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Negative Ion Chemical Ionization Mass Spectral (NICIMS) Studies. Reactions of Metal Schiff Base Complexes with Methane: Gas Mixtures

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The gaseous negative ion reactions of four and five coordinate cobalt(II), nickel(II), and copper(II) Schiff base complexes with gas mixtures have been studied. The gas mixtures contain methane (~90%) and about 10% of the gases O_2, NO, CO, and PF_3. Intense parent negative ions were formed by secondary electron capture processes under moderate chemical ionization conditions. It was observed that the gaseous parent negative ion reacts with the added gas molecule to form the addition product MLX^- where X = O_2, NO, CO, or PF_3, L = Schiff base ligand, and M = Ni(II) or Co(II). The abundance of the MLX^- secondary ion was greatest in CH_4–O_2 mixtures. The relative abundance of MLX^- for the other gas mixtures varied approximately in the manner $MLNO^- > MLCO^- > MLPF_3^-$. For CuL systems, no MLX^- ions were detected. The significant aspects of these results are presented and discussed. Comparisons of the reactivity of these compounds in solution and in the solid state with the gas phase reactions are discussed.

Introduction

Positive and negative ion mass spectra of coordination compounds and organometallic compounds have been studied in order to correlate mass spectra with molecular structures [1–4]. More recently negative ion mass spectra at ion source pressures of approximately 10^{-5} Torr have been reported [5–8]. Under these conditions negative ions are produced by secondary electron capture. In an effort to enhance secondary electron capture processes, the negative ion mass spectra of volatile metal chelates have been measured using chemical ionization methods [9–11]. Reagent gases employed in the studies have included methane [9, 10], methane-d_4 [10], methane–argon [9], isobutane [9, 10] and fluorine-containing gases [11]. Using nitrogen, isobutane, and methane–argon [9] reagent gases, parent negative ions were noted for a variety of metal acetylacetonate compounds. For Schiff base complexes secondary ions were discovered [10, 11] along with parent negative ions when using a selection of reagent gases. In view of the interest in the reactions of metal compounds with small molecules [12–16], it appeared that an investigation of the reactions of potential ligand molecules with the negatively charged coordination compound species in the gas phase would be of interest.

In earlier studies [17] of organic molecules under chemical ionization conditions it was noted that functional groups could be identified using NO as the reagent gas. In another study [18] using ICR techniques, the reactions of CO, PF_3, and NO with negative ions from $(C_5H_5)Co(CO)_2$ have been examined to investigate the relative π acceptor ability of CO and PF_3. The results of the ICR study indicate that PF_3 is a stronger π acceptor ligand than CO in the reactions with $C_5H_5CoCO^-$ in the gas phase.

In this paper the results of a study of the reactions of gaseous negative ions derived from Schiff base coordination compounds with simple molecules are presented. Of particular interest in this study are the reactions of O_2, NO, CO, and PF_3 with the gaseous metal complex negative ion under chemical ionization conditions. The gases were selected to take advantage of the potential reactivity of these molecules with the Schiff base complexes of Co(II), Ni(II), and Cu(II). The information from such a study could suggest analytical reagent gases for detecting coordination compounds, provide information on the manner in which the reactions are dependent on the metal ion and the reagent gas, and indicate the influence of the ligand and complex structure on the nature of the ion–molecule reactions.

Experimental

Instrumentation and Procedures

A modified [10, 11] Hitachi Perkin–Elmer RMU-6 single focusing mass spectrometer was used in this

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study. Although the details of the modifications and the operating procedures have been presented [10, 11], a brief summary will be given here. The stainless steel ion source ion volume dimensions are 15 X 14 X 11 mm. Electrons entered the ionization chamber through a 4.0 X 0.25 mm slit and ions were repelled into the analyzer region through an 8.0 X 0.5 mm ion exit slit. Repeller potentials ranged from 0–5V. The ion source temperature was maintained at 150–200 ℃ depending on the sublimation temperature of the metal complex. Samples were introduced into the ion source using a gas tight direct insertion probe. Sample temperatures were 180–200 ℃ for SALHTDA* and SALDPT* compounds and 160–170 ℃ for SALDAPE** and SALDAPS** complexes.

Pressure in the ion source was measured using a model 144 MKS Baratron capacitance manometer. Gases were stored in an all glass vacuum system and introduction into the ion source was controlled by stainless steel fine metering valves. The reagent gas pressure for these studies ranged from 0.20 to 0.30 Torr. Measurements of the spectra at various percent gas compositions were carried out by metering in methane to obtain the appropriate partial pressure and then the added simple gas compound to maintain a constant pressure. For measurement of the relative intensities reported in the table, a 90% methane–10% "added gas" mixture was used.

The differential pumping system included a 6″ Varian-NRC diffusion pump (2400 l/sec) for the ion source envelope and a smaller 3″ Hitachi pump (360 l/sec) for the analyzer region. At a methane ion source pressure of 0.3 Torr, the ion source envelope pressure was less than 3×10^{-5} Torr and the analyzer pressure was lower than about 3×10^{-6} Torr.

Mass spectra were mass calibrated using high boiling PFK or tris(perfluorobutyl)amine (PFBA). The coordination compounds caused some contamination of the ion source. However, with repeated cleaning (2–3 weeks) of the repeller and inner surfaces of the ion source chamber, the reproducibility of the spectra was ±10% in relative abundance.

Reagent Gases and Coordination Compounds

Methane (99.97%) isobutane (99.0%), nitric oxide (99.0%), and carbon monoxide (99.99%), were obtained from Matheson Gas Products, East Rutherford, N.J. Oxygen (99.6%) was purchased from Airco Inc., Montvale, N.J., and PF_3 (98%) was supplied by Ozark Mahoning Co., Tulsa, Okla.

The metal complexes were prepared by methods described in the literature [19–22]. Low voltage and 70ev EI mass spectra were measured to examine the purity of the compounds. The mass spectra for all compounds were found to be identical to those measured earlier [21]. No significant "ion source exchange" reactions [21, 23] were noted at chemical ionization conditions in this study.

Results

The negative ion mass spectra of Schiff base complexes with methane under chemical ionization conditions are reported elsewhere [10, 11, 24]. The previous results indicate that hydrocarbon moieties are incorporated into the metal complex negative ions to give the secondary ions. The results for the present study, summarized in Table I, indicate that the dominant secondary ions produced are those involving addition and/or reaction of the small molecule with the parent negative ion. For O_2, NO, and CO mixtures with methane, the important secondary ions with cobalt and nickel complexes are MLX^-, where M = Co(II), Ni(II), L = Schiff base ligand, and X = O_2, NO, or CO. For all of the copper complexes, only parent molecular ion (P^-) and/or fragment ions similar to these noted in pure methane were detected [24]. For methane mixtures with CO and PF_3 additional ions were detected where hydrocarbon moieties or F and PF_3 species were incorporated in the secondary ion, respectively. The formation of the adduct secondary ion, MLX^-, occurs by reaction of ML^- with the neutral simple molecule. In all instances at CH_4 source pressures of 0.2–0.3 Torr the significant negative ion was ML^- [10, 11]. For the 10% simple gas (X) 90% methane mixtures at 0.2–0.3 Torr no X^- ions were detected. In some experiments in CH_4–NO mixtures at a pressure of about 0.3 Torr, low intensity (≃1.0%) NO_x^- (x = 1,2) ions were detected. Because of the low intensity of these ions it is reasoned that they are not directly involved in ion–molecule reactions.

To examine the ion formation processes in detail the relative intensities of the product ions were studied as a function of the percent small molecule in the methane mixtures. The total pressure in these experiments was maintained at a constant value. The results are presented in graphic form in Figure 1 for O_2 and NO reactions with CoSALHTDA and in figure 2 for O_2 interaction with CoSALDPT. Similar curves were noted for the other gases and for the nickel complexes. In each of these curves the intensity of the parent molecular ion decreases as the percent of the small molecule in the mixture increases. Concurrent with the depletion in CoL^- intensity, the $CoLX^-$ relative intensity increases with increasing percent of small molecule in the mixture. For $(P-2)^-$ in CoSALDPT–O_2 the percent abundance is relatively unchanged as the percent O_2 in the

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*SALHTDA: N,N′-bis(salicylidene)heptanediamine; SALDPT: N,N′-bis(salicylidene)-3,3′-bis(aminopropyl)amine.

**SALDAPE: N,N′-bis(salicylidene)-3,3′-bis(aminopropyl)-ether. SALDAPS: N,N′-bis(salicylidene)-3,3′-bis(aminopropyl)sulfide.

TABLE I. Chemical Ionization Mass Spectra. Schiff Base Complexes: 90% Methane–10% Gas Mixtures.

Compound	CH_4/O_2				CH_4/NO					
	$(P-2)^-$	$(P-1)^-$	P^-	$(P+32)^-$	$(P-4)^-$	$(P-2)^-$	P^-	$(P+30)^-$	$(P+46)^-$	[a]
CoSALHTDA	–	–	1.4	100	–	–	63.6	100	15.6	
CoSALDAPE	–	–	2.5	100	–	–	51.9	100	2.9	
CoSALDAPS	–	–	6.8	100	–	–	71.8	100	12.7	
CoSALDPT	13.4	11.0	4.0	100	22.6	100	13.2	37.7	5.7	9.4
NiSALHTDA	–	–	100	23.5	–	–	16.6	100	10.0	
NiSALDAPE	–	–	100	33.2	–	–	63.9	100	–	
NiSALDAPS	–	–	100	26.6	–	–	38.9	100	–	
NiSALDPT	–	–	35.1	100	–	–	75.4	100	–	
CuSALHTDA	–	–	100	–	[b]	–	–	–	–	
CuSALDAPE	–	–	100	–	[b]	–	–	–	–	
CuSALDAPS	–	–	100	–	[b]	–	–	–	–	
CuSALDPT	–	–	100	–	–	–	100	–	–	

Compound	CH_4/CO				CH_4/PF_3							
	$(P-2)^-$	P^-	$(P+14)^-$	$(P+28)^-$	$(P-2)^-$	P^-	$(P+35)^-$	$(P+36)^-$	$(P+37)^-$	$(P+38)^-$	$(P+85)^-$	$(P+86)^-$
CoSALHTDA	–	100	1.2	7.7	–	100	–	6.4	–	3.8	–	3.8
CoSALDAPE	–	100	1.4	16.0	–	100	–	1.6	–	–	–	3.5
CoSALDAPS	–	100	0.7	1.8	–	100	–	–	–	–	–	–
CoSALDPT	9.6	100	–	3.4	11.0	100	21.0	–	10.1	–	1.7	–
NiSALHTDA	–	100	1.0	–	–	100	–	–	–	–	–	2.9
NiSALDAPE	–	100	–	0.3	–	100	–	–	–	–	–	3.7
NiSALDAPS	–	100	–	0.2	–	100	–	–	–	–	–	–
NiSALDPT	–	100	–	0.4	–	100	–	–	–	–	–	4.0
CuSALHTDA	[b]				[b]							
CuSALDAPE	[b]				[b]							
CuSALDAPS	[b]				[b]							
CuSALDPT	[b]				[b]							

[a] $(P+28)^-$ $[(CoSALDPT-2H)NO]^-$. [b] These copper complexes were not studied with these gas mixtures (see text).

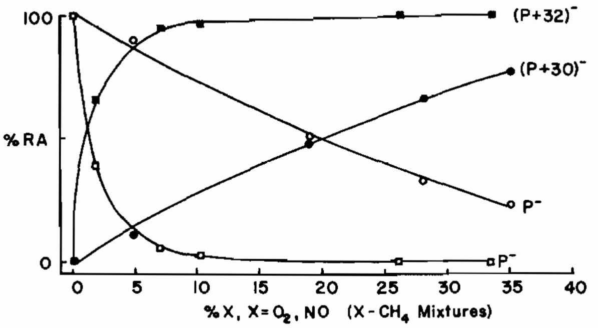

Figure 1. Variation in $CoLO_2^-$, $CoLNO^-$, and CoL^- % in abundance for four coordinate CoSALHTDA, *vs.* % O_2 and % NO. □ $[CoSALHTDA]^-$: ■ $[CoSALHTDA{\cdot}O_2]^-$ $CH_4{\cdot}O_2$ Mixture. ○ $[CoSALHTDA]^-$: ● $[CoSALHTDA{\cdot}NO]^-$ $CH_4{\cdot}NO$ Mixture.

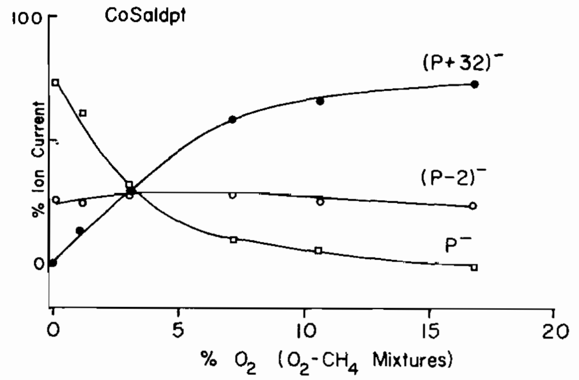

Figure 2. Variation of % Ion Current for $CoLO_2^-$, $(CoL-H_2)^-$ and CoL^- for five coordinate CoSALDPT *vs* % O_2 in O_2–CH_4 mixtures. □ $CoSALDPT^-$ ● $CoSALDPT{\cdot}O_2^-$ ○ $(CoSALDPT-H_2)^-$.

mixture is increased. These results taken with the fact that no intense X^- ions were detected in these experiments, support the notion that the $CoLX^-$ ions are formed via the processes

$$CoL + e^- \rightarrow CoL^- \tag{1}$$

$$CoL^- + X \rightarrow CoLX^- \tag{2}$$

In reaction 1, the neutral complex yields the parent negative ion by secondary electron capture and this ion combines with the small molecule to produce $CoLX^-$. It is reasonable that similar processes yield the $NiLX^-$ secondary ions.

All of the copper complexes were studied in CH_4–O_2 mixtures and CuSALDPT was investigated in CH_4–NO and CH_4–CO mixtures. Under the experimental conditions employed to obtain high intensities of secondary ions, no $CuLX^-$ ions were detected. It is estimated from the instrumental detection limits that if $CuLX^-$ ions are formed with X = O_2, NO, and CO the relative intensity must be less than 10^{-3} %. However, intense CuL^- ions and some fragment ions were noted in the selected copper complexes. An extensive study of the copper compounds was not carried out due to the fact that no $CuLX^-$ secondary ions were detected for the CuL compounds producing the most intense CuL^- ions. Also from a comparison of the reactivity of the copper compounds (Table I) with that for other nickel and cobalt complexes [10, 11], it was judged, that if CuL^- did not react with O_2 to produce $CuLO_2^-$ and if $CuSALDPT^-$ did not react with NO, then the probability of detecting $CuLX^-$ ions for the other complexes upon reaction with CO or PF_3, would be small.

The fragment ions noted in the copper complexes are produced by loss of ligand moieties and by formation of protonated ligand ions, *i.e.* $(L + 2)^-$, where L represents the coordinated ligand. The important ions detected were $(P - 27)^-$, $(P - 57)^-$, and $(P - 94)^-$. The relative abundance of these species was about 10% in all cases. It is suggested that $(P - 27)^-$ involves loss of the neutral HCN; $(P - 57)^-$ may correspond to the loss of $H(CH_2)_4$ or $HN(CH_2)_3$ from the ligand, and $(P - 94)^-$ could arise by elimination of $-C_7H_{10}-$ or $-NC_6H_8-$ from the hydrocarbon bridge.

Metastable peaks were noted for all of the nickel complexes in the CH_4–O_2 and CH_4–NO mixtures. For cobalt complexes metastable peaks were detected in the CH_4–O_2 and CH_4–CO gas mixtures. A summary of the metastable data is presented in Table II. The calculated metastable mass was determined using the most abundant isotope of the metal ion; Co, 59 and Ni, 58 amu. The metastable results are

TABLE II. Metastable Transitions For $MLX^- \rightarrow ML^- + X$ Ion Decomposition.

$ML{\cdot}X^-$	M* (Measured) (amu)	M* (Calculated) (amu)
CoSALHTDA·O_2	365.1	365.4
CoSALDAPE·O_2	367.3	367.4
CoSALDAPS·O_2	383.2	383.3
CoSALDPT·O_2^{a}	364.4	364.5
CoSALHTDA·CO	369.1	368.9
CoSALDAPE·CO	370.6	370.8
CoSALDAPS·CO	387.1	386.8
CoSALDPT·CO	370.1	369.9
NiSALHTDA·O_2	364.3	364.4
NiSALDAPE·O_2	366.2	366.4
NiSALDAPS·O_2	382.5	382.3
NiSALDPT·O_2	365.5	365.4
NiSALHTDA·NO	366.1	366.1
NiSALDAPE·NO	367.8	368.1
NiSALDAPS·NO	384.3	384.1
NiSALDPT·NO	367.0	367.1

^{a}The process here is $CoSALDPT{\cdot}O_2^- \rightarrow (CoSALDPT - H)^- + HO_2$.

consistent with decomposition of the MLX^- ion according to reaction (3).

$$MLX^- \rightarrow ML^- + X \qquad (3)$$

Only for $[CoSALDPT - O_2]^-$ is the metastable process indicative of a decomposition involving the formation of HO_2:

$$[CoSALDPT - O_2]^- \rightarrow [CoSALDPT - H]^- + HO_2 \qquad (4)$$

The reactions leading to the formation of secondary ions in CH_4–PF_3 mixtures do not involve simple addition of PF_3. No abundant PF_n^- ions were detected so it is concluded that the parent negative ion is the primary ion. The reactions for the cobalt complexes are similar to those noted [10, 11] when CF_4 and SO_2F_2 were used as reagent gases. In CoSALHTDA and CoSALDAPE the dominant reactions appear to involve loss of hydrogen from the complex upon incorporation of PF_3 and F_2 into the product as illustrated

$$\underset{}{CoL^-} + PF_3 \rightarrow \underset{(P+86)^-}{[(CoL - 2H)PF_3]^-} + H_2 \qquad (5)$$

$$CoL^- + PF_3 \rightarrow \underset{(P+36)^-}{[(CoL - 2H)F_2]^-} + PFH_2 \qquad (6)$$

An additional reaction for the two cobalt complexes is

$$CoL^- + PF_3 \rightarrow \underset{(P+38)}{[CoLF_2]^-} + PF \qquad (7)$$

The nickel compounds react with PF_3 in a manner similar to that for cobalt (Reaction 5) in that the only secondary ion detected was $[P + 86]^-$, $[(NiL - 2H)PF_3]^-$. For CoSALDAPS and NiSALDAPS no secondary ions were detected in the CH_4–PF_3 mixtures even though the parent negative ion intensity for each compound was large.

For CoSALDPT, a five coordinate complex, the reaction with PF_3 includes the loss of H_2 and H. For the formation of $(P + 85)^-$ a possible reaction is

$$[CoSALDPT)^- + PF_3 \rightarrow [(CoSALDPT - 3H)PF_3]^- + H_2 + H \qquad (8)$$

A similar reaction may lead to $(P + 35)^-$ for CoSALDPT:

$$[CoSALDPT]^- + PF_3 \rightarrow [(CoSALDPT - 3H)F_2]^- + PH_2F + H \qquad (9)$$

The loss of a single hydrogen atom from the complex accompanies the formation of $(P + 37)^-$:

$$CoSALDPT^- + PF_3 \rightarrow [(CoSALDPT - H)F_2]^- + PHF \text{ (or PF + H?)} \qquad (10)$$

The additional ions, P – 2 and P – 4 noted for five coordinate CoSALDPT, were also observed in the spectra using CH_4 alone as the reagent gas. It is probable that these ions are formed by hydrogen loss from the ligand in $CoSALDPT^-$ upon secondary electron capture.

Discussion

The results in Table I may be interpreted to suggest that the reaction center is at the metal ion. If secondary ions were produced by reactions at ligand sites, then the significant difference in secondary ion products and relative abundances noted for Co(II), Ni(II), and Cu(II) complexes for all ligands would not be expected. For reaction processes at the ligand it is reasonable that similar secondary ions and more constant relative abundances would be noted.

The nature of the added gas also influences the relative abundance of the parent and secondary ions. For the cobalt complexes the $CoLX^-/CoL^-$ ion ratio varies with X in the manner $O_2 > NO > CO$. For NO and CO this variation parallels the suggested [25] π donor strength of the ligand. Because of competing reactions it is not possible to include PF_3 in the series, although it is recognized that the $Co(L - H)X^-/CoL^-$ ratio is smallest for secondary ions in the CH_4–PF_3 mixture. The addition reactions in CH_4–X gas mixtures proceed with almost complete exclusion of any reactions of ML^- with methane. Only in the CH_4–CO mixture is any $(P + CH_n)^-$ ion detected. For the four coordinate cobalt complexes (SALHTDA, SALDAPE, and SALDAPS) and for four coordinate NiSALHTDA, $(P + 14)^-$ ions were detected in low abundance.

The reactions of four and five coordinate nickel and cobalt complexes in the CH_4–O_2 and CH_4–NO mixtures and for four and five coordinate cobalt complexes in the CH_4–CO mixture are characteristically different. The structures for CoSALHTDA [26], CoSALDAPE [27], and CoSALDAPS [27] are reportedly four coordinate tetrahedral while CoSALDPT [19] is five coordinate trigonal bipyramid. NiSALHTDA, NiSALDAPE and NiSALDAPS are reported [28] to be similar in structure to square planar NiSALEN [29, 30], while NiSALDPT adopts [31, 32] a structure intermediate between trigonal bipyramid and square pyramid. For the five coordinate CoSALDPT compound the base peak is $(P + 32)^-$ in the CH_4–O_2 mixture and additional intense ions are noted at $(P - 2)^-$ and $(P - 1)^-$. For the four coordinate cobalt species only P^- and $(P + 32)^-$ were detected. In CH_4–NO mixtures the most intense ion for CoSALDPT is $(P - 2)^-$ while for the four coordinate tetrahedral complexes, $(P + 30)^-$ is most abundant. Although the $(P + 28)^-$ ions in the CH_4–CO mixture are not intense, $(P - 2)^-$ is noted for CoSALDPT but not for the four coordinate compounds. For four coordinate nickel species the P^- ion is most abundant while the $(P + 32)^-$ abundance is about 20–35% in CH_4–O_2. For the five coordinate NiSALDPT compound, the secondary ion $[NiSALDPT \cdot O_2]^-$ is the most abundant species (100%) and $NiSALDPT^-$ is about 30% abundant. Use of the three other methane gas mixtures for nickel compounds was less successful in revealing characteristic spectral differences between four and five coordinate complexes.

The nickel and copper complexes have similar structures so it is significant that the electronic nature of the metal ion appears to be important for the reactions reported here. The copper and nickel four coordinate complexes are planar while the five coordinate CuSALDPT and NiSALDPT complexes have structures intermediate between trigonal bipyramid and square pyramid [29, 30, 33, 34] geometries. Thus even though the structures of the parent compounds involved in the ion-molecule reactions are similar, CuL^- ions do not react with O_2 whereas intense secondary ions were detected for the nickel complexes. It is suggested that this difference in reactivity may be related to the electronic nature of the metal ion in the ML^- species. Upon electron capture it is likely that the electron may be captured into a metal orbital producing d^{10} copper in CuL^- and d^9 nickel in NiL^-. It is reasoned that the completed d^{10} configuration is more stable and thus less reactive toward O_2 incorporation. If copper is formally Cu(I) in the CuL^- ion it is interesting that O_2 is unreactive in the gas phase since Cu(I) species are [15] readily oxidized to Cu(II) in condensed phases.

Comparison of gas phase behavior with solution and solid behavior of these nickel and cobalt compounds is informative. It is reported that NiSALDAPE [34] and NiSALDAPS [34] are not oxygenated in air and/or when moist. CoSALDAPS and CoSALDAPE do not react with O_2 [27]. The five coordinate cobalt complex, CoSALDPT, oxygenates [27] rapidly in solution. It is significant that all nickel and cobalt negative ion species studied in this work react with O_2. The results lend support the notion [15] that the mechanism for reaction is one in which O_2 is reduced to O_2^-. The apparent "reduction" of cobalt and nickel in the ML^- ion may aid in providing additional electron density at the metal reaction site to produce O_2^- in the adduct secondary ion.

Formulation of the cobalt secondary ion as $[CoL \cdot (X^-)]$ species is favored by examining the MLX^-/ML^- ratio for the X ligand species, X = O_2, NO, and CO. It is reasoned that a larger $CoLX^-/CoL^-$ ratio would be found if electron transfer from CoL^- to X occurs upon formation of the secondary ion. Furthermore if electron transfer is important then the probability of transfer would be related to the electron affinity of X. The ion ratios vary according to the scheme $MLO_2^- > MLNO^- > MLCO^-$, where the average calculated ratios are approximately 28 for MLO_2^-; 1.6 for $MLNO^-$ and 0.085 for $MLCO^-$. This ion ratio behavior indicates that the largest ratio is found for the X ligand with the greatest electron affinity [37]: $EA(O_2) = 0.44$ ev; $EA(NO) = 0.024$ ev, and $EA(CO) = -1.8$ ev. From these results and the concept of electron transfer noted [15, 38] for stabilizing MLX^- species it is proposed that these secondary ions be formulated as $[ML \cdot (X^-)]$ species. It is of interest to point out that a similar correlation of $CoLX^-/CoL^-$ ratios has been observed [36] for the reaction of gaseous square planar cobalt Schiff base complex negative ions, ML^-, with O_2 and NO.

However, it must be recognized that localization of the electron on X is an extreme simplification. If the complex negative ion is formulated as $[ML(X^-)]$ decomposition of this ion should yield X^- + ML. A search for a metastable process for this decomposition was not successful. The only ion decomposition reaction involves loss of neutral X and production of ML^- from MLX^-.

The formation of secondary ions where X = NO and CO suggests that these X species could be added to metal complexes in reduced oxidation states. It is likely that addition of CO would not be as probable as NO addition since the abundance of $MLCO^- \ll MLNO^-$. If the mode of attachment of NO and CO to the metal is similar to that for O_2, then these ligands would be bound as NO^- and CO^-. However, bonding by nitric oxide in many transition metal compounds is viewed [13] with NO bound as NO^+. If $MLNO^-$ is represented as $(ML \cdot NO^-)$, it might be expected that the ion ratio for $MLNO^-/ML^-$ would increase with increasing ligand donor strength so that formation of $MLNO^-$ or $ML \cdot (NO^-)$ would be favored. Such a variation would be predicted from the notion that greater electron density at the metal ion would favor NO^- ligand formation. It is known [26, 27, 34] that the approximate ligand strength for the four coordinate ligands is SALHTDA ≃ SALDAPS > SALDAPE. From the results in Table I the $NiLNO^-/NiL^-$ ion ratios vary in the manner NiSALHTDA (6.02) > NiSALDAPS (2.57) > NiSALDAPE (1.92) for nickel. The favorable correlation with ligand donor strength for nickel may suggest that the added nitric oxide should be formulated as NO^- in $NiLNO^-$.

The $CoLNO^-/CoL^-$ ratio shows little dependence on the donor nature of the ligand. For the four coordinate complexes the average ion ratio varies according to the scheme CoSALDAPE (1.93) > CoSALHTDA (1.57) > CoSALDAPS (1.39). The relative donor strength for the ligands is SALDAPS > SALHTDA > SALDAPE. The characteristic difference in the behavior of the cobalt complexes toward NO compared to the nickel complexes may be related to the fact that the nickel compounds are square planar while the cobalt compounds are tetrahedral. The difference may be rationalized by recognizing that electron donation to NO from the d_{z^2} orbital in the NiL^- ion would be favored since the d_{z^2} is filled in d^9 NiL^-. It has been shown [39] that axial perturbation in square planar complexes aids in raising the energy of the d_{z^2} orbital. Thus an increase in the ligand field strength would provide further aid in raising the d_{z^2} energy level and promote electron donation from NiL^- to NO. On the other hand, electron donation to NO from the t_{2g} orbitals in the tetrahedral CoL^- ion appears not to be influenced by the ligand strength. The suggested d^8 configuration for CoL^- would yield two half filled t_{2g} orbitals. It is reasoned that these partially filled orbitals are less likely to become involved in electron donation to NO and that increasing the field strength of the ligand does not enhance donor ability of these t_{2g} levels.

The five coordinate MSALDPT compounds of cobalt and nickel react to give secondary ions with O_2, NO, and CO. Consideration of the $(MSALDPT\cdot X)^-/(MSALDPT)^-$ ratios for $X = O_2$, NO and CO for M = Co(II) and Ni(II) is supportive of the suggestion that electron transfer to produce $[MSALDPT\cdot(X^-)]$ may be the best description for ion formulation. For cobalt and nickel the $(MLX)^-/(ML)^-$ ion ratios vary in a manner related to the electron affinity [37] of the X ligand. The experimental ratios for cobalt are $CoLO_2^-$ (25) > $CoLNO^-$ (2.9) > $CoLCO^-$ (0.34) and for nickel the ratios are $NiLO_2^-$ (2.9) > $NiLNO^-$ (1.3) > $NiLCO^-$ (0.004), (L = SALDPT). The relative magnitude of the ion ratios decreases as the electron affinity of the X gas molecule decreases. It is reasonable that electron transfer to X is more important for the five coordinate compounds than for the four coordinate compounds. Since electron density at M in the ML^- ion is no doubt greater for the five coordinate species electron donation to stabilize X^- in the MLX^- ion would be favored.

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References

1 M. R. Litzow and T. R. Spalding, "Mass Spectrometry of Inorganic and Organometallic Compounds, "Elsevier, Amsterdam (1973).
2 J. G. Dillard, *Chem. Rev., 73,* 589 (1973).
3 J. B. Westmore, *Chem. Rev., 76,* 695 (1976).
4 J. Lewis and B. F. G. Johnson, *Acta Chem. Rev., 1,* 245 (1968).
5 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, *Org. Mass Spectrom., 13,* 20 (1978).
6 D. R. Dakternieks, I. W. Fraser, J. L. Garnett and I. K. Gregor, *Org. Mass Spectrom., 12,* 370 (1977).
7 *Idem, Talanta, 23,* 701 (1976).
8 I. W. Fraser, J. L. Garnett, I. K. Gregor and K. J. Jessop, *Org. Mass Spectrom., 10,* 69 (1975).
9 S. R. Prescott, J. E. Campana and T. H. Risby, *Anal. Chem., 49,* 1501 (1977).
10 E. Baumgartner and J. G. Dillard, *Org. Mass Spectrom.*
11 E. Baumgartner and J. G. Dillard, *Org. Mass Spectrom.*
12 J. S. Valentine, *Chem. Rev., 73,* 235 (1973).
13 T. Moeller, *J. Chem. Ed., 23,* 542 (1946).
14 D. J. Hodgson and J. A. Ibers, *Inorg. Chem., 1,* 2345 (1968).
15 R. G. Wilkins, *Adv. Chem. Sec., 100,* 111 (1971).
16 K. Kustin, I. A. Taub and E. Weinstock, *Inorg. Chem., 5,* 1079 (1966).
17 D. F. Hunt and J. F. Ryan, *Chem. Comm.,* 620 (1972).
18 R. R. Corderman and J. L. Beauchamp, *Inorg. Chem., 12,* 3135 (1977).
19 L. Sacconi and I. Bertini, *J. Am. Chem. Soc., 88,* 5180 (1966).
20 L. W. Lane and L. T. Taylor, *J. Coord. Chem., 2,* 295 (1973).
21 L. T. Taylor and J. G. Dillard, *Inorg. Chem., 13,* 2621 (1974).
22 M. Hariharan and F. L. Urbach, *Inorg. Chem., 8,* 556 (1969).
23 W. C. Gilbert, L. T. Taylor and J. G. Dillard, *J. Am. Chem. Soc., 95,* 2477 (1973).
24 J. G. Dillard and E. Baumgartner, *Inorg. Chim. Acta* (submitted for publication).
25 F. Basolo and R. G. Pearson, "Mechanisms of Inorganic reactions," Wiley, New York (1967) p. 538.
26 H. Weigold and B. O. West, *J. Chem. Soc. A,* 1310 (1967).
27 R. H. Niswander, A. K. St. Clair, S. R. Edmondson and L. T. Taylor, *Inorg. Chem., 14,* 478 (1975).
28 A. G. King and L. T. Taylor, *Inorg. Nucl. Chem., 33,* 3057 (1971).
29 R. H. Holm, *J. Am. Chem. Soc., 82,* 5632 (1960).
30 R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem., 7,* 82 (1966).
31 M. Seleborg, S. L. Holt and B. Post, *Inorg. Chem., 10,* 1501 (1971).
32 M. DiVaira, P. L. Orioli and L. Sacconi, *Inorg. Chem., 10,* 553 (1971).
33 D. Hall and T. N. Waters, *J. Chem. Soc.,* 2644 (1960).
34 A. K. St. Clair, *M. S. Thesis,* Virginia Polytechnic Institute and State University (1972).
35 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev., 13,* 339 (1974).
36 E. Baumgartner and J. G. Dillard (unpublished results).
37 H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data, 6,* Suppl. 1 (1977).
38 F. Basolo, B. M. Hoffman and J. A. Ibers, *Accts. Chem. Res., 8,* 384 (1975).
39 W. M. Coleman and L. T. Taylor, *Inorg. Chem., 10,* 2195 (1971).