Inorganica Chimica Acta, *155* (1989) 221–225

Reactions of *N*,*N*′-Ethylenebis(salicylideneiminato)metal(II) Complexes with Electrons, Halide Ions and Halogen Radicals in Gaseous Plasmas

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(Received June 10, 1988)

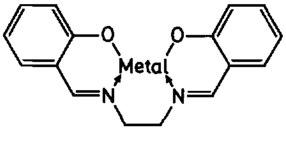
Abstract

Results of the gas phase reactions between a series of *N*,*N*′-ethylenebis(salicylideneiminato)metal(II) complexes (metal = Co, Ni, Cu, Zn) and electrons, radicals and negative ions contained in plasmas of the halogenated reagent gases NF_3, CF_2Cl_2 and CF_3Br are presented. Resonance electron capture and nucleophilic addition of a halide ion to the metal complexes compete as the two primary ionization processes in the gaseous plasmas. The relative abundances of ions arising from these processes are interpreted in terms of the ease of reduction and the Lewis acidities of the complexes respectively. Fluoride ions also induce negative ion formation by proton abstraction. In competition with the ionization processes, halogen radicals react with the metal complexes to produce new complex species which are detected as a result of their ionization by either resonance electron capture or nucleophilic halide addition.

Introduction

Recently we have described the use of negative ion chemical ionization (NICI) mass spectrometry with halogenated reagent gases as a method for examining the gas-phase negative ion chemistry of transition-metal coordination compounds [1–4]. Studies such as these are of significance because they provide information on fundamental aspects of metal complex chemistry, including Lewis acid and oxidation–reduction behavior under solvent-free conditions. The reagent gases, NF_3, CF_2Cl_2 and CF_3Br, have been shown to be convenient sources of fluoride, chloride and bromide ions, respectively, and facilitate the investigation of ion/molecule reactions involving nucleophiles of varying base strengths with a range of substrates including metal complexes [1–4]. Anions arising from Lewis acid–base addition [1–4] and Brφnsted acid–base proton tansfer reactions between halide ions and metal complexes [2, 4] have been identified previously as have nucleophilic displacement reactions at transition-metal centres [2, 3]. Inorganic ions may be the end products in NICI plasmas as a result of initial fast reactions between radicals and metal complexes followed by ionization of the reaction products. Radical/molecule reactions involving oxidative-addition [2, 3] and ligand displacement [1–3] have been identified in previous studies.

In this paper we present the results of a study of the gas phase negative ion chemistry of a series of metal(II) complexes of the non-macrocyclic tetradentate ligand, *N*,*N*′-ethylenebis(salicylideneimine)[†] for the metals cobalt, nickel, copper and zinc (herein abbreviated as Metal(salen) (1)[§]) in NF_3, CF_2Cl_2 and CF_3Br gaseous plasmas. Mechanisms based on competing bimolecular processes including resonance electron capture and several ion/molecule reactions are proposed to account for formation of the negative ions identified in the mass spectra. Chemical factors such as the ease of reduction and Lewis acidity of the complexes, as well as the Brφnsted basicity of the halide ions, are shown to be the principal influences on the types and relative abundances of negative ions formed.



Metal(salen)

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[†] Available commercially as *N*,*N*′-bis(salicylidene)ethylenediamine and *N*,*N*′-ethylenebis(salicylimine).

[§] Listed in Chemical Abstracts as [2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[phenolato]]metal(II).

0020-1693/89/$3.50

Experimental

The Metal(salen) complexes were prepared and purified by established procedures [5]. The free ligand, *N,N'*-ethylenebis(salicylimine) (Strem Chemical, Newburyport, MA, U.S.A.), was used as purchased in these preparations. The metal complexes were vacuum dried at 100 °C for 16 h and gave satisfactory elemental analyses.

The NCI mass spectra were obtained with a VG MM-16F single focusing mass spectrometer fitted with a dual EI/CI ion source (VG Analytical Instruments, Altrincham, Cheshire, U.K.). The principal instrumental parameters were as follows: ion source pressure, 0.1 torr; filament emission current, 500 μA; primary electron energy, 50 or 100 eV; repeller voltage, 0 to -1 V; ion accelerating voltage, -4 kV.

NF_3 (Spectra Gases, Newark, NJ, U.S.A.), CF_2Cl_2 and CF_3Br (Pacific Chemical Industries, Sydney, N.S.W., Australia) were used as reagent gases as purchased. In the absence of added analyte molecules, the NCI mass spectra of NF_3, CF_2Cl_2 and CF_3Br consisted principally of $[F]^-$, $[Cl]^-$ and $[Br]^-$, respectively (*ca.* 99% of the total ion current).

The technique of selected ion monitoring [6] was used as described previously [4, 7] to quantify the molecular ion charge which was generated from each complex under negative ionization conditions where argon was used as the electron-energy-moderating/collisional stabilization gas.

An isotopic cluster simulation program [8] was used to confirm the empirical formulae of ion assignments based on *m/z* and to deconvolute overlapping isotopic clusters.

Results and Discussion

In the absence of added analyte molecules, the negative ion mass spectra of the halogenated reagent gases are very simple. NF_3, CF_2Cl_2 and CF_3Br each undergo dissociative electron capture rapidly in the presence of low energy electrons to yield $[F]^-$, $[Cl]^-$ and $[Br]^-$, respectively [2]. In addition to abundant halide ions, the reagent gas plasmas also contain populations of thermalized electrons and free-radicals. An analysis of the processes leading to the formation of reactive ionic and radical species in these gaseous NICI plasmas has been given previously [2].

Upon addition of Metal(salen) complexes to the NICI plasmas, a variety of metal-containing negative ions are formed, several of which contain one or more halogen atoms. Table 1 lists the assigned formulae and relative abundances of the ions identified in the NF_3, CF_2Cl_2 and CF_3Br negative ion

TABLE 1. Percentage of the Total Ion Current (*TIC*) Carried by Ions in the NF_3, CF_2Cl_2 and CF_3Br NCI Mass Spectra of the Metal(salen) Complexes [a, b, c]

Ion	Reagent gas/metal											
	NF_3				CF_2Cl_2				CF_3Br			
	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn
$[\mathrm{Metal}^{II}\cdot L\cdot X_2-H-H_2]^-$	3		0.1	0.5	d	d		5				0.4
$[\mathrm{Metal}^{II}\cdot L\cdot X_2H-H_2]^-$	2		0.3	1	d	d						
$[\mathrm{Metal}^{II}\cdot L\cdot X]^-$	44	0.6		33	63	67	25	19	91	52	4	9
$[\mathrm{Metal}^{II}\cdot L\cdot X-H_2]^-$	11	6	5	4	16	13	15	2	2	2	0.9	0.2
$[\mathrm{Metal}^{I}\cdot L\cdot X-H]^-$	2	1	3	0.4	2	4	3					
$[\mathrm{Metal}^{II}\cdot L\cdot A]^-$ [e]	3	0.2	0.1	1	1							
$[\mathrm{Metal}^{II}\cdot L\cdot A-H_2]^-$ [e]	0.9		0.2	0.6	1							
$[\mathrm{Metal}^{I}\cdot L]^-$ [f]	15	14	29	4	1	3	17	0.1	0.8	4	62	0.1
$[\mathrm{Metal}^{I}\cdot L-H_2]^-$ [g]	4	6	2	22	1	0.3	5	0.5	0.2	0.3	2	9
$[\mathrm{Metal}^{II}\cdot L-H]^-$	14	51	49	30								
$[\mathrm{Metal}^{II}\cdot L-H-H_2]^-$	2	21	10	3								
$[\mathrm{Metal}^{II}\cdot X_3]^-$					15	13		74	5	41		90
$[\mathrm{Metal}^{I}\cdot X_2]^-$							34				31	
$[X]^-/TIC$	1.4	1.5	1.1	0.54	6.0	2.2	7.8	3.0	3.0	7.4	10	1.7
Temperature (°C)	220	230	250	310	270	250	250	300	250	260	320	315

[a] All isotopes of all atoms included. [b] $L = C_{16}H_{14}N_2O_2$. [c] X corresponds to F, Cl and Br in the NF_3, CF_2Cl_2 and CF_3Br mass spectra, respectively. [d] Not resolved due to iron-metal exchange in the ion source. [c] A = CN, HF_2 in the NF_3 mass spectra, F in the CF_2Cl_2 mass spectra. [f] $[\mathrm{Metal}^{II}\cdot L]^{-\cdot}$ in the case of Zn(salen). [g] $[\mathrm{Metal}^{II}\cdot L-H_2]^{-\cdot}$ in the case of Zn(salen).

mass spectra of the Metal(salen) complexes. Since the products of exothermic reactions will be excited initially, it is assumed that stabilization of each excited ion by collision with reagent gas molecules, M, is necessary to prevent fragmentation or back-reaction.

Each of the mass spectra listed in Table 1 contain a molecular ion, $[\text{Metal}\cdot\text{L}]^-$ ($L = C_{16}H_{14}N_2O_2$), formed by resonance capture of a low energy electron [9] into the lowest unoccupied or singly occupied molecular orbital of the metal complex. Formation of these ions with the cobalt, nickel and copper complexes in a number of reagent gases has been noted previously [10, 11]. With these Metal(salen) complexes (metal = Co, Ni, Cu), the electron capture process may be represented by reactions (1) and (2). Since resonance electron capture can only occur with molecules possessing positive electron affinities, the capture process is exothermic and initially produces an excited molecular ion, $[\text{Metal}^{\text{I}}\cdot\text{L}]^{-*}$, which may be stabilized by collisions with reagent gas molecules, represented by M [12]. As the cobalt, nickel and copper complexes each have unoccupied or singly occupied 3d orbitals on the metal (electron configurations $3d^7$–$3d^9$), resonance electron capture is likely to occur into a metal-based orbital. Hence, resonance electron capture with these complexes may be considered to entail a gas-phase, one-electron reduction which produces $[\text{Metal}^{\text{I}}\cdot\text{L}]^-$. This conclusion is supported by the behaviour of these complexes in solution where analogous $[\text{Metal}^{\text{I}}\cdot\text{L}]^-$ ions may be generated by electrochemical methods [13–15] and may even be isolated as complex salts such as $[\text{Na}[\text{Metal}^{\text{I}}\cdot\text{L}](\text{tetrahydrofuran})_2]$ [16]. In solution, the reduction potentials of these complexes decrease in the order, Cu > Co > Ni [13–15]. In order to compare the ease of reduction of the complexes in the gas phase with their solution-based reduction potentials, the technique of selected ion monitoring was used to measure the number of coulombs of molecular ion charge which could be generated from a given quantity of complex [4, 6, 7]. This measurement was made using argon as the buffer gas to prevent the formation of all ions except the molecular ion. The relative molecular ion charges measured for each complex, normalized to Ni(salen) which produced the least charge, varied as follows: Co, 3.4; Ni, 1.0; Cu, 6.7. That is, the tendency of the complexes to undergo reduction by resonance electron capture also decreases in the order, Cu > Co > Ni, in qualitative agreement with the solution-based reduction potentials.

$$\text{Metal}^{\text{II}}\cdot\text{L} + e^- \longrightarrow [\text{Metal}^{\text{I}}\cdot\text{L}]^{-*} \qquad (1)$$

$$[\text{Metal}^{\text{I}}\cdot\text{L}]^{-*} + \text{M} \longrightarrow [\text{Metal}^{\text{I}}\cdot\text{L}]^- + \text{M} \qquad (2)$$

The low relative abundances of the molecular ion in the mass spectra of the zinc complex indicate that this complex undergoes resonance electron capture considerably less readily than its cobalt, nickel and copper analogues. This is consistent with the inability of zinc(II) to accommodate an extra electron in a 3d orbital because of its $3d^{10}$ configuration. Resonance electron capture by the zinc complex probably produces a π-anion, $[\text{Metal}^{\text{II}}\cdot\text{L}]^{-\cdot}$, where the captured electron resides in the lowest π^* antibonding orbital of the ligand; reaction (3).

$$\text{Metal}^{\text{II}}\cdot\text{L} + e^- \xrightarrow{\text{M}} [\text{Metal}^{\text{II}}\cdot\text{L}]^{-\cdot} \qquad (3)$$

It is noteworthy that none of the mass spectra contain organic ions corresponding to the free ligand or ligand fragments, arising from fragmentation of the excited molecular ion, $[\text{Metal}\cdot\text{L}]^{-*}$. With metal(II) complexes containing two bidentate ligands, fragmentation of $[\text{Metal}\cdot\text{L}_2]^{-*}$ to give $[\text{L}]^-$ and $\text{Metal}^{\text{I}}\cdot\text{L}$ is commonly observed [2, 3, 9]. It is apparent that the tetradentate nature of the ligand in Metal(salen) complexes stabilizes the excited molecular ion against fragmentation because additional bonds would have to be broken for comparable eliminations to occur.

In competition with resonance electron capture, the metal complexes may react with the abundant halide ions in the plasmas by nucleophilic addition; reaction (4). This ion/molecule association is likely to be exothermic, so that the halide addition leads initially to an excited adduct ion, $[\text{Metal}^{\text{II}}\cdot\text{L}\cdot\text{X}]^{-*}$, which may be stabilized by collisions with reagent gas molecules to form $[\text{Metal}^{\text{II}}\cdot\text{L}\cdot\text{X}]^-$; reaction (5). As the metal complexes are coordinatively unsaturated and display well established Lewis acid properties in solution [17], and the halide ions are recognized Lewis bases [18], it is probable that nucleophilic addition is a Lewis acid–base process where the halide ion bonds directly to the metal. Hence, the $[\text{Metal}^{\text{II}}\cdot\text{L}\cdot\text{X}]^-$ ions are likely to be square-pyramidal species **2** [17], in which the metal is bonded to an XN_2O_2 donor atom set. It is significant that Zn(salen) forms halide adduct ions readily even though it has only a limited tendency to undergo resonance electron capture. Similar behaviour has been observed [1–3] with other zinc(II) complexes which do not undergo resonance electron capture at all but do form abundant halide adduct ions. This behaviour is consistent with the proposed Lewis acid–base formation mechanism for the halide adduct ions, but is difficult to reconcile with an alternative two-step mechanism which has been suggested [11] involving formation of the molecular ion by resonance electron capture followed by reaction of this ion with the reagent gas.

$$\text{Metal}^{\text{II}}\cdot\text{L} + [\text{X}]^- \longrightarrow [\text{Metal}^{\text{II}}\cdot\text{L}\cdot\text{X}]^{-*} \qquad (4)$$

$$[\mathrm{Metal^{II}\cdot L\cdot X}]^{-*} + \mathrm{M} \longrightarrow [\mathrm{Metal^{II}\cdot L\cdot X}]^{-} + \mathrm{M} \qquad (5)$$

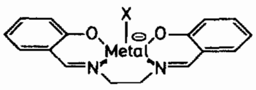
$$[\mathrm{Metal^{II}\cdot L\cdot X}]^{-*} \longrightarrow [\mathrm{Metal^{II}\cdot L{-}H}]^{-} + \mathrm{HX} \qquad (6)$$

Table 2 lists the $[\mathrm{Metal^{II}\cdot L\cdot X}]^-/[\mathrm{Metal^{I}\cdot L}]^-$ ion ratios in the mass spectra of the cobalt, nickel and copper complexes. Evaluation of these ion ratios in combination with the relative tendencies of the complexes to form $[\mathrm{Metal\cdot L}]^-$ indicates that the Lewis acidities of the complexes towards halide ions decrease in the order, Co > Ni > Cu. The Lewis acidity of the zinc complex with respect to this series is uncertain due to the low abundance of molecular ion in the zinc spectra, but may be intermediate between cobalt and nickel judging by the $[\mathrm{Metal^{II}\cdot L\cdot X}]^-/[\mathrm{Metal^{II}\cdot L{-}H}]^-$ ion ratios in the NF_3 mass spectra. Several factors are probably operative in determining this Lewis acidity order. Cobalt(II) and Zinc(II) complexes are generally not constrained by electronic factors to exhibit a particular geometry [19]. Hence, the metal in Co(salen) and Zn(salen) is free to rise above the N_2O_2 donor atom plane to achieve optimum coordination of an apical Lewis base [17, 19]. In contrast, electronic factors cause four-coordinate nickel(II) and copper(II) complexes to favour square-planar geometry and somewhat restrict the ability of the metal to leave the donor atom plane upon coordination of an additional Lewis base [17, 19]. With square-planar copper(II) complexes, a diminished tendency to coordinate additional ligands is also often associated with the Jahn–Teller effect [19]. Furthermore, the entropy of base addition to 'rigid' complexes such as square-planar copper complexes may be more unfavourable than with more flexible complexes such as those of zinc and cobalt [20].

The NF_3 NICI mass spectra of the metal complexes contain a prominent ion of the form, $[\mathrm{Metal^{II}\cdot L{-}H}]^-$. This ion is absent from the CF_2Cl_2 and CF_3Br mass spectra. Formation of the $[\mathrm{Metal^{II}\cdot L{-}H}]^-$ ion is attributed to elimination of HF from the excited fluoride adduct, $[\mathrm{Metal^{II}\cdot L\cdot F}]^{-*}$, before collisional stabilization has occurred; reaction (6). In effect, reactions (4) and (6) in combination constitute a proton transfer reaction from $\mathrm{Metal^{II}\cdot L}$ to $[\mathrm{F}]^-$. Formation of the $[\mathrm{Metal^{II}\cdot L{-}H}]^-$ ion occurs only in the NF_3 plasma because the fluoride ion is a substantially stronger Brønsted base than the other halide ions in the gas phase [21]. Since the fluoride ion is not a sufficiently strong base to abstract a proton from aryl or alkyl molecules [21], however, it may be inferred that the $[\mathrm{Metal^{II}\cdot L{-}H}]^-$ ions arise due to abstraction of a methine proton adjacent to one of the aromatic rings (**3**). Hydrogen atoms attached to sp^2 hybridized carbon atoms are generally more acidic than HF in the gas phase [21].

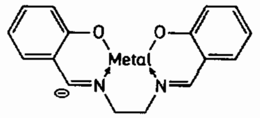
TABLE 2. $[\mathrm{Metal^{II}\cdot L\cdot X}]^-/[\mathrm{Metal^{I}\cdot L}]^-$ Ion Ratios Observed in the NF_3, CF_2Cl_2 and CF_3Br NCI Mass Spectra of the Cobalt, Nickel and Copper(salen) Complexes

X	Metal		
	Co	Ni	Cu
F	2.9	0.043	
Cl	63	22	1.5
Br	110	13	0.065



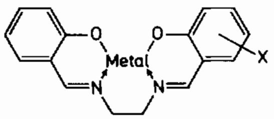
$[\mathrm{Metal^{II}.L.X}]^-$

2



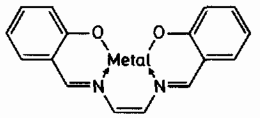
$[\mathrm{Metal^{II}.L-H}]^-$

3



$(\mathrm{Metal^{II}.L.X-H})$

4



$(\mathrm{Metal^{II}.L-H_2})$

5

Prior to ionization by either electrons or halide ions, the metal complexes may undergo fast radical/molecule reactions in the plasmas to give neutral adduct or elimination species which can further interact with electrons or halide ions to give the detected negative ion end products. Formation of the ions, $[\mathrm{Metal^{I}\cdot L\cdot X{-}H}]^-$ and $[\mathrm{Metal^{II}\cdot L\cdot X_2{-}H}]^-$, is attributed to radical/molecule reactions. A bimolecular encounter between a halogen radical and $\mathrm{Metal^{II}\cdot L}$ in the plasma can lead to homolytic displacement of a hydrogen atom to produce a molecule of the form, $(\mathrm{Metal^{II}\cdot L\cdot X{-}H})$ (**4**), reaction (7). As with $\mathrm{Metal^{II}\cdot L}$, $(\mathrm{Metal^{II}\cdot L\cdot X{-}H})$ may be ionized by either resonance electron capture or nucleophilic halide addition to give the ions $[\mathrm{Metal^{I}\cdot L\cdot X{-}H}]^-$ and $[\mathrm{Metal^{II}\cdot L\cdot X_2{-}H}]^-$, respectively; reactions (8) and (9). It has been demonstrated that the abundances of ions derived from radical reactions in the ion source increase relative to the molecular ion as the filament electron emission current is increased, and such processes can therefore be identified readily by examining relative ion abundances as a function of variations in filament electron emission currents [22, 23]. Consistent with a radical formation mechanism, the abundances of $[\mathrm{Metal^{I}\cdot L\cdot X{-}H}]^-$ and $[\mathrm{Metal^{II}\cdot L\cdot X_2{-}H}]^-$ were seen to increase relative to both $[\mathrm{Metal\cdot L}]^-$ and $[\mathrm{Metal^{II}\cdot L\cdot X}]^-$ as the filament emission current was increased over the range 100–1000 μA.

$$\mathrm{Metal^{II}\cdot L} + \mathrm{X^{\bullet}} \longrightarrow (\mathrm{Metal^{II}\cdot L\cdot X{-}H}) + \mathrm{H^{\bullet}} \qquad (7)$$

$$(\mathrm{Metal}^{II}\cdot \mathrm{L}\cdot \mathrm{X{-}H}) + e^- \xrightarrow{M} [\mathrm{Metal}^{I}\cdot \mathrm{L}\cdot \mathrm{X{-}H}]^- \tag{8}$$

$$(\mathrm{Metal}^{II}\cdot \mathrm{L}\cdot \mathrm{X{-}H}) + [\mathrm{X}]^- \xrightarrow{M} [\mathrm{Metal}^{II}\cdot \mathrm{L}\cdot \mathrm{X_2{-}H}]^- \tag{9}$$

Formation of the ions, $[\mathrm{Metal}^{I}\cdot X_2]^-$ and $[\mathrm{Metal}^{II}\cdot X_3]^-$, is also attributed to radical/molecule reactions because the abundances of these ions increased relative to $[\mathrm{Metal}\cdot L]^-$ with increasing filament emission currents. It appears that due to the exceptionally high electron affinities of halogen radicals, the salen ligand may be displaced from the Metal(salen) complexes by these radicals; reaction (10). The ligand displacement produces a metal halide molecule, $\mathrm{Metal}^{II}\cdot X_2$, which can capture an electron to form $[\mathrm{Metal}^{I}\cdot X_2]^-$ or coordinate an additional halide ion to yield $[\mathrm{Metal}^{II}\cdot X_3]^-$; reactions (11) and (12). Similar radical-induced ligand displacement processes have been identified previously with bis(β-ketoenolato)metal(II) complexes in gaseous halogenated plasmas [1–3].

$$\mathrm{Metal}^{II}\cdot \mathrm{L} + 2\mathrm{X}^{\bullet} \longrightarrow \mathrm{Metal}^{II}\cdot \mathrm{X}_2 + \mathrm{L}^{\bullet\bullet} \tag{10}$$

$$\mathrm{Metal}^{II}\cdot \mathrm{X}_2 + e^- \xrightarrow{M} [\mathrm{Metal}^{I}\cdot \mathrm{X}_2]^- \tag{11}$$

$$\mathrm{Metal}^{II}\cdot \mathrm{X}_2 + [\mathrm{X}]^- \xrightarrow{M} [\mathrm{Metal}^{II}\cdot \mathrm{X}_3]^- \tag{12}$$

With the exception of $[\mathrm{Metal}^{I}\cdot X_2]^-$ and $[\mathrm{Metal}^{II}\cdot X_3]^-$, each of the negative ions presently described is accompanied by an ion two daltons lower in mass such as, for example, $[\mathrm{Metal}\cdot L]^-$, $[\mathrm{Metal}\cdot L{-}H_2]^-$; $[\mathrm{Metal}^{II}\cdot L\cdot X]^-$, $[\mathrm{Metal}^{II}\cdot L\cdot X{-}H_2]^-$. Formation of these satellite ions may be due, at least in part, to a common dehydrogenation process, reaction (13).

$$[\mathrm{Ion}]^- \longrightarrow [\mathrm{Ion{-}H_2}]^- + \mathrm{H_2} \tag{13}$$

It is probable that the two hydrogen atoms eliminated come from adjacent hydrogen atoms of the ethylene bridge as this would enable the two aromatic systems to become linked into one conjugated network (5). Evidence supportive of reaction (13) was obtained by performing an accelerating voltage (V_{acc}) experiment [24] on an MS-902 double focusing mass spectrometer. Using Co(salen) as a test compound, because of the presence of the monoisotopic Co atom, and methane as the NCI moderating gas, the $[\mathrm{Co}^{I}\cdot L{-}H_2]^-$ ion was focused at V_{acc} = 8 kV then, with the field strengths of the electric (E) and magnetic (B) sectors held constant, V_{acc} was increased. Under these conditions, where only ions which fragment to form $[\mathrm{Co}^{I}\cdot L{-}H_2]^-$ may reach the detector [24], a peak resulting from H_2 loss from $[\mathrm{Co}^{I}\cdot L]^-$ was observed. Thermal dehydrogenation of the Metal(salen) complexes may also contribute to formation of the $[\mathrm{Ion{-}H_2}]^-$ ions as dehydrogenation as represented in reaction (14) has been noted [25] from thermogravimetric studies with similar metal complexes containing an ethylene bridge. Were $(\mathrm{Metal}^{II}\cdot L{-}H_2)$ and similar molecular species to form as the products of thermolysis processes, they would be expected to undergo the same series of reactions as $\mathrm{Metal}^{II}\cdot L$ with electrons, halide ions and halogen radicals to yield a parallel series of product ions.

CAS Registry Numbers: Co(salen), 14167-18-1; Ni(salen), 14167-2-5; Cu(salen), 14167-15-8; Zn-(salen), 14167-22-7.

Acknowledgement

Partial support of this work by the Australian Research Grants Committee is acknowledged.

References

1 G. W. Dillow and I. K. Gregor, *Inorg. Chim. Acta, 86* (1984) L67.
2 G. W. Dillow and I. K. Gregor, *Inorg. Chem., 27* (1988) 2102.
3 G. W. Dillow and I. K. Gregor, *Inorg. Chim. Acta, 150* (1988) 207.
4 G. W. Dillow and I. K. Gregor, *Org. Mass Spectrom., 23* (1988) 777.
5 W. C. Gilbert, L. T. Taylor and J. G. Dillard, *J. Am. Chem. Soc., 95* (1973) 2477.
6 B. J. Millard, *Quantitative Mass Spectrometry*, Heyden, London, 1978, Ch. 2 and 6.
7 I. K. Gregor and M. Guilhaus, *Talanta, 31* (1984) 55.
8 M. Guilhaus, *Ph.D. Thesis*, University of New South Wales, Australia, 1983.
9 I. K. Gregor and M. Guilhaus, *Mass Spectrom. Rev., 3* (1984) 39.
10 E. Baumgartner, T. C. Rhyne and J. G. Dillard, *J. Organomet. Chem., 171* (1979) 387.
11 E. Baumgartner and J. G. Dillard, *Org. Mass Spectrom., 14* (1979) 360.
12 D. F. Hunt and F. W. Crow, *Natl. Bur. Stand. (U.S.) Spec. Publ., 519* (1979) 601.
13 D. F. Rohrbach, W. R. Heineman and E. Deutsch, *Inorg. Chem., 18* (1979) 2536.
14 C. Gosden, K. P. Healy and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, (1978) 972.
15 C. Gosden, J. B. Kerr, D. Pletcher and R. Rosas, *J. Electroanal. Chem., 117* (1981) 101.
16 G. Fachinetti, C. Floriani, P. F. Zanazzi and A. R. Zanzari, *Inorg. Chem., 18* (1979) 3469.
17 M. Calligaris, G. Narden and L. Randaccio, *Coord. Chem. Rev., 7* (1972) 385, and refs. therein.
18 W. B. Jensen, *The Lewis Acid–Base Concepts*, Wiley-Interscience, New York, 1980, Ch. 7.
19 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 4th edn., 1980, Ch. 21.
20 D. R. Dakternieks and D. P. Graddon, *Aust. J. Chem., 26* (1973) 2537.
21 J. E. Bartmess and R. T. McIver, in M. T. Bowers (ed.), *Gas Phase Ion Chemistry*, Vol. 2, Academic Press, New York, 1979.
22 C. N. McEwen, *Mass Spectrom. Rev., 5* (1986) 521.
23 C. N. McEwen and M. A. Rudat, *J. Am. Chem. Soc., 101* (1979) 6470; *103* (1981) 4343.
24 K. R. Jennings, in M. L. Gross (ed.), *High Performance Mass Spectrometry*, American Chemical Society, 1978, p. 3.
25 S. Dilli, A. M. Maitra and E. Patsalides, *J. Chem. Soc., Chem. Commun.*, (1979) 133.