bis(salicylidene)ethylenediiminenickel(II). These reactions represent a new type of ring-opening reaction of aziridine.

Introduction

In the course of a study of the complexes formed by aziridines[1] and *N*-(aminoalkyl)aziridines,[2] we have investigated complexes of the Schiff bases derived from reactions of salicylaldehyde with *N*-(2-aminoethyl)aziridine, AEA, and *N*-(3-aminopropyl)aziridine, APA.[3] The salicylidene Schiff bases of unsymmetrically N-substituted diamines have been studied extensively as ligands.[4–13] This work is the first report in which the third donor atom of a potentially tridentate salicylaldimine ligand is the nitrogen of an aziridine ring. Furthermore, a unique ring-opening reaction has been discovered in which both carbon–nitrogen bonds are cleaved under mild conditions in the presence of nickel(II) and copper(II).

The aziridine ring is well known as an alkylating agent, mutagen, antimicrobial and sterilant, and the sizable literature on aziridine chemistry has been reviewed thoroughly by Dermer and Ham.[14] The use of metal ions in facilitating ring-opening reactions of aziridine has been explored with Al(III)[15] and iron(III)[16]

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