

Negative Ion Mass Spectral Studies of Polydentate Schiff Base Compounds: the Formation of Negative Ions Using Chemical Ionization Conditions for Co(II), Ni(II) and Cu(II) Complexes

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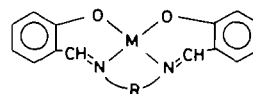
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The negative ion mass spectra of polydentate Schiff base complexes with Co(II), Ni(II), and Cu(II) have been measured using chemical ionization conditions. Methane, methane- d_4 and isobutane were used as the reagent gases. Molecular negative ions were detected for all complexes. Secondary ions produced via ion/molecule reactions were noted for complexes with Co(II) and for some complexes with Ni(II). Since no reagent gas negative ions were detected, it is reasoned that the ion/molecule reactions occur by interaction of the metal complex molecular negative ion with the neutral reagent gas. For Cu(II) complexes only molecular negative ion and fragment ions were detected. It is suggested that electron configuration at the metal ion is a significant controlling factor in these reactions.

Introduction

Negative ion mass spectra of metal Schiff base complexes have been reported by several investigators [1–3]. Reproducible negative ion mass spectra have been measured [4] for a series of copper β -diketonates by operating the ion source at 4×10^{-6} Torr [5] where secondary electron capture processes are significant. More recently, the production of negative ions from transition metal complexes using chemical ionization mass spectrometry has been investigated for metal β -diketonates [6] and tetradentate Schiff base ligands [7]. The chemical ionization mass spectra are characterized by the presence of abundant molecular negative ions. For cobalt and nickel complexes [7, 8] ion/molecule reactions involving the molecular negative ion and the reagent gas were also noted. The present study was initiated to further examine the influence of metal ion and ligand donor properties on secondary ion formation in Schiff base complexes. In addition, it was of interest to compare the nature of the gas phase reac-

tions for metal complexes with different structures and coordination geometries. In this work the negative ion formation processes have been studied for four and five coordinate complexes of Cu(II), Ni(II), and Co(II) in the presence of methane, methane- d_4 and isobutane as reagent gases. The four coordinate complexes are metal MSALHTDA, MSALDAPE, and MSALDAPS compounds (Structures Ia, b, c) while five coordinate metal complexes are MSALDPT (Structure Id).



- Ia Salhtda R = C₇H₁₄
Ib Saldape R = C₃H₆OC₃H₆
Ic Saldaps R = C₃H₆SC₃H₆
Id Saldpt R = C₃H₆NHC₃H₆

M = Cu(II), Ni(II), Co(II)

Experimental

The mass spectrometer used in this investigation and the experimental procedures employed have been described [7]. The relative abundances are mono-isotopic values in that all isotopes of a given metal complex ion are included in the measured ion current. SALHTDA and SALDPT compounds were sublimed at 180–200 °C into the ion source using the direct insertion probe. SALDAPE and SALDAPS complexes were introduced via sublimation at 160–170 °C. Methane and methane- d_4 reagent gas pressures were 0.2–0.3 Torr while spectra were measured at 0.1–0.2 Torr when using isobutane.

The reagent gases were purchased from commercial sources. Methane (99.97%) and isobutane (99.0%) were obtained from Matheson Gas Products, East Rutherford, N.J. Methane- d_4 (99% isotopic purity) was supplied by Merck, Sharp and Dohme of Canada, Ltd., Isotope Division. The gases were used as received.

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TABLE I. Negative Ion Mass Spectra of Copper Schiff Base Compounds.

CuSalhtrda				CuSaldape				CuSaldaps				CuSaldpt			
M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀
301	(M-98) ⁻	0.6	1.8	-	-	-	-	-	-	-	-	343	(M-57) ⁻	2.1	1.0
305	(M-94) ⁻	10	12	338	L ⁻	0.4	0.4	-	-	-	-	337	L ⁻	0.4	0.6
372	(M-27) ⁻	7	1.4	340	(L+2) ⁻	3.8	9.8	356	(L+2) ⁻	100	100	339	(L+2) ⁻	2.5	3.1
399	M ⁻	100	100	401	M ⁻	100	100	417	M ⁻	39	37	400	M ⁻	100	100

TABLE II. Negative Ion Mass Spectra of Nickel Schiff Base Compounds.

NiSalhtrda				NiSaldape				NiSaldaps				NiSaldpt			
M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀	M/Z	Ion	CH ₄	iC ₄ H ₁₀
324	(M-70) ⁻	1.4	1.1	-	-	-	-	370	(M-42) ⁻	1.3	-	324	(M-71) ⁻	1.5	0.8
336	L ⁻	0.7	1.6	338	L ⁻	2.7	0.6	354	L ⁻	1.2	1.3	-	-	-	-
338	(L+2) ⁻	5	14	340	(L+2) ⁻	9	8	356	(L+2) ⁻	23	19	-	-	-	-
394	M ⁻	100	100	396	M ⁻	100	100	412	M ⁻	100	100	395	M ⁻	100	100
408	(M+14) ⁻	0.9	0.4	-	-	-	-	-	-	-	-	-	-	-	-

TABLE III. Negative Ion Mass Spectra of Cobalt Schiff Base Compounds.

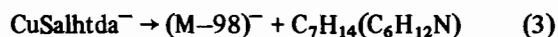
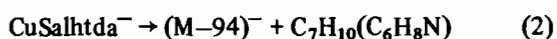
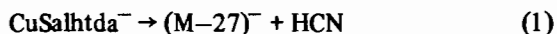
CoSalhtrda				CoSaldape				CoSaldaps				CoSaldpt			
Ion	CH ₄	CD ₄	iC ₄ H ₁₀	Ion	CH ₄	CD ₄	iC ₄ H ₁₀	Ion	CH ₄	CD ₄	iC ₄ H ₁₀	Ion	CH ₄	CD ₄	iC ₄ H ₁₀
M ⁻	100	100	100	M ⁻	100	100	100	M ⁻	100	100	100	(M-2) ⁻	9	18	2
(M+14) ⁻	1.1	-	0.3	(M+14) ⁻	1.7	-	1.5	(M+14) ⁻	1.4	-	1.2	M ⁻	100	100	100
(M+16) ⁻	-	0.6	-	(M+16) ⁻	-	<0.1	-	(M+16) ⁻	-	<0.1	-	(M+15) ⁻	2.1	-	7
												(M+18) ⁻	-	3.2	-

The metal complexes were prepared according to methods described in the literature [2, 9–11]. The purity of the complexes was examined using low pressure positive ion mass spectra. The mass spectra were in agreement with those previously reported [2]. With the copper compounds ions formed by 'exchange' of copper with iron from the ion source were noted in the low pressure spectra. The 'exchange' ions were not detected in the negative ion spectra measured using chemical ionization conditions.

Results and Discussion

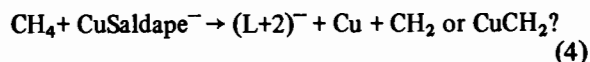
The negative ion mass spectra measured using chemical ionization conditions with methane, methane- d_4 and isobutane are summarized in Tables I, II, and III for Cu(II), Ni(II), and Co(II) compounds, respectively. The monoisotopic abundances are given as a percentage of the most abundant ion. Under the experimental conditions employed here, no negative ions arising from the reagent gas were detected. The mass spectra are characterized by a) abundant molecular negative ions which are formed principally via secondary electron capture processes, b) fragment ions produced by loss of ligand moieties, and c) secondary ions generated via ion/molecule reactions. The copper complexes produced the greatest abundance of negative ions under the experimental conditions used here. This result is similar to that noted previously [2] where the intensity of molecular negative ion for Schiff base complexes varied in the manner $Cu > Ni > Co$. In these studies at high pressures no significant difference in the relative intensities of the nickel- and cobalt-containing molecular negative ions was noted. It is likely that at high pressures, where secondary electron capture processes are important, electron attachment is equally probable in the partially filled d orbitals of the tetrahedral cobalt complexes and the empty orbitals of the square planar nickel compounds. The large intensity of the copper-containing ions may be related to the formation of a stable d^{10} configuration on copper in the molecular negative ion.

In the tetracoordinate copper compounds CuSalhtda, CuSaldape and CuSaldaps the molecular negative ion (M^-) is an intense ion. The M^- ion is not the base peak in the spectrum of CuSaldaps. For five coordinate CuSaldpt the M^- ion is the most abundant. The prominent fragment ions detected in CuSalhtda and in CuSaldpt are formed by cleavage of bonds in the ligand portion of M^- . The probable reactions for the decomposition of CuSalhtda are



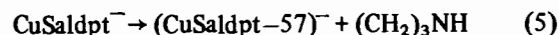
The loss of HCN occurs from the coordinated nitrogen of the amine. The removal of C_7H_{10} and C_7H_{14} , probably occurs from the hydrocarbon bridge. In the process for C_7H_{10} loss the hydrocarbon hydrogen may be transferred to the coordinated nitrogens or to copper. It is not possible to speculate on the bonding site for the hydrogens in the $(M-94)^-$ ion. The loss of 98 mass units probably occurs from the hydrocarbon bridge and it is likely that C_7H_{14} is removed. Alternatively, it is possible that loss of 94 could correspond to C_6H_8N and removal of 98 could be $C_6H_{12}N$. However, it is reasoned that removal of C_7H_{10} and C_7H_{14} for the $(M-94)^-$ and $(M-98)^-$ ions, respectively would maintain nitrogen coordination to copper which is deemed favorable in stabilizing the fragment ions.

For the CuSaldaps and CuSaldape four coordinate complexes fragmentation of the ligand is not a prominent process although the formation of ligand negative ions was observed. The $(L+2)^-$ ion was noted in CuSaldape and in CuSaldaps. For CuSaldaps $(L+2)^-$ was the most intense ion in the spectrum when using methane or isobutane as the reagent gas. It is probable that $(L+2)^-$ arises via reaction of the reagent gas with the complex as illustrated using CH_4



From the present results it is not possible to identify the neutral products.

Five coordinate CuSaldpt interacts with methane and isobutane to produce an abundant molecular negative ion plus $(M-57)^-$, $(L+2)^-$ and L^- . The molecular negative ion, $(M-57)^-$ and L^- are no doubt produced following secondary electron capture by the neutral complex. The $(L+2)^-$ ion probably arises by a process like reaction 4 above. The $(P-57)^-$ fragment ion may be formed by loss of a portion of the hydrocarbon bridge in the ligand. It is suggested that loss of 57 occurs by removal of the $(CH_2)_3NH$ moiety, thus reducing the coordination number of copper from five to four in the reaction

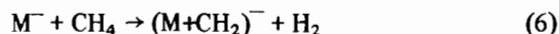


For all of the copper complexes no ion/molecule reaction products were produced by incorporation of hydrocarbon moieties. The intensity of the molecular negative ions was large in all complexes, and it was determined that if any secondary ions are formed their relative abundance must be less than 0.001%. In a previous study [7] it was found that these same copper complexes did not react with simple gases (O_2 , NO , CO , PF_3) in mixtures with methane. Further no ion/molecule processes were detected for the reactions of square planar copper complexes with

methane and isobutane [8]. It must thus be concluded that the inability of the copper complex negative ions to participate in ion/molecule reactions is related to the stability of the d^{10} electron configuration on copper. From this study where five coordinate pyramidal and additional four coordinate square planar complexes have been investigated, it appears that changes in geometric structure, or ligand donor strength, are not effective in enhancing the likelihood of ion/molecule reactions. These studies do not yield any information on the probability of reactions of negative ions with neutral copper complexes. However, since the neutral complexes capture electrons to form M^- ions, it is probable that negative ions could react with neutral copper complexes to produce ion/molecule product ions containing copper via nucleophilic reactions in the gas phase.

The negative ion spectra for nickel complexes are presented in Table II. For all nickel compounds the molecular negative ion is the most abundant ion in the presence of methane or isobutane. For the four coordinate compounds the formation of L^- ions occurs by fragmentation of the molecular ion while $(L+2)^-$ must arise via a reaction of the molecular negative ion with methane or isobutane. The process may be similar to that described for the copper compounds (reaction 4). Loss of 70 mass units $(M-70)^-$, from NiSalhtda⁻ is believed to correspond to cleavage of carbon-carbon bonds in the hydrocarbon (R) bridge, to produce C_5H_{10} and $(M-70)^-$. In NiSaldaps the $(M-42)^-$ ion may be produced by loss of C_3H_6 from the thiol bridge in the molecular negative ion. Upon loss of C_3H_6 the coordination by nitrogen and oxygen ligand donor atoms would be maintained and any steric restrictions for potential sulfur coordination would be diminished.

Of particular interest in the negative ion mass spectrum for NiSalhtda is the detection of $(M+14)^-$ in the presence of methane or isobutane. In other studies of the reactions of nickel Schiff base complex negative ions with hydrocarbons, the formation of $(M+14)^-$ was shown [7, 8] to occur via the reaction (illustrated for CH_4)



In this process the H_2 produced arises from methane. For square planar NiSalhtda it is likely that $(M+14)^-$ is formed according to reaction 6. No negative ions from the reagent gases (CH_4 or $i-C_4H_{10}$) were detected in this study so reaction 7 is not reasonable for $(M+14)^-$ production.



In reaction 6 the nickel-containing molecular negative ion may be viewed as a d^9 species. Evidence has been presented previously [1-5] to suggest that reduction

of the metal occurs upon electron capture. Capture of an electron into a metal orbital would yield Ni(I). As a reduced metal formation of the nickel- CH_2 bond would be enhanced. It could be reasoned that the availability of additional electron density on the metal could facilitate bond formation between carbon and the non-bonded electrons in the d_{z^2} orbital of nickel (I). The final geometric configuration for $(M+CH_2)^-$ would be five coordinate and could adopt a square pyramidal or trigonal bipyramidal configuration. The square pyramidal configuration would be most likely since little geometric rearrangement would be necessary and the d_{z^2} orbital would contain a pair of electrons in the d^9 Ni(I) configuration.

For the other four coordinate nickel complexes, NiSaldape and NiSaldaps, no $(M+14)^-$ ion was detected. It should be mentioned that the absolute intensity of M^- in NiSaldape and NiSaldaps was much less than that for NiSalhtda. Under these conditions, it is probable that the primary ion intensity was not sufficient to yield detectable $(M+14)^-$ secondary ions. Because the structures of NiSaldape, NiSaldaps and NiSalhtda are similar, since NiSalhtda reacted with methane and isobutane to yield $(M+CH_2)^-$, and since M^- ions were detected for all three four-coordinate nickel compounds, the inability to detect $(M+14)^-$ in NiSaldape and NiSaldaps, is attributed to the low absolute intensity of M^- , rather than any inability of M^- to react with the reagent gases.

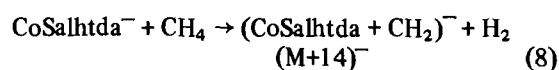
The abundant ions in NiSaldpt were M^- and $(M-71)^-$. The molecular negative ion is formed via secondary electron capture and $(M-71)^-$ is produced via decomposition of M^- . The loss of 71 mass units is attributed to elimination of $(CH_2)_2NH(CH_2)_2$ from the molecular negative ion. It is reasoned that the loss of $(CH_2)_2NH(CH_2)_2$ occurs from the bridging amine portion of the ligand. Because of this loss, the $(M-71)^-$ ion would be a four coordinate species.

No secondary ions were detected in NiSaldpt, although the intensity of the M^- ion was at least as great as that for M^- in NiSalhtda. The inability of NiSaldpt⁻ to react with methane may be due to structural or electronic factors. The significant observation is that square planar nickel complex negative ions NiSalen⁻, NiOaben⁻ [8] and NiSalhtda⁻ (Table II) react with methane to yield $(M+CH_2)^-$ whereas five coordinate NiSaldpt⁻ does not yield a detectable ion/molecule product ion.

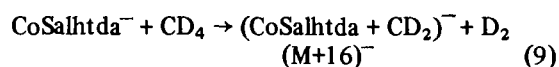
The negative ion mass spectral data for cobalt complexes in Table III reveal that molecular negative ions, fragment ions, and secondary ions (ion/molecule product ions) are detected in the presence of methane, methane- d_4 , and isobutane. The spectra are devoid of any significant fragment ions except for the presence of $(M-2)^-$ in CoSaldpt. It is particularly significant to note that the ion/molecule product ion is different for the four and five coordinate com-

plexes. The complexes CoSalhtda, CoSaldape, and CoSaldaps have tetrahedral structures [12, 13] and interact with methane and isobutane to yield $(M+14)^-$ ions. The five coordinate trigonal bipyramid CoSaldpt complex [9] reacts with the hydrocarbon gases CH_4 and $i\text{-C}_4\text{H}_{10}$ to yield the $(M+15)^-$ ion.

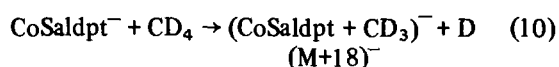
That no negative ions of the reagent gases were detected, supports the notion that the secondary ions are formed via reactions of the metal complex negative ions with methane and isobutane. The proposed reaction between tetrahedral four coordinate CoSalhtda⁻, CoSaldape⁻, and CoSaldaps⁻ molecular negative ions with methane is (illustrated for CoSalhtda⁻)



That incorporation of CH_2 from the reagent gas occurs was confirmed by measuring the mass spectra in the presence of CD_4 . The formation of $(M+16)^-$ in CoSalhtda supports the reaction



The $(M+16)^-$ ion was barely detectable ($<0.1\%$) in the CD_4 spectra of CoSaldape and CoSaldaps, so it is suggested that reactions 8 and 9 also occur for these four coordinate complexes. The five coordinate complex CoSaldpt⁻ molecular negative ion reacts with methane and isobutane to yield the $(M+15)^-$ secondary ion. That the incorporation of additional 15 mass units occurs only by loss of H from CH_4 was confirmed by the formation of $(M+18)^-$ when the mass spectrum of CoSaldpt was measured in CD_4 ; reaction [10]



The formation of $(M+\text{CH}_2)^-$ ions in the tetrahedral cobalt complexes contrasts with the ion/molecule processes for square planar and trigonal bipyramid cobalt complexes. For square planar CoSalen, CoOaben, and CoSalophen [8] and for CoSaldpt (Table III), the important secondary ion is $(M+\text{CH}_3)^-$. For the molecular negative ion, all complexes would adopt a d^8 Co(I) electron configuration. For the tetrahedral CoSalhtda, CoSaldape, and CoSaldaps compounds the added electron would be captured into one of the degenerate t_{2g} orbitals leaving two unpaired electrons in the t_{2g} levels. It is suggested that the two electrons of this t_{2g} level may facilitate cobalt- CH_2 bond formation. Sharing of the cobalt electrons in these degenerate levels apparently favors the bonding by CH_2 . That planar cobalt compounds and trigonal bipyramid com-

plexes react with methane to yield $(M+\text{CH}_3)^-$ ions must be related to differences in structure or more probably to different electron configurations when compared to tetrahedral cobalt complexes.

For the square planar and trigonal bipyramid or square pyramid complexes, capture of the attached electron could occur into the highest d level, say either d_{z^2} for a trigonal bipyramid geometry or $d_{x^2-y^2}$ for square planar or square pyramid structures. Capture of the electron to yield a diamagnetic ion structure would not likely facilitate or favor Co- CH_3 bond formation since in the resulting ion no cobalt-carbon electron sharing would be possible. It is suggested that the mode of cobalt-carbon (CH_3) bond making would involve one of the unpaired d electrons on cobalt and the carbon free electron of CH_3 . By comparison with the tetrahedral complexes, it may be suggested that electrons in degenerate levels, t_{2g} , favor Co- CH_2 type ion/molecule products while unpaired electrons in non-degenerate levels would facilitate Co- CH_3 bonded structures.

The relative intensities of the $(M+\text{CH}_2)^-$ ions in CoSalhtda, CoSaldape and CoSaldaps do not differ within experimental error, so there is evidently no significant influence due to ligand strengths on the extent of secondary ion formation. It is noted that the relative abundance of $(M+\text{CH}_3)^-$ in CoSaldpt is slightly larger than that for the tetrahedral compounds. Whether this difference is of important significance in characterizing the different four and five coordinate complexes cannot be judged without additional measurements. However, the important observation reported herein is that the production of ion/molecule product ions appears to be strongly influenced by the structure, geometrical and/or electronic, of the molecular negative ion.

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