

Science Foundation (Grant GP-30485X), Hoffmann-La Roche, Chevron Research, and the Mobil Foundation for support of this research.

Registry No. Isobutylamine, 75-64-9; 3,5-dibromopyridine, 625-92-3; *N,N'*-diisobutyl-3,5-diaminopyridine, 52165-28-3; *N*-isobutyl-

3-amino-5-bromopyridine, 52165-29-4; 9,10-diketostearoyl chloride, 52165-30-7; 3,5-diaminopyridine, 4318-78-9; *N,N'*-bis(9,10-diketostearoyl)-3,5-diaminopyridine, 52165-31-8; *N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine, 52165-32-9; *N,N'*-diisobutyl-*N,N'*-bis(9,10-diketostearoyl)-3,5-diaminopyridine, 52165-33-0; *N,N'*-diisobutyl-*N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine, 52165-34-1; chloro [*N,N'*-diisobutyl-*N,N'*-bis(9,10-hydroxyiminooxyminatostearoyl)-3,5-diaminopyridine]cobalt(III), 52216-80-5.

Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Mass Spectrometric Study of Polydentate Schiff Base Coordination Complexes. II. Cobalt(II), Nickel(II), and Copper(II) Complexes of *N,N'*-Bis(salicylidene)heptanediamine, *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl)amine, *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl) Ether, and *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl) Sulfide

LARRY T. TAYLOR and JOHN G. DILLARD*

Received April 3, 1974

AIC402200

Positive and negative ion mass spectra have been measured for the coordination compounds of cobalt(II), nickel(II), and copper(II) with SALHTDA,¹ SALDPT,² SALDAPE,³ and SALDAPS.⁴ Intense molecular ions were detected in both the positive and negative ion mass spectra. Fragmentation patterns are reported and many decomposition reactions are confirmed by metastable transitions. Ionization potentials of the uncomplexed ligand and the metal complexes are reported. The measured ionization potentials reflect the nature of the bonding of the ligand to the metal ion. Parent molecular negative ions are formed *via* direct electron capture at near-zero electron energies.

Introduction

The significance of metal coordination compounds in biological systems is recognized.⁵ In many instances metal coordination compounds of Schiff bases have been suggested as models to describe energy transfer in naturally occurring systems. In such instances the coordination sphere about the metal ion is believed to play an important role in determining the nature of the model system.

In a similar way the importance of Schiff base ligand donor atoms in influencing the ionization potentials and mass spectral fragmentation patterns has been demonstrated.⁶ In previous studies⁶ tetradentate model ligand systems were investigated. The strength of the donor atoms (N and O) was found to influence directly the magnitude of the ionization potential of the metal-Schiff base complex and the formation of various parent molecular negative ions.

In this paper positive and negative ion mass spectra and ionization potentials of cobalt(II), nickel(II), and copper(II) complexes of potentially pentadentate Schiff base ligands are reported. The donor atom containing chain that joins azomethine linkages is found to influence the ionization potential. In addition evidence is presented regarding the formation of five-coordinate species in the gas phase.

Experimental Section

Mass spectra and ionization potentials for positive ions and resonance-capture appearance potentials for negative ions were ob-

tained using an Hitachi Perkin-Elmer RMU-7 mass spectrometer described earlier.⁷ Samples were introduced into the mass spectrometer using the direct insertion probe. Samples were heated to 190–210° to effect sublimation. The ion source temperature was maintained at about 10–20° above the solid inlet temperature. Upon removal from the mass spectrometer, all samples, except Co(SALDAPE), showed no evidence of thermal decomposition. In the case of Co(SALDAPE) decomposition appeared to begin at about 200°, so spectra and ionization measurements were carried out at about 180–190°. Data acquisition for the energetic measurements was accomplished using the MADCAP IV data acquisition program and a Digital PDP8/I computer. The electron energy scales were calibrated with Xe and Kr for positive ions (ionization potentials 12.13 and 13.99 eV, respectively)⁸ and SF₆ for negative ions (0.08 eV).⁹ Mass calibration at 50 eV and at other electron energies was accomplished using perfluorokerosene.⁷

Ionization efficiency curves for the parent molecular ions were parallel to the curve for the calibrant ions Xe⁺ and Kr⁺ so the semi-logarithmic method¹⁰ was used. The data in Table V represent the averages of no less than 10 separate measurements, and the quoted precision represents one standard deviation. It is anticipated that the accuracy of the ionization potentials is better than 0.5 eV. The vertical ionization potential measured here will deviate from the true adiabatic value if the potential energy representations for the neutral complex, ML, and the singly charged complex ion, ML⁺, differ significantly. In such an instance the measured electron impact value would represent the formation of ML⁺ in an excited electronic and/or vibrational state.

Complexes of SALDPT were prepared by the method of Sacconi and Bertini.¹¹ The other complexes were synthesized by a general procedure which involved adding a stoichiometric amount of an appropriate metal(II) acetate dissolved in ethanol to a refluxing

(1) SALHTDA = *N,N'*-bis(salicylidene)heptanediamine.

(2) SALDPT = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl)amine.

(3) SALDAPE = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl) ether.

(4) SALDAPS = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl) sulfide.

(5) *Advan. Chem. Ser.*, No. 100 (1972).

(6) W. C. Gilbert, L. T. Taylor, and J. G. Dillard, *J. Amer. Chem. Soc.*, **95**, 2477 (1973).

(7) J. G. Dillard, *Inorg. Chem.*, **8**, 2148 (1969).

(8) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxal, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

(9) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

(10) F. P. Lossing, A. W. Tickner, and W. A. Brice, *J. Chem. Phys.*, **19**, 1254 (1951).

(11) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

ethanol solution of the previously prepared ligand and NaOH.¹²⁻¹⁴ All cobalt(II) complexes were prepared under a nitrogen atmosphere. Each complex was washed thoroughly with absolute ethanol and dried for 12 hr *in vacuo* prior to mass spectrometric investigation.

The compounds appeared, from the low-voltage mass spectra, to be pure (99%). However, as in previous studies,^{6,15} ions appeared at *m/e* values near the parent molecular ion which could be attributed to compounds formed by exchange of the metal in the complex with iron. In all instances the contribution of the Fe(complex) species was less than 1% in relative abundance. The intensity did increase with increasing ion source block temperatures. Spectra and other measurements were carried out at temperatures where the Fe(complex) species was always less than 1%.

The parent molecular ions detected in the positive and negative ion mass spectra were first order in measured analyzer tube pressure. Ion currents were measured at 50 eV for positive ions and at near 0 eV for negative ions. As in previous studies⁷ these results indicate that the parent molecular ions are formed by direct ionization (positive ions) and resonance-capture (negative ions) processes and that no ion-molecule or secondary reactions are responsible for the formation of the ions.

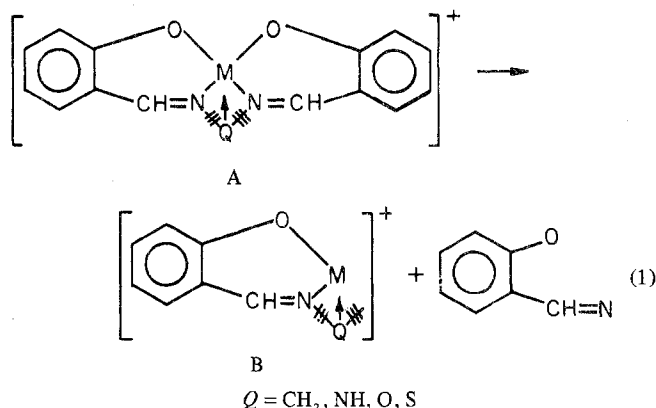
Results and Discussion

I. Spectra. Positive Ions. The dominant metal-containing ions for the complexes are presented in Tables I-IV for M-(SALHTDA), M(SALDPT), M(SALDAPE), and M(SALDAPS), respectively. The tabulated relative abundance (RA) represents the monoisotopic abundance for the chemical composition indicated. The proposed probable formula is suggested from a comparison of the various fragmentation patterns of the compounds studied and by comparison with previously established fragmentation processes for Schiff base-metal complexes.⁶ The *m/e* values quoted are calculated for the most abundant isotope of the elements present. In the effort to clarify the fragmentation processes a survey of the mass spectra for metastable ions was carried out. A summary of the calculated and observed metastables is presented also in Tables I-IV. The calculated values are based on the most abundant isotopes of the elements in the ion using the *m/e* values given in columns 2, 4, and 6 of Tables I-IV for the parent and fragment ions.

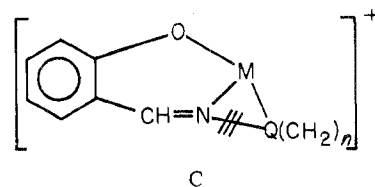
The positive ion spectra of nickel(II), cobalt(II), and copper(II) complexes are strikingly similar. The spectrum of each complex is characterized by an intense molecular ion which is the most abundant ion in the spectrum. This abundance coupled with the relatively abundant doubly charged parent molecular ions and the dominance of metal-containing fragment ions demonstrates the high stability of the molecular ions and suggests a rather large metal-donor atom bond energy in the ion. In contrast to the observations in earlier studies of Schiff base complexes^{6,16,17} no polymeric species were detected in these compounds. The spectra were scanned to *m/e* values at least 3 times that of the parent molecular ion and no significant polymeric species were detected. The relative abundance of any polymeric species in the gas phase must be 0.1% or less. If any molecular polymers exist, they must be destroyed at the temperatures required to sublime the samples or the stability of the polymer ions produced upon electron impact is such that no polymer ionic species are collected in the mass spectrometer.

The dissociative processes for the complexes are represented

by a series of competitive and consecutive fragmentation reactions. Formation of fragment ions for all the compounds occurs by loss of C₆H₄OCH₂ from the parent ion. The fragmentation process likely proceeds *via* a hydrogen migration from a bridging hydrocarbon chain to yield the neutral C₆H₄OCH₂ such that nitrogen remains coordinated to the metal ion. In competition with the loss of C₆H₄OCH₂ is cleavage of the metal-nitrogen bond by loss of C₇H₅ON. See eq 1.

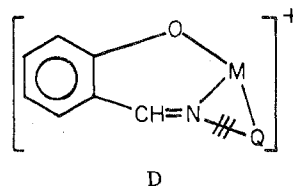


Processes for the formation of type C ions could occur *via*



fragmentation of the hydrocarbon chain or by fragmentation of the parent molecular ion. Limited metastable data indicate that some type C ions [*m/e* 262, Co(SALDPT); *m/e* 279, Cu(SALDPT); *m/e* 282, Cu(SALDAPE); *m/e* 279, Ni(SALDAPS)] are formed from the parent molecular ion.

The second most abundant group of ions except for M-(SALHTDA) are those containing a potentially three-coordinate ligand and having a possible structure D. Also formed



in significant abundance from M(SALDPT), M(SALDAPE), and M(SALDAPS) are ions at 1, DH⁺, and 2, DH₂⁺, mass units above the D⁺ ions. These species are produced predominantly from the parent ion in all instances. Of importance here is the significant difference in abundance between the cobalt and nickel D⁺, DH⁺, and DH₂⁺ ions compared to copper. In the M(SALDAPS) compounds the difference is most pronounced. The abundance of the DH₂⁺ ion for Cu(SALDAPS) is about 73%, whereas the abundances for the DH₂⁺ ions in Co(SALDAPS) and Ni(SALDAPS) are significantly less. Furthermore the D⁺ ions for Ni(SALDAPS) and Co(SALDAPS) are much more abundant than D⁺ from Cu(SALDAPS). These data appear to relate to the ability of Cu(II) to be more easily reduced than Co(II) or Ni(II). A similar observation is noted for the D type ions in M-(SALDAPE) and M(SALDPT), although the differences in relative abundances are not as striking.

The remaining metal-containing ions for M(SALDPT), M-

(12) L. W. Lane and L. T. Taylor, *J. Coord. Chem.*, **2**, 295 (1973).

(13) A. K. St. Clair, M.S. Thesis, Virginia Polytechnic Institute and State University, June 1972.

(14) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).

(15) J. K. Terlow and J. J. deRidder, *Org. Mass. Spectrom.*, **5**, 1127 (1971).

(16) E. P. Dudek, E. Chaffee, and G. Dudek, *Inorg. Chem.*, **7**, 1257 (1968).

(17) J. Charalambous and M. J. Frager, *J. Chem. Soc. A*, 2645 (1970).

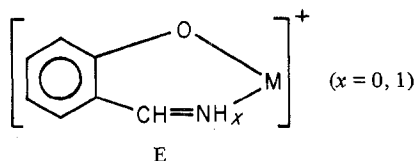
Table I (Continued)

Co		Ni		Cu		Ion	Propose probable ion structure, M ⁺	Probable process M ₁ ⁺ → M ₂ ⁺	Metastable processes						
RA ^a	m/e	RA	m/e	RA	m/e				Co	Obsd	Ni	Obsd	Cu	Obsd	
4.6	193			1.1	197	t									
8.1	192	6.9	191	2.7	196	u									
13.3	180	17.0	179	6.9	184	v									
18.9	179	7.2	178	3.7	183	w									
8.4	178	5.2	177	4.7	182	x									
8.0	177					y									
9.7	165	4.3	164	1.7	169	z	c-C ₇ H ₆ -O-M	u → z	141.8	141.6	140.8	140.5			
6.6	59	3.7	58	4.3	63	aa	M ⁺								
2.6	197.5	2.6	197	3.0	199.5	bb	P ²⁺								

^a RA = relative abundance.

(SALDAPE), and M(SALDAPS) at lower masses are produced predominantly from the D⁺, DH⁺, and DH₂⁺ ions. Loss of heteroatom groups from these ions is confirmed by metastable transitions in Tables I-IV. No metastable data were obtained which could support fragmentation of the parent ion to produce the lower fragment ions, *i.e.*, [C₆H₅OCHN(CH₂)_nM]⁺, M = Co, Ni, Cu, n = 1-3 (except for m/e 220 in Co(SALDPT)).

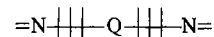
The third group of abundant metal-containing ions is those in which the ligand is bidentate, *i.e.*, structure E. For this



series of ions, those with x = 1, 2 are formed by rearrangement. Presumably the hydrogen is on the ligand for x = 1, and for x = 2 one is on the ligand and one is on the metal. The abundances of the x = 1, 2 ions for nickel and cobalt are generally greater than those of copper. This result is probably related to the stability of the ligand-copper bond. If copper is reduced in these ions, then the metal-ligand bond would be weaker and the abundance would be expected to be smaller.

Another significant comparison between the various mass spectra relates to the elimination of stable H_nQ molecules from the parent ion. In the mass spectra of the cobalt and nickel complexes where Q = NH, O, and S, loss of H₂S is noted for M(SALDAPS), while elimination of OH is noted for the M(SALDAPE) compounds. In Co(SALDPT) and Ni(SALDPT) loss of NH₃ and NH₃ + H from the parent ion is suggested. The loss of NH₃ + H in the M(SALDPT) complexes could of course be loss of H₂O which would involve the SALDPT ligand oxygen. However, since this type of loss was not noted in the spectra of M(SALDAPS) (H₂S + H) and M(SALDAPE) (H₂O + H) for cobalt and nickel, it is reasoned that loss of ammonia and atomic hydrogen occurs.

The behavior of copper with respect to H_nQ loss stands in contrast to that noted for cobalt and nickel. Loss of H_nQ is not observed for copper. If such fragment ions are formed, their abundance must be less than 0.1%. However, in the copper complexes loss of C₃H₅N or C₄H₇ is noted. From these low-resolution measurements it is not possible to distinguish between C₄H₇ and C₃H₅N loss. However, it is believed that loss of C₃H₅N is likely *via* a hydrogen migration process. In addition, for the pentadentate ligand complexes no fragment ion corresponding to loss of the bridging



group or portions of the bridging group is noted except for loss of C₃H₅N in the copper compounds and loss of H_nQ in nickel and cobalt compounds as already discussed. This result is in contrast to the observation in previous studies⁶ of OABEN and SALEN ligand complexes where loss of C₂H₄ from the diamine bridge was observed. Thus in the mass spectra of the complexes with potentially pentadentate ligands the fragmentation patterns are generally similar for the three metals studied. However, certain significant differences are noted between the spectra of the nickel and cobalt complexes and those of the copper compounds.

The complexes with SALHTDA are not potentially five-coordinate and thus important differences between the analogous pentadentate complexes are noted. The fragmentation patterns for the metal complexes are similar in that the dominant ion is the parent molecular ion. Fragmentation of the parent ion occurs by loss of C₆H₄CH₂O and C₆H₄CHON as noted for the pentadentate ligands. However the lower mass fragment ions are not abundant except for the series of ions F where R = C₇H₁₄ for M = Cu and R = C₇H₁₂

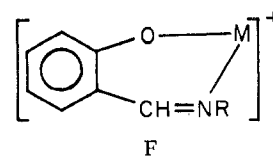
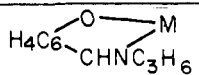
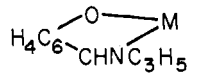
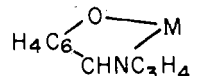
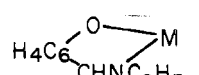
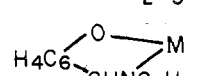
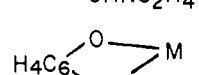
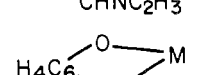
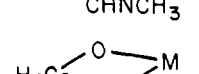
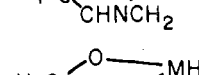
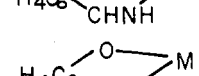
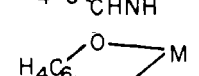
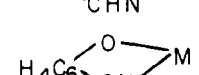


Table II (Continued)

Co		Ni		Cu		Probable proposed ion structure	Probable process $M_1^+ \rightarrow M_2^+$	Metastable processes						
RA	m/e	RA	m/e	RA	m/e			Co		Ni		Cu		
					Ion			Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	
9.6	220	19.3	219	13.7	224	s		a → s	122.2	122.3				
5.7	219	3.1	218	3.9	223	t								
2.7	218					u								
4.2	207	0.5	206	0.9	211	v								
3.7	206	2.2	205	13.1	210	w		s → w			196.4	196.7		
7.9	205	2.2	204	2.0	209	x								
6.0	193	6.3	192	3.5	197	y								
4.5	192	2.8	191	21.4	196	z		w → z	178.9	178.8				
12.5	180	8.6	179	11.8	184	aa		z → aa	168.7	168.5				
16.0	179	8.6	178	10.3	183	bb								
8.4	178	6.9	177	11.3	182	cc								
4.6	177	1.9	176			dd								
4.9	165	3.1	164	4.2	169	ee	$c-C_7H_6-O-M$	z → ee	141.8	141.6				
2.9	59	6.8	58	10.6	63	ff	M^+							
5.4	198	5.0	197.5	4.5	200	gg	P^{2+}							

for M = Co and Ni. In the case of cobalt and nickel the F ion may be stabilized by a π interaction of the metal with the C_7H_{12} hydrocarbon group. On the other hand for copper the stability of the F ion may be the result of a copper-carbon σ -type bond in the ion.

One additional fragmentation process noted for Cu-(SALHTDA) is the loss of C_7H_{10} from the parent to yield a low-abundance ion. For cobalt and nickel no removal of the hydrocarbon bridge is noted. This result compares with the fragmentation of the pentadentate ligands where for copper, loss of C_3H_5N was noted, but only loss of H_nQ was observed for the cobalt and nickel compounds. In other tetradentate Schiff base metal chelates fragmentation of the hydrocarbon bridge has been noted.^{6,18}

A comparison between the mass spectra of the four-coordinate M(SALHTDA) and the potentially five-coordinate M-(SALDPT), M(SALDAPE), and M(SALDAPS) complexes

suggests that the presence of the characteristic D^+ , DH^+ , and DH_2^+ ions in the spectra of potentially five-coordinate species and their absence in the four-coordinate complexes may provide a method for determining the coordination geometry of the complex in the gas phase. It may be imagined that upon ionization an electron is removed from an orbital with significant metal character (as will be discussed later in this paper) thereby reducing the electron density in the metal and enhancing ligand coordination to the metal. In the case of the five-coordinate ligands the M-Q interaction would be enhanced upon ionization and subsequent fragmentation of the parent ion would be controlled in part by the coordinating power of Q. In the SALHTDA complexes no Q atom is present to stabilize the ion so fragmentation of the hydrocarbon chain occurs easily and the abundance of the F ions is very small compared to that of ions where the ligand may utilize its maximum coordinative powers, i.e., "D" type ions. In competition with the formation of the "D" type ions for pentadentate ligands is the process where H_nQ loss occurs. It is noted that this process, even though thermodynamically

(18) K. S. Patel, K. L. Rinehart, and J. C. Bailar, *Org. Mass Spectrom.*, **4**, 441 (1970).

Table III. Monoisotopic Mass Spectra and Fragmentation Processes for M(SALDAPE) Complexes (50 eV)

Co		Ni		Cu		Ion	Probable proposed ion structure	Probable process $M_1^+ \rightarrow M_2^+$	Metastable processes					
RA	<i>m/e</i>	RA	<i>m/e</i>	RA	<i>m/e</i>				Co		Ni		Cu	
								Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	
100	397	100	396	100	401	a								
	1.4		0.5			b		$a \rightarrow b$		362.7	362.9			
					1.2	c								
	7.7		4.6		5.8	d								
	5.6		1.2			e								
					4.1	f		$a \rightarrow f$				198.3	198.2	
	0.6		2.1		0.4	g								
	0.5				1.1	h								
	1.4				0.4	i								
	7.0		1.0		0.3	j								
	0.4		5.7		13.9	k		$a \rightarrow k$				146.0	146.0	
	11.4		14.4		3.8	l		$a \rightarrow l$			140.6	140.5		
	20.9		10.6		2.4	m		$a \rightarrow m$ $j \rightarrow m(\text{Co})$	140.3 222.8	140.4 222.7	139.5	139.5	143.6 143.5	
	11.6		16.7		29.1	n		$m \rightarrow n(\text{Ni})$ $k \rightarrow n(\text{Cu})$ $m \rightarrow n(\text{Cu})$			204.1	204.0	207.4 209.1	207.3 209.2
			1.6		0.5	o						204.1	204.0	
			3.5		3.1	p								
	1.1		1.5		2.4	q		$n \rightarrow q$			191.9	191.7		
	3.5		2.2			r								

Table III (Continued)

Co		Ni		Cu		Ion	Probable proposed ion structure	Probable process $M_1^+ \rightarrow M_2^+$	Metastable processes					
RA	<i>m/e</i>	RA	<i>m/e</i>	RA	<i>m/e</i>				Co		Ni		Cu	
								Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	
1.5	193	0.9	192	1.1	197	s								
4.0	192	2.4	191	22.3	196	t		q → t	178.9	178.8			182.9	182.8
8.6	180	10.9	179	2.6	184	u		t → u					172.7	172.6
9.1	179	9.7	178	8.1	183	v								
5.9	178	7.0	177	7.1	182	w								
3.1	177			1.7	181	x								
3.8	165	3.5	164	3.9	169	y	c-C ₇ H ₆ -O-M	t → y			140.8	140.8	145.7	145.8
2.8	59	2.9	58	6.8	63	z	M ⁺							
4.4	198.5	5.3	198	3.5	200.5	aa	P ²⁺							

favorable due to the formation of H_nQ, is not as important as the formation of the "D" type ions. Whereas the formation of ions by loss of H_nQ may suggest that Q is weakly coordinated, the large abundance of the "D" type ions certainly suggests that the M-Q interaction may be appreciable in the gaseous parent molecular ions and "D" fragment ions.

Negative Ions. The 50-eV negative ion spectrum is characterized by the parent molecular ion. No significant fragmentation of the parent ion occurs. Some low intensity (~5%) fragment negative ions are noted in the copper complexes. Although careful *m/e* assignment of the fragment ions was not carried out, the approximate mass corresponds to loss of 106 or 107 mass units. Thus the fragmentation is similar to that noted in complexes of SALEN and OABEN.⁶ Although no attempt was made to measure accurately the relative absolute intensities of the parent ions for the different complexes, for the same analyzer tube pressure the parent negative ion intensity varied as Cu > Ni > Co for all four ligands. For the different ligands the intensity varied approximately as M(SALDAPS) ≈ M(SALHTDA) ≈ M(SALDPT) > M-(SALDAPE). If the electron producing the negative ion is captured by a metal d orbital, it is reasonable that the copper ions would be most intense since a d¹⁰ configuration would be attained. It is not clear why the observed variation of parent negative ion intensity among the different ligands is observed.

II. Energetics. The measured ionization potentials for the four free ligands H₂SALHTDA, H₂SALDPT, H₂SALDAPS, and H₂SALDAPE and for the twelve complexes are presented in Table V. The ionization energies of the complexes are all lower than that of the free ligand and approximately equal to the values for the free metals. The decrease in ionization energy upon complexation is related to the presence of the metal ion in the compound. As noted from previous studies,⁶ it is suggested that the electron removed in the ionization process may be from an orbital where the metal ion makes a significant contribution. The variation in the ionization potentials among the various ligands is more important than the variation among the metals and offers strong support that the electron being removed is from a metal-like orbital.

In particular the ionization potentials of the M(SALHTDA) complexes are slightly higher than those of M(SALEN).⁶ These data support a previous observation⁶ that lower ionization potentials are expected with an increase in ligand field strength provided no gross structural or electronic changes have taken place. SALHTDA²⁻ is known to be a weaker ligand;¹⁹ therefore, higher ionization potentials for M-(SALHTDA) are expected relative to M(SALEN). However, it should be emphasized that when the respective standard deviations are taken into account,⁶ the values are comparable. The greater ionization potential for Co(SALHTDA) relative to Co(SALEN) may arise from the fact that Co(SALHTDA) is tetrahedral and Co(SALEN) is square planar.²⁰ No such structural changes are observed with the analogous Ni(II) and Cu(II) complexes.

Comparison of the ionization potentials of the potentially five-coordinate ligand complexes with those for SALHTDA²⁻ reveals that there is a significantly lower ionization potential for all the compounds except Cu(SALDAPE), Cu(SALDAPS), and Ni(SALDAPE). For the M(SALDPT) compounds all the values are lower than that for M(SALHTDA) by about 0.3–0.4 eV. Since it is known with certainty from other structural and physical evidence^{11,21} that the M(SALDPT) complexes are high spin five-coordinate, it is reasonable that the additional electron density on the metal ion brought about by a fifth coordinating group would tend to reduce the ionization potential of the complex. The lowering would occur, however, only if the electron were removed from an orbital to which the metal makes a significant contribution. Otherwise, if the electron were removed from a predominantly ligand orbital, the ionization potential would be expected to increase.

An additional factor, the difference in spin state between high-spin Ni(SALDPT) and low-spin Ni(SALHTDA), could be an important molecular parameter influencing the variation in ionization potentials. For the nickel complexes no

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Table IV. Monoisotopic Mass Spectra and Fragmentation Processes for M(SALDAPS) Complexes (50 eV)

Co		Ni		Cu		Ion	Probable proposed ion structure	Probable process $M_1^+ \rightarrow M_2^+$	Metastable processes					
RA	<i>m/e</i>	RA	<i>m/e</i>	RA	<i>m/e</i>				Co		Ni		Cu	
								Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	
100	413	100	412	100	417	a								
		0.5	379			b								
6.6	379	1.4	378			c		a → c	347.8	348.0	346.8	347.0		
				1.0	362	d								
2.5	307	2.0	306	7.6	311	e								
				4.7	298	f								
1.2	280	4.2	279	0.5	285	g		a → g			188.9	189		
3.3	279	1.5	278	11.0	284	h								
9.7	266	12.1	265			i								
0.2	254	11.5	253	73.2	258	j		a → j					159.6 159.5	
4.8	253	8.4	252	7.8	257	k								
17.5	252	38.2	251	6.4	256	l		a → l i → l	153.8 153.9	152.9 153 237.7 237.8	157.1 157.3			
7.5	220	29.3	219	4.0	224	m		l → m(Ni) j → m(Cu)			191.1 191.1	194.5 194.6		
5.5	219	13.8	218	3.8	223	n								
7.3	218	9.6	217	10.5	222	o								
1.9	207	6.2	206	1.1	211	p								
0.9	206	9.7	205	10.0	210	q		o → q					198.5 198.5	
2.4	205	2.9	204	4.1	209	r								

Table IV (Continued)

Co		Ni		Cu		Ion	Probable proposed ion structure	Probable process $M_1^+ \rightarrow M_2^+$	Metastable processes					
RA	m/e	RA	m/e	RA	m/e				Co		Ni		Cu	
								Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	
1.3	193	3.9	192	1.0	197	s								
5.8	192	12.5	191	10.3	196	t		q → t				182.9	182.7	
3.0	180	15.3	179	4.6	184	u								
8.2	179	15.2	178	6.4	183	v								
4.1	178	13.0	177	6.5	182	w								
3.5	177	6.3	176	2.4	181	x								
4.8	165	11.7	164	3.8	169	y	c-C ₇ H ₆ -O-M	t → y		140.8	140.6	145.7	145.6	
2.2	59	7.1	58	5.3	63	z	M ⁺							
2.4	206.5	9.7	206	3.2	208.5	aa	P ²⁺							

Table V. Ionization Potentials (eV)

H ₂ SALHTDA	8.26 ± 0.06	H ₂ SALDAPE	8.40 ± 0.10	H ₂ SALDAPS	8.51 ± 0.10	H ₂ SALDPT	8.31 ± 0.07
Co(SALHTDA)	7.78 ± 0.08	Co(SALDAPE)	7.53 ± 0.10	Co(SALDAPS)	7.58 ± 0.07	Co(SALDPT)	7.31 ± 0.07
Ni(SALHTDA)	7.69 ± 0.09	Ni(SALDAPE)	7.61 ± 0.06	Ni(SALDAPS)	7.44 ± 0.07	Ni(SALDPT)	7.41 ± 0.08
Cu(SALHTDA)	7.81 ± 0.07	Cu(SALDAPE)	7.75 ± 0.05	Cu(SALDAPS)	7.78 ± 0.06	Cu(SALDPT)	7.54 ± 0.08

definitive arguments regarding this point can be made. Experiments are in progress to discover how changes in spin state for complexes of identical geometry influence the ionization potentials.

The nickel complexes of SALDAPE²⁻ and SALDAPS²⁻ are believed to be weakly five-coordinate low spin. These assignments are based primarily on infrared and visible spectra.¹² A correlation between ionization potential and the donor ability of Q is noted. The ionization potential increases in the order CH₂ > O > S > NH for a variation in the ligand donor strength of NH > S > O > CH₂. These results compare favorably with the previous work.⁶

For the Cu(II) complexes of SALDAPE²⁻ and SALDAPS²⁻, wherein the secondary N-H is replaced with much poorer coordinating atoms (*i.e.*, an ether oxygen and a thioether sulfur), the ionization potentials are higher relative to the analogous complexes with SALDPT²⁻ and approximately equal to those of Cu(SALHTDA). The copper complexes Cu(SALDAPE) and Cu(SALDAPS) are believed¹³ to have a distorted square-planar structure. Since the complexes are four-coordinate, the result that the ionization potentials approximate those for Cu(SALHTDA) is reasonable.

The cobalt complexes with SALDAPE²⁻ and SALDAPS²⁻ are tetrahedral four-coordinate compounds. It would be expected that the ionization potentials should approximate those of Co(SALHTDA). Examination of the data in Table V indicates that the ionization potentials of Co(SALDAPE) and Co(SALDAPS) are lower than that for Co(SALHTDA). The ionization potential data and the mass spectra suggest that some Co-Q (Q = S or O) interaction occurs. This is in contrast to other structural data. No reasonable explanation for the differences in interpretation of the data emerges although the data may suggest a slightly different structure in the gas phase. It is an open question as to what factors would cause such a change.

Thus for nickel and copper complexes a good correlation of alterations and trends in ionization potentials with complex coordination geometry is found. On the other hand the correlation for Co(SALDAPS) and Co(SALDAPE) is poor. Where there is conclusive evidence for five-coordinate geometry, the ionization potential data appear to reflect the change in electron density on the metal ion and should provide an additional diagnostic tool for structure elucidation.

For the parent negative ions the ionization efficiency curves were determined over the energy range from near 0 to 10 eV. For each compound only one resonance-capture peak was observed. In every compound the resonance-capture curve was identical with that for SF₆⁻ (the calibrant). The parent ion [M(SALX)]⁻ (X = HTDA, DPT, DAPE, DAPS) ion current measured at the resonance maximum was first order in pressure, consistent with a primary process. That the complexes capture thermal electrons to yield intense parent negative ions compares with the observation⁶ of [M(SALEN)]⁻ ions in the M(SALEN) complexes (M = Co, Ni, Cu). On the other hand, one might expect that increased electron density on the metal for the five-coordinate species would prohibit electron capture. Such prohibition was noted in electron-capture processes for M(OABEN) compounds. For the compounds of interest in this study it must be reasoned that the added fifth coordinating atom is not as effective in increasing electron density on the metal as the strong four-coordinate ligand OABEN. This point is also supported by the fact that the IP's for the M(OABEN) complexes are lower than those of the M(SALX) complexes studied here. Alternatively the alteration in coordination geometry may yield unoccupied orbitals in the complex which facilitate electron capture.

From the negative ion energetic studies there appears to be no correlation with the ability of the metal to be reduced. It might be expected that the Cu(SALX) complexes would form negative ions more readily than those of nickel or co-

balt since copper could be reduced to Cu(I). However, the only difference noted was that the approximate relative intensity of the $[\text{Cu}(\text{SALX})]^-$ ions was greater than that for $[\text{Ni}(\text{SALX})]^-$ and $[\text{Co}(\text{SALX})]^-$.

Registry No. $\text{H}_2\text{SALHTDA}$, 52279-42-2; $\text{Co}(\text{SALHTDA})$,

17084-78-5; $\text{Ni}(\text{SALHTDA})$, 52358-03-9; $\text{Cu}(\text{SALHTDA})$, 52279-50-2; $\text{H}_2\text{SALDAPE}$, 52279-43-3; $\text{Co}(\text{SALDAPE})$, 52279-51-3; $\text{Ni}(\text{SALDAPE})$, 52279-52-4; $\text{Cu}(\text{SALDAPE})$, 52279-53-5; $\text{H}_2\text{SALDAPS}$, 52279-44-4; $\text{Co}(\text{SALDAPS})$, 52279-54-6; $\text{Ni}(\text{SALDAPS})$, 52279-55-7; $\text{Cu}(\text{SALDAPS})$, 52358-04-0; H_2SALDPT , 52279-45-5; $\text{Co}(\text{SALDPT})$, 15306-22-6; $\text{Ni}(\text{SALDPT})$, 15391-40-9; $\text{Cu}(\text{SALDPT})$, 15391-22-7.

Contribution from the Research School of Chemistry, The Australian National University, Canberra, 2600, Australia, and Chemistry Department I, University of Copenhagen, Copenhagen, Denmark

Hydrolysis and Nitrosation of the $(\text{NH}_3)_5\text{CoNCO}^{2+}$ Ion. Evidence for $(\text{NH}_3)_5\text{CoNHCOOH}^{2+}$ and $(\text{NH}_3)_5\text{Co}^{3+}$ Intermediates

D. A. BUCKINGHAM, D. J. FRANCIS, and A. M. SARGESON*

Received April 8, 1974

AIC40231T

$(\text{NH}_3)_5\text{CoNCO}^{2+}$ hydrolyzes (1 M H^+) by consecutive reactions to yield first $(\text{NH}_3)_5\text{CoNH}_2\text{CO}_2\text{H}^{3+}$ ($-\text{d}[\text{cyanato}]/\text{d}t = k_1K_1[\text{H}^+][\text{cyanato}]$) and then by three parallel paths to form $(\text{NH}_3)_5\text{CoOH}_2^{3+}$, $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$, and $\text{Co}(\text{NH}_3)_5^{3+}$ ($-\text{d}[\text{carbamate}]/\text{d}t = [(k_2' + k_2'')[\text{H}^+] + k_3K_2][\text{carbamate}]/(K_2 + [\text{H}^+])$). The aqua- and O-bonded carbamate complexes arise from the k_2 paths and the hexaammine arises from the deprotonated N-bonded carbamate intermediate (k_3). Essentially the rate-determining step for the nitrosation reaction is the same as that for acid hydrolysis. Subsequently in a somewhat faster step NO^+ adds to the N-deprotonated carbamate intermediate to generate N_2 and CO_2 and the $\text{Co}(\text{NH}_3)_5^{3+}$ intermediate. The latter is characterized by the competition ratio for H_2O , Cl^- , and NO_3^- and is shown to be the same as that observed in previous examples of induced aquation.

Introduction

The existence and nature of the five-coordinate intermediate $(\text{NH}_3)_5\text{Co}^{3+}$ has been the subject of several investigations.¹⁻⁶ Common competition ratios between nucleophiles in solution have been observed from several sources of this intermediate²⁻⁶ but there is a need for additional support for its existence. The recent preparation by Balahura and Jordan⁷ of $[(\text{NH}_3)_5\text{CoNCO}](\text{ClO}_4)_2$ leads to the possibility that coordinated NCO^- would be susceptible to nitrosation by NO^+ like free NCO^- ion, to produce coordinated N_2 and CO_2 .⁸ Such species are good leaving groups in cobalt(III) amine chemistry^{2,3} and the reactive intermediate $[(\text{NH}_3)_5\text{Co}]^{3+}$ could be expected. This paper gives evidence to support the existence of such an intermediate in the form of its competition properties for nucleophiles such as H_2O , Cl^- , NO_3^- , and HNO_2 .

During some preliminary acid hydrolysis experiments of the $(\text{NH}_3)_5\text{CoNCO}^{2+}$ ion unusual kinetics and products were observed. This reaction was therefore reexamined⁷ in more detail and the new results also form a major part of the paper.

Experimental Section

Preparation of $[(\text{NH}_3)_5\text{CoNCO}](\text{ClO}_4)_2$. The following method was developed to improve the yields of the isocyanato complex re-

ported by Balahura and Jordan.⁷ The addition of molecular sieves or triethylamine to the reaction mixture had no effect on the yield. The use of trimethyl or triethyl phosphate as the reaction solvent resulted in appreciably lower yields of the isocyanato complex. Reaction temperature, reaction time, and order of reagent addition appeared to be the most critical factors.

Finely ground, reagent grade urea (15 g) was dissolved in *N,N*-dimethylacetamide (100 ml) and the solution heated to 135° . $[(\text{NH}_3)_5\text{CoOH}_2](\text{ClO}_4)_3$ (12 g) was added to the stirred solution and kept at 135° for 25 min. 2-Butanol (1 l.) was added to the warm solution to precipitate the crude product which was then fractionally recrystallized from water by addition of NaClO_4 . Six fractions were collected and further fractionated to yield three products, $[(\text{NH}_3)_5\text{CoNCO}](\text{ClO}_4)_2$ (8.1 g, 80%), $[(\text{NH}_3)_5\text{Co}](\text{ClO}_4)_3$, and a pink material which was not characterized but was presumed to be $[(\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2](\text{ClO}_4)_3$.⁷ *Anal.* Calcd for $[(\text{NH}_3)_5\text{CoNCO}](\text{ClO}_4)_2$: C, 3.12; H, 3.94; N, 21.83; Co, 15.28. Found: C, 3.1; H, 3.9; N, 21.8; Co, 15.3. The uv-visible spectrum (in H_2O , ϵ_{504} 134.8, ϵ_{356} 88.3 $\text{M}^{-1}\text{cm}^{-1}$) and the infrared spectrum ($\nu_3(\text{C-N})$ 2262 cm^{-1} in KBr disk) of the complex agreed with those reported previously.⁷ The pure complex yielded only one 2+ band on elution from Dowex 50W-X2 (Na^+ form) cation-exchange resin with 1.0 *M* NaClO_4 (pH \sim 5) and only one 3+ band after reaction in HCl (0.08 *M*) for 30 min followed by elution from Dowex 50W-X2 (H^+) with 3 *M* HCl. The 3+ band was characterized from its uv-visible spectrum to be $(\text{NH}_3)_5\text{Co}^{3+}$ ion in agreement with the earlier study.⁷

Product Analysis. Acid Hydrolysis. In a typical experiment, acid (50 ml, $\mu = 2.0$, HClO_4 , HCl, or HNO_3) and an aqueous solution of $[(\text{NH}_3)_5\text{CoNCO}](\text{ClO}_4)_2$ (0.2 g in 50 ml) were simultaneously added to a beaker and stirred for 10 min at 25° . The reaction solution was then diluted (about three times) and neutralized to pH 6 with NaOH. The solution was rapidly sorbed on a Dowex 50W-X2 (Na^+ form) cation-exchange resin and washed with distilled water. The products were eluted separately: 2+ ions with 1 *M* NaClO_4 (pH \sim 5), $(\text{NH}_3)_5\text{CoOH}_2^{2+}$ with 1.0 *M* NaClO_4 (pH 10), and $(\text{NH}_3)_5\text{Co}^{3+}$ with 3 *M* HCl. By lowering the pH to 2 with 1.0 *M* HClO_4 , the $(\text{NH}_3)_5\text{CoOH}_2^{2+}$ was converted to $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ thereby preventing decomposition of the hydroxo species. Concentrations were determined by uv-visible and/or atomic absorption spectroscopy. The above procedure took less than 60 min from reaction initiation and was necessary to minimize hydrolysis of minor products. Unless the reaction solution was neutralized and rapidly sorbed, complete hydrolysis of the initial 2+ ion to $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ occurred in the time (\sim 24 hr) required to sorb, elute, and analyze the fractions. Partial anation of the $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ to $(\text{NH}_3)_5\text{CoX}^{3+}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^-) also occurred in these long experiments.

* To whom correspondence should be addressed at The Australian National University.

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