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Negative Ion Mass Spectra – Chemical Ionization Conditions: Fluorine-Containing Reagent Gases and Schiff Base Coordination Compounds

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The negative ion mass spectra of Schiff base complexes with copper(II), nickel(II), and cobalt(II) have been measured using chemical ionization conditions. Fluorine-containing reagent gases, CF_4*,* SO_2F_2*, and* SF_6*, have been employed to initiate ion/molecule reactions with some of the complexes. Copper(II) complexes are unreactive with any of the reagent gases. Electron capture and dissociative electron capture reactions are important for copper compounds. The addition of* F_2^- *and* F^- *moieties to the nickel compounds was noted when using* SO_2F_2 *as the reagent gas. With cobalt compounds reactions of the complex molecular negative ion with* CF_4 *produced* $(M+69)^-$ *as the dominant secondary ion. Reactions of negative ions from* SO_2F_2 *and* SF_6 *with the cobalt complexes proceeded via incorporation of* F_2^- *and* F^- *species in the secondary ion.*

Introduction

The formation of gaseous negative ions in coordination compounds may occur via resonance electron capture [1], dissociative resonance capture [1], secondary electron capture [2–4] and ion/molecule reactions [5–7]. For many organometallic and coordination compounds, electron capture into predominantly metal orbitals and reduction of the metal are believed to be the significant aspects of electron capture [2–6, 8–10]. For metal compounds with electron capture sites on the ligand, the electron attachment process appears to leave the metal unreduced [10, 11]. The negative ion mass spectra of copper(II) β-diketonate compounds have been measured under conditions where secondary electron capture is the mode of molecular negative ion formation [2b]. For all copper compounds studied [2b] the molecular negative ion and the ligand negative ion were the dominant ions in the spectra. It has been a consistent observation that molecular negative ions and ligand negative ions are formed under experimental conditions where secondary electron capture is favored [2–6, 9–11]. Production of these characteristic ions facilitates a determination of molecular weights and the nature of the ligand. These characteristics also facilitate the analysis of complex mixtures of metal complexes.

The production of negative ions using chemical ionization conditions has been the subject of recent studies [5–7]. For a group of metal β-diketonates the molecular negative ion is the most abundant ion when methane, isobutane, nitrogen, and argon–10% methane were used as reagent gases [7]. The production of $(M+O_2)^-$ was noted in the spectra of some complexes when methane that contained trace quantities of water was used as the reagent gas [7]. The reactions of simple gas molecules (O_2, NO, CO and PF_3) with the molecular negative ions of Schiff base complexes have been studied [5]. The incorporation of $-CH_2$ groups in nickel complexes and $-CH_3$ moieties into cobalt compounds has been noted in the negative ion chemical ionization spectra with methane and isobutane as the reagent gases [6]. The reaction processes were found to depend on the electronic nature of the metal ion and on the coordination geometry of the metal complex [5, 6].

The present investigation was carried out to explore the use of fluorine-containing reagent gases for measuring negative ion chemical ionization mass spectra. Among the questions of interest in this study were 1) what is the effect of the reagent gas on the formation of secondary ions via ion/molecule reactions, 2) what structural factors in the metal complex exert an influence on the formation of secondary ions, 3) how do electronic effects in the molecular negative ion influence the nature of secondary ion formation, and 4) what is the role of the reagent gas in promoting secondary electron capture? The coordination compounds selected for study include a group of tetrahedral and square planar four coordinate compounds and a five coordinate trigonal bipyramid complex. The fluorine-containing reagent gases were CF_4, SO_2F_2, and SF_6.

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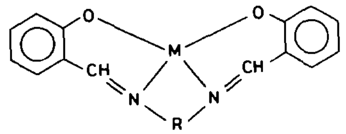
TABLE I. Negative Ion Mass Spectra at Chemical Ionization Conditions for Schiff Base Complexes using Fluorine-Containing Reagent Gases (Relative Abundance).

	CuSalhtda			CuSaldape			CuSaldaps			CuSaldpt		
Ion	CF_4	SO_2F_2	SF_6	CF_4	SO_2F_2	SF_6	CF_4	SO_2F_2	SF_6	CF_4	SO_2F_2	SF_6
$(M-2)^-$	–	–	–	–	–	–	–	–	–	–	25	–
M^-	100	100	–	100	100	–	100	100	–	100	100	–
	NiSalhtda			NiSaldape			NiSaldaps			NiSaldpt		
$(M-2)^-$	–	–	–	–	–	–	–	–	–	–	42	–
M^-	100	100	–	100	100	–	100	100	–	100	100	–
$(M+19)^-$	–	9	–	–	–	–	–	–	–	–	3.5	–
$(M+38)^-$	–	21	–	–	–	–	–	–	–	–	1.4	–
	CoSalhtda			CoSaldape			CoSaldaps			CoSaldpt		
$(M-2)^-$	–	–	–	–	–	–	–	–	–	27	41	100
M^-	100	100	–	100	100	–	100	100	–	100	100	89
$(M+19)^-$	–	7	100	–	45	100	–	86	100	–	2.3	–
$(M+38)^-$	–	9	67	–	16	–	–	27	12	–	–	–
$(M+69)^-$	1.6	–	–	1.1	–	–	1.5	–	–	2.8	–	–

Experimental

The metal complexes were prepared according to methods in the literature [12–15]. The Schiff base compounds are four coordinate compounds with nitrogen and oxygen donor atoms (Ia–Ic) and five coordinate complexes with nitrogen and oxygen donor atoms (Id).



Ia $R = C_7H_{14}$	Salhtda; N,N'-Bis(salicylidene)-heptanediamine
Ib $R = C_3H_6OC_3H_6$	Saldape; N,N'-Bis(salicylidene)-3,3'-bis(aminopropyl)ether
Ic $R = C_3H_6SC_3H_6$	Saldaps; N,N'-Bis(salicylidene)-3,3'-bis(aminopropyl)sulfide
Id $R = C_3H_6NHC_3H_6$	Saldpt; N,N'-Bis(salicylidene)-3,3'-bis(aminopropyl)amine

The purity of the compounds was determined from C, H and N analysis and from measurements of the low voltage positive ion mass spectra. The spectra were identical to those reported earlier [14]. The negative ion methane chemical ionization spectra were like those measured in previous studies [16].

Reagent gases were purchased from commercial suppliers. The fluorine-containing gases CF_4 (Freon-14) 99.7%; SO_2F_2, 99.5%; and SF_6, 99.8% were obtained from Matheson Gas Products, East Rutherford, N.J. The gases were used as received without additional purification. The positive ion mass spectra of the gases revealed no impurities that would interfere with these studies.

The mass spectrometer used in this study was a modified Hitachi Perkin-Elmer RMU-6 [5, 6]. Reagent gas pressures were approximately 0.1 Torr for all three reagent gases. Sample compounds were sublimed into the ion source at 160–170 °C for Saldape and Saldaps compounds and at 180–200 °C for the Salhtda and Saldpt complexes. The reagent gas pressures and sample sublimation temperatures were selected to optimize negative ion intensities. The electron energy and repeller potential were also adjusted to attain maximum negative ion currents. The mass spectra reported correspond to monoisotopic spectra in that ion currents from all isotopic species in the ion cluster are included in the evaluation.

Results and Discussion

Negative ion mass spectra for copper(II), nickel(II), and cobalt(II) Schiff base complexes measured under chemical ionization conditions with the reagent gases CF_4, SO_2F_2, and SF_6 are summarized in Table I.

For copper compounds molecular negative ions, M^-, were detected for all complexes with CF_4 and SO_2F_2 as reagent gases. For CuSaldpt an intense ion at (M–2) was detected with SO_2F_2 as the reagent gas.

The formation of the M^- ions occurs via secondary electron capture and the $(M-2)^-$ ion in CuSaldpt is produced by dissociation capture:

$$\text{CuSaldpt} + e^- \rightarrow (\text{CuSaldpt}-2\text{H})^- + H_2 \qquad (1)$$

No copper-containing negative ions were detected when SF_6 was employed as the reagent gas. This observation is no doubt related to the high electron capture cross section for SF_6, and the large amount of SF_6 present in the ion source compared to the copper complexes. Since the formation of M^- and SF_6^- must occur via secondary electron capture, and because of the large quantity of SF_6 and the great tendency for SF_6 to form SF_6^- by thermal electron capture [17, 18], the production of copper-containing molecular ions is not realized under the experimental conditions employed. The intensity of the molecular negative ions was found to vary in the manner $CF_4 > SO_2F_2 > SF_6$. This variation is related to the probability for negative ion formation in the reagent gas. Thus, the most intense copper-containing negative ions are detected in the presence of CF_4 where no abundant CF_n^- (n = 1–4) ions are produced. The lower abundance of metal-containing ions in SO_2F_2 is related to the effective competition of SO_2F_2 with the copper complexes for secondary electrons.

No secondary ions produced via ion/molecule reactions were detected in any of the copper complexes with any of the reagent gases. The non reactivity of the M^- ions with neutral reagent gas compounds has been attributed to the inert d^{10} configuration of copper in the molecular negative ion [5, 6]. The inability of negative ions from SO_2F_2 and from SF_6 to react may be related to the fact that the reagent gas negative ions usually react by fluoride ion transfer. If this process occurs at copper in the molecule, the addition of F^- would alter the electron configuration on copper to $d^{10}s^1$. It is reasoned that such a bonding configuration would not be favorable on copper.

The negative ions produced with the nickel complexes include the molecular negative ion in CF_4 and SO_2F_2, and secondary product ions in SO_2F_2. A nickel-containing negative ion M^- was detected when SF_6 was used as the reagent gas with NiSaldpt. For other compounds only SF_6^- and SF_5^- ions were noted with SF_6 as the reagent gas. The formation of the M^- ions occurs via secondary electron capture. The production of NiSaldpt$^-$ in all gases, and particularly in the presence of SF_6, indicates that NiSaldpt competes favorably with the reagent gases for secondary electrons and that the capture cross section for NiSaldpt$^-$ formation must be large when compared with that for SF_6^- formation from SF_6.

The $(M+19)^-$ and $(M+38)^-$ ions were detected in NiSalhtda and in NiSaldpt with SO_2F_2 as the reagent gas. No secondary negative ions were noted for NiSaldape and for NiSaldaps. Although the M^- ion was the most abundant metal-containing ion in SO_2F_2 for these complexes, the absolute ion intensity was quite low. A similar situation was noted for NiSaldape and NiSaldaps in the negative ion spectra with methane and isobutane as the reagent gas [16]. It was reasoned that the inability to detect secondary ions for NiSaldape and for NiSaldaps in CH_4 and i-C_4H_{10} was due to the low intensity of the molecular negative ion and thus the low probability for detecting the reaction product according to reaction 2:

$$M^- + CH_4 \rightarrow (M+CH_2)^- + H_2 \qquad (2)$$

A similar condition may be significant for the reaction of NiSaldape and NiSaldaps with SO_2F_2, in that combination of M^- with SO_2F_2 is not observed because the absolute intensity of M^- is low.

Processes for the formation of $(M+19)^-$ and $(M+38)^-$ in NiSalhtda and in NiSaldpt could occur as summarized in reactions 3–6 for NiSalhtda.

$$\text{NiSalhtda}^- + SO_2F_2 \longrightarrow (\text{NiSalhtda} + F)^- + SO_2F \qquad (3)$$

$$\text{NiSalhtda}^- + SO_2F_2 \longrightarrow (\text{NiSalhtda} + F_2)^- + SO_2 \qquad (4)$$

$$\text{NiSalhtda} + SO_2F_2^- \longrightarrow (\text{NiSalhtda} + F)^- + SO_2F \qquad (5)$$

$$\text{NiSalhtda} + SO_2F_2^- \longrightarrow (\text{NiSalhtda} + F_2)^- + SO_2 \qquad (6)$$

Various attempts were made to identify the primary ion NiSalhtda$^-$ or $SO_2F_2^-$. From measurements and comparisons of the resonance capture curve for $SO_2F_2^-$, NiSalhtda$^-$, and (NiSalhtda + $F_2)^-$ it was not possible to identify the reagent ion since both NiSalhtda$^-$ and $SO_2F_2^-$ ions are produced via thermal electron capture and thus both ionization efficiency curves are identical. The ionization efficiency curves for the product ions were identical to those for NiSalhtda$^-$ and $SO_2F_2^-$. Attempts to vary NiSalhtda pressure by increasing the sublimation temperature usually led to decomposition of the complex. Increasing the SO_2F_2 pressure led to an increase in the $SO_2F_2^-$ ion current and a proportionate increase in the secondary ion currents, $(M+F_2)^-$ and $(M+F)^-$. These results suggest that reactions 5 and 6 are responsible for $(M+F_2)^-$ and $(M+F)^-$ ion formation. Because it was not possible to vary the NiSalhtda pressure and thus the M^- ion current at constant SO_2F_2 pressure, the contributions of reactions 3 and 4 to secondary ion formation cannot be assessed. It could be argued that the reactions of NiSalhtda, NiSaldape, and NiSaldaps should be similar since these complexes have similar structures and that the inability to detect secondary ions in NiSaldape and in NiSaldaps, is due to the low intensity of NiSaldape and NiSaldaps. This argument would support reactions 3 and 4 as the mode of secondary ion formation with SO_2F_2 as the reagent gas. As noted above, the present experimental results do not conclusively support either pair (3 and 4, or 5 and 6) of reactions.

The formation of secondary ions for cobalt complexes was observed with the three reagent gases. Only in the reactions of ions from SF_6 and CoSaldpt were no ion/molecule products detected. With CF_4 as the reagent gas the negative ions detected where M^- (molecular negative ion) from the complexes and $(M+69)^-$. No CF_n^- negative ions were detected under the experimental conditions used. The reactions leading to the $(M+69)^-$ ion can only be

$$M^- + CF_4 \longrightarrow (M+CF_3)^- + F \tag{7}$$

since M^- was the only primary ion detected. The CoSalhtda, CoSaldape and CoSaldaps complexes are tetrahedral [19, 20] while CoSaldtp is trigonal bipyramid [12]. The incorporation of CF_3 moieties into the negative molecular ion may occur by the formation of a cobalt–carbon bond. In the M^- ions it has been suggested [5, 14] that cobalt(I) is produced so that electron sharing in the t_{2g} cobalt orbitals would be the mode of bonding in $(M+CF_3)^-$. In reactions of CH_4 and cobalt Schiff base negative ions [16] the $(M+CH_2)^-$ ion was detected with the tetrahedral cobalt complexes. That incorporation of CF_2 moieties into M^- in these same complexes is not observed, must be related to the thermochemistry of the reaction. Formation of $(M+CH_2)^-$ proceeds with the loss of H_2 and the bonding of CH_2 to the metal. By comparison the formation of F_2 upon possible incorporation of CF_2 into M^- with cobalt complexes releases less energy, about 272 Kg/mol [21].

The formation of $(M+CF_3)^-$ occurs via reaction 7 where the cobalt carbon bond formation leads to stability in the secondary ion. For this reaction it is imagined that the t_{2g}^4 electron configuration for cobalt in the M^- ion, provides sufficient electron density to form a stable Co–CF_3 bond. It has been noted [22, 23] that fluoroalkyl cobalt compounds are more stable than the alkyl derivatives. That $(M+CF_3)^-$ ions are formed with CF_4 whereas the $(M+CH_2)^-$ ions are produced with CH_4 [16] may also be related to a greater stability of the fluorocarbon–cobalt bond in $(M+CF_3)^-$. The preparation of compounds with Co–CF_3 bonds has been reported for a series of Schiff base complexes of cobalt [23]. In the reactions, cobalt is reduced to Co(I) and the perfluoroalkyl cobalt derivative is formed presumably by an oxidative addition process [23]. The reaction in solution is similar to those noted here in that reduced cobalt, Co(I), is believed to be the most reasonable form of cobalt in the M^- ions.

Reaction of $CoSaldpt^-$ with CF_4 also yields the $(M+CF_3)^-$ ion. It is interesting to note also that the relative intensity for $(M+CF_3)^-$ in CoSaldpt is greater than that for $(M+CF_3)^-$ in the tetracoordinate compounds. The greater abundance for $(CoSaldpt + CF_3)^-$ may be related to the notion that CoSaldpt adopts a trigonal bipyramid structure and attachment of an electron in $CoSaldpt^-$ occurs in the d_{z^2} orbital. It is reasoned that additional electron density at cobalt due to this attached electron and also due to the fifth ligand enhances the formation of $(CoSaldpt + CF_3)^-$.

In the presence of SO_2F_2 all four complexes yield a molecular negative ion, M^-, as the most abundant ion in the spectrum. For five coordinate CoSaldtp, the $(M-2)^-$ ion is also detected in high abundance. The M^- ion is formed by secondary electron capture and $(M-2)^-$ is produced via a dissociative capture process. It is not possible to specify the ligand position from which H_2 is lost to form $(M-2)^-$ in CoSaldpt.

The ion/molecule reactions noted in the presence of SO_2F_2 are similar to those studied with square planar cobalt complexes. The important ions are $(M+F)^-$ and $(M+F_2)^-$ for the tetracoordinate species but only $(M+F)^-$ is detected for five coordinate CoSaldpt. At least two reactant ions could yield the secondary ion $(M+F_2)^-$ as illustrated for CoSaldpt,

$$SO_2F_2^- + CoSalhtda \longrightarrow (CoSalhtda + F_2)^- + SO_2 \tag{8}$$

or

$$SO_2F_2 + CoSalhtda^- \longrightarrow (CoSalhtda + F_2)^- + SO_2 \tag{9}$$

In reaction 8 $SO_2F_2^-$ transfers F_2^- to the neutral complex while in reaction 9 the $CoSalhtda^-$ negative ion abstracts F_2 from SO_2F_2. Attempts to identify the $(CoSalhtda + F_2)^-$ precursor ion(s) by measuring the ionization efficiency curves for $CoSalhtda^-$ for $SO_2F_2^-$, and for $(CoSalhtda + F_2)^-$ were uninformative since both potential precursor ions have identical electron capture ionization efficiency curves. Measurement of the variation in secondary ion current as a function of metal complex pressure was not successful because increasing the sublimation temperature over a range necessary to obtain significant increases in M^- ion current, led to decomposition of the complex. Increasing the SO_2F_2 pressure gave results similar to those obtained with SO_2F_2 and the nickel complexes. From this behavior it is suggested that a primary reactant ion is $SO_2F_2^-$. Because the pressure of the complex could not be varied, contributions of reaction 9 cannot be evaluated. It is reasonable that process 8 plays a significant role in these systems since fluorosulfur compounds are known to participate in F_n^- transfer processes [24–27].

Formation of $(M+F_2)^-$ in the four coordinate compounds may be suggestive of a process in which the tetrahedral cobalt complexes either add F^- and F to attain a six coordinate $(M+F_2)^-$ ion or add F_2^- to obtain a five coordinate geometry in $(M+F_2)^-$. The observation that five coordinate CoSaldpt reacts to yield only $(M+F)^-$ might be interpreted to suggest that six coordinate geometries are preferred in the cobalt-containing product ions. It is not apparent why NiSaldpt and CoSaldpt reactions in SO_2F_2 are dissimilar, unless the nature of the bonding in the ion/molecule product ions is different for the two metals and unrecognized electronic effects dictate the nature of the reaction processes.

Reactions of the tetrahedral metal complexes in the presence of SF_6 yield $(M+F)^-$ as the dominant ion. In CoSalhtda and in CoSaldape, $(M+F_2)^-$ is also detected. No molecular negative ions were noted for the tetrahedral complexes whereas an abundant (89%), although not intense, $CoSaldpt^-$ ion was detected. The $(M-2)^-$ ion in CoSaldpt arises by dissociative attachment of a secondary electron. No ion/molecule product ions were detected from CoSaldpt in the presence of SF_6. That no molecular negative ions were detected with the tetrahedral complexes indicates that SF_6 acts as a scavenger for the secondary electrons. Since SF_6^- is the only primary ion produced the $(M+F)^-$ and $(M+F_2)^-$ ions must arise via the reactions (where M = neutral metal complex),

$$SF_6^- + M \longrightarrow SF_5 + (M+F)^- \qquad (10)$$

$$SF_6^- + M \longrightarrow SF_4 + (M+F_2)^- \qquad (11)$$

The large abundance of the $(M+F)^-$ and $(M+F_2)^-$ ions may be related to the ability of the complexes to adopt five and perhaps six coordinate geometries. That the cobalt compounds react with SF_6^- while the corresponding nickel complexes do not, may be related to the electronic structure of the metal. The square planar structure of the nickel compounds is not believed to be an important factor here since square planar cobalt complexes of Schiff base ligands react [28] with SF_6^- to produce $(M+F)^-$ and $(M+F_2)^-$ ions.

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References

1 J. G. Dillard, *Chem. Rev., 73,* 589 (1973).
2 D. R. Dakternieks, I. W. Fraser, J. L. Garnett and I. K. Gregor, a) *Talanta, 23,* 701 (1976); b) *Org. Mass Spectrom., 12,* 370 (1977).
3 J. A. Wilson, I. W. Fraser, J. L. Garnett and I. K. Gregor, *Org. Mass Spectrom., 10,* 1047 (1975).
4 I. W. Fraser, J. L. Garnett and I. K. Gregor, *Chem. Commun.,* 365 (1974).
5 E. Baumgartner and J. G. Dillard, *Inorg. Chim. Acta, 32,* 11 (1979).
6 E. Baumgartner, T. C. Rhyne and J. G. Dillard, *J. Organometal. Chem., in press.*
7 S. R. Prescott, J. E. Campana and T. H. Risby, *Anal. Chem., 49,* 1501 (1977).
8 R. E. Sullivan, M. E. Lupin and R. W. Kiser, *Chem. Commun.,* 655 (1969).
9 I. W. Fraser, J. L. Garnett and I. K. Gregor, *Inorg. Nucl. Chem. Lett., 10,* 925 (1974).
10 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, *Org. Mass Spectrom., 13,* 20 (1978).
11 M. R. Blake, I. W. Fraser, J. L. Garnett, I. K. Gregor and R. Levot, *Chem. Commun.,* 1004 (1974).
12 L. Sacconi and I. Bertini, *J. Am. Chem. Soc., 88,* 5180 (1966).
13 L. W. Lane and L. T. Taylor, *J. Coord. Chem., 2,* 295 (1973).
14 L. T. Taylor and J. G. Dillard, *Inorg. Chem., 13,* 2620 (1974).
15 M. Hariharan and F. L. Urbach, *Inorg. Chem., 8,* 556 (1969).
16 J. G. Dillard and E. Baumgartner, *Inorg. Chim. Acta in press.*
17 A. J. Ahearn and N. B. Hannay, *J. Chem. Phys., 21,* 119 (1953).
18 W. M. Hickam and R. E. Fox, *J. Chem. Phys., 25,* 642 (1956).
19 H. Weigold and B. O. West, *J. Chem. Soc. A,* 1310 (1967).
20 R. H. Niswander, A. K. St. Clair, S. R. Edmondson and L. T. Taylor, *Inorg. Chem., 14,* 478 (1975).
21 H. M. Rosenstock, K. Draxal, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data, 6,* Suppl. 1 (1977).
22 P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem., 1,* 143 (1964).
23 A. van den Bergen, K. S. Murray and B. O. West, *J. Organometal. Chem., 33,* 89 (1971).
24 T. C. Rhyne and J. G. Dillard, *Inorg. Chem., 10,* 730 (1971).
25 J. A. Stockdale, D. R. Nelson, F. J. Davis and R. N. Compton, *J. Chem. Phys., 56,* 3336 (1972).
26 J. C. Haartz and D. H. McDaniel, *J. Am. Chem. Soc., 95,* 3562 (1973).
27 M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc., 99,* 4992 (1977); *98,* 1433 (1976).
28 E. Baumgartner and J. G. Dillard (unpublished results).