Inorg. Chem. **1995,** *34,* 4117−4122

Comparative Chemical-Ionization and Electron-Ionization Mass Spectra of Salen Complexes with Metals of the First Transition Series[†]

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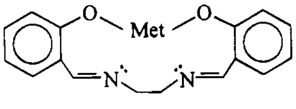
Received October 20, 1994[⊗]

Positive-ion methane chemical-ionization (CI) mass spectra and 70 and 18 eV electron-ionization (EI) mass spectra are obtained for *N,N'*-bis(salicylidene)ethylenediamine, H_2salen, and for Met(salen) where Met = TiO, VO, CrCl, Mn, FeCl, Co, Ni, Cu, and Zn. Comparison of the relative abundances of the ions from the various compounds under these modes of ionization elucidates the gaseous ion chemistry. This is understood by considering the preferred oxidation states of the metals and whether the molecular ion results from electron loss at a metal or a ligand site. For Met = VO, Mn, Co, Ni, and Cu, the complexes ionize at the metal and, except for Cu(salen), undergo little EI fragmentation at 70 eV. For Met = TiO, CrCl, FeCl, and Zn, the complexes ionize at the ligand and undergo more extensive EI fragmentation. Many of the CI and EI processes involve loss or transfer of H_2 from the ethylene bridge of the ligand. Cyclized ionic or neutral fragments account for some of the low-energy processes observed. Conclusions are supported by collision-induced-dissociation mass spectra. Under 70 eV EI, elimination of CuH from $[CuC_8H_7NO]^{\bullet +}$ has been invoked to account for the abundant $[C_8H_6NO]^+$ from Cu(salen), but the latter fragment is now found to be significant also for Mn(salen) and Zn(salen).

Introduction

Mass spectrometry is a familiar analytical technique, but it is also an effective method for investigating the gaseous ion chemistry arising from known molecules. The mass spectrometry of metal chelates, including complexes such as those of diketones, thiodiketones, oximes, carboxylic acids, macrocycles, and Schiff bases, has been reviewed.[1,2] In our earlier study of dimethylglyoxime metal complexes, we compared chemical ionization (CI) and electron ionization (EI) mass spectra and identified some previously unrecognized or misassigned fragments and thermal effects.[3]

Salen, $C_{16}H_{14}N_2O_2$, is the Schiff base form of H_2(salen) or *N,N'*-bis(salicylidene)ethylenediamine. It forms tetradentate chelates with transition metals, which are coordinatively unsaturated, as shown.



Salen derivatives of transition metals have been used in solution as biomimetic catalysts for oxygen atom transfer,[4] as catalysts for enantioselective epoxidations[5] and aziridinations,[6] as catalysts for mediating organic redox reactions,[7] and as mediators for other oxidative processes.[8] These and related compounds also are interesting structurally.[9] Salen and porphyrin ligands are capable of supporting metals in a variety of oxidation states, and oxidation of the metal or of the ligand (such as in porphyrin ferryl complexes[10]) is possible. It is therefore important to understand the fundamental oxidation chemistry of (salen)metal complexes. Previous mass spectrometric studies have reported 70 eV electron-ionization spectra for Met(salen), where Met = 2 H, Co, Ni, and Cu.[11−14] These show abundant molecular ions $[M]^{\bullet +}$,[15] with important fragments $[MetC_8H_7NO]^{\bullet +}$ or $[M - {}^1/_2(\text{salen})]^{\bullet +}$, $[MetC_7H_6O]^{\bullet +}$ by loss of HCN from the preceding ion, and $[C_8H_6NO]^+$ by loss of MetH from $[M - {}^1/_2\ (\text{salen})]^{\bullet +}$ especially when Met = Cu. Fragmentation pathways of metal complexes have been rationalized in terms of the valence-change concept.[13] This considers possible charge transfer between metal and ligand depending on the availability to the metal of various oxidation states, which often are those found in its condensed-phase chemistry.

[†] Presented in part at the 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2−6, 1995.

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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(15) We use the radical ion symbol for metal-containing species to indicate an electron-number parity opposite to that of the original neutral molecule. Thus, for example, if Met has an odd number of electrons, then M is an odd-electron species and $[M]^{\bullet +}$ is even.

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Table 1. Relative Abundances of Ions from Met(salen) as Percent of Total[a] (CH_4 CI)

	Met									
ion	2 H	TiO	VO	CrCl[b]	Mn	FeCl[c]	Co	Ni	Cu	Zn
$[M + C_3H_5]^+$	3 (309)	3 (371)	1 (374)		1 (362)			1 (365)	2 (370)	3 (371)
$[M+C_2H_5]^+$	12 (297)	12 (359)	9 (362)	3 (382)	11 (350)	1 (386)	5 (354)	8 (353)	10 (358)	13 (359)
$[M + H]^+$	73 (269)	74 (331)	68 (334)	11 (354)	59 (322)	12 (358)	65 (326)	70 (325)	66 (330)	73 (331)
$M^{\bullet +}$	7 (268)	7 (330)	23 (333)	11 (353)	17 (321)	6 (357)	27 (325)	20 (324)	21 (329)	10 (330)
$[M - H]^+$	1 (267)	5 (329)		2 (352)	12 (320)		3 (324)		1 (328)	1 (329)
$[MH - HCl]^+$				48 (318)		73 (322)				

[a] Only principal ions are tabulated; isotope peaks are excluded (*m/z* values in parentheses). [b] Also $[MH - Cl]^{\bullet +}$, 25% (*m/z* 319). [c] Also $[MH - HCl - C_3H_3N]^+$, 8% (*m/z* 269).

The present work was undertaken to test and expand upon the earlier conclusions by studying systematically the influence of a wider range of first-row transition metals, oxometals, and chlorometals on the gaseous positive-ion chemistry of their salen complexes. This work gives methane chemical-ionization results and more complete EI results at 70 eV as well as 18 eV for the four previously studied complexes and for those where Met = TiO, VO, CrCl, Mn, FeCl, and Zn, which have not been reported previously. CI typically shows low-energy processes arising from the protonated molecule or from molecular adducts with the methane-plasma ions, but it may also show the molecular ion by charge transfer and hydride abstraction from the original molecule. Low-energy EI enhances the relative abundances of the molecular ion and of its low-energy fragmentations, which may involve rearrangements. Collision-induced-dissociation (CID) mass spectra for some of the ions resulting from EI of the Ni and Cu complexes are used to further elucidate their behavior.

Experimental Section

The (salen)metal complexes were prepared according to literature procedures.[16] EI and CI data were obtained using a Finnigan 1020B quadrupole mass spectrometer. This instrument, its operation, and the methods of data reduction, identification of sample vs impurity peaks, and isotope-ratio confirmation are described elsewhere.[17]

Acetonitrile solutions of each of the solid samples, except the Zn complex, were made. Zn(salen) was dissolved in methanol, in which its solubility is higher. To decrease the risk of oxidation, solutions of the Mn and Co complexes were made under N_2 in a glovebag. Samples of solutions containing several micrograms of complex were gently evaporated in Pyrex tubes; these were introduced into the mass spectrometer, evacuated, and heated at 2 °C/s while full spectra were scanned every 2 s.

CID data were obtained using a Finnigan TSQ 45 triple-quadrupole mass spectrometer. The first quadrupole selected the ion to be studied, which was activated by collision with argon gas in the second quadrupole. Cited collision energies refer to the laboratory frame. The third quadrupole, operating at 2 s per scan, subsequently mass-analyzed the product ions.

Results

For most complexes the maximum total ion count occurred between 330 and 375 °C, with the oxo complexes at the higher end of this range. For ClCr(salen) and Zn(salen) this temperature was significantly higher, and for H_2(salen) it was lower. For Co(salen) and Zn(salen) the ion-count-versus-temperature peaks were unusually broad (>50 °C), implying that these complexes do not have sharp sublimation points. A spectrum of ClV(salen) was sought unsuccessfully, although a weak but recognizable $[M]^{\bullet +}$ peak was found at 70 eV. Similarly Cl_2V(salen), which evidently does not sublime intact, gave neither a characteristic spectrum nor a molecular ion. The spectra resulting from both of these complexes, however, are essentially that of OV(salen). The latter may be formed by reaction of the chlorovanadium complexes with residual water or oxygen. The spectra of Cu(salen) and Zn(salen) showed interference from H_2(salen) under CI but not EI, suggesting that H_2(salen) is produced in a nonionic, possibly heterogeneous, thermal reaction between these complexes and methane. A negative-ion methane CI study of Co(II) complexes including Co(salen) showed evidence of thermal oxidative addition of alkyl radicals from the methane plasma to the complexes, but this was a minor process for Co(salen),[18] and such reactions do not seem to affect the present results. Contributions from thermal reactions in the ion source or from other impurities are excluded from the reported spectra. Because, even for pure substances, mass spectra may be temperature-dependent, comparisons of ion abundances among spectra of different compounds are not strictly quantitative. A 25 eV CID spectrum of the molecular ion of Cu(salen) is similar to the EI spectrum and confirms the origins of the EI fragments.

The CI results are given in Table 1, and the EI results in Table 2. Some examples of graphical spectra are shown as obtained at 70 eV for Met = TiO, CrCl, and Zn in Figures 1–3, respectively. In some cases low ion counts prevented acquisition of reliable CID data, but qualitatively significant CID results are considered in the Discussion. Relative EI and CI *ion* abundances (not spectral peak intensities) are listed in the tables as percent of total for the principal ions after removing recognizable contributions from impurities. Abundances were obtained by correcting for the isotopologs of chemically different species which contribute to the same mass peak. These corrections are significant for ions containing a polyisotopic metal or chlorine, as well as ^{13}C for the heavier ions. Those ions whose relative abundances are greater at 18 eV than at 70 eV are suggestive of low-energy processes and are noted in Table 2.

Chemical assignments for the ions are based on the known

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Table 2: Relative Abundances of Ions from Met(salen) as Percent of Total[a] (EI at 70 eV)

ion	Met TiO[b]	VO	Cr[c]	Mn[d]	FeCl	Fe[e]	Co[f]	Ni	Cu	Zn
$M^{\bullet+}$	10^g (330)	27^g (333)	17^g (318)	16^g (321)	12^g (357)	8^g (322)	20^g (325)	18^g (324)	10^g (329)	12^g (330)
M^{2+}	6 (165)	3 (166.5)	6 (159)	*h* (160.5)		4 (161)	6 (162.5)	4 (162)	3 (164.5)	2 (165)
$[M - H]^+$	7 (329)			2 (320)		5^g (321)				
$[M - H_2O]^+$	9^g (312)	4 (315)								
$[M - C_2H_4]^{\bullet+}$ or $[M - H_2CN]^+$				2 (293)			2 (297)			3 (302)
$[MetC_8H_7NO]^{\bullet+}$					6 (224)		2 (192)	12 (191)	12^g (196)	
$[MetC_7H_7NO]^{\bullet+}$	3 (185)	2 (188)	2 (173)				4 (180)	2 (179)		
$[MetC_7H_6NO]^+$	2 (184)	3 (187)	5 (172)	3 (175)		2 (176)	4 (179)			3 (184)
$[MetC_7H_5NO]^{\bullet+}$	2 (183)	3 (186)	3 (171)	2 (174)		2 (175)	3 (178)	4 (177)	2 (182)	
$[MetC_7H_4NO]^+$	4 (182)	3 (185)	3 (170)	3 (173)		3 (174)	3 (177)			
$[MetC_7H_6O]^{\bullet+}$		4 (173)	5 (158)	3^g (161)	3 (197)		7 (165)	11 (164)	3 (169)	
$[MetC_7H_5O]^+$		2 (172)	2 (157)	3 (160)		*i* (161)				
$[MetC_6H_5O]^+$	5 (157)	2 (160)	3 (145)							
$[MetC_6H_4O]^{\bullet+}$	3 (156)	3 (159)	5 (144)	3 (147)		2 (148)	2 (151)	2 (150)		
$[MetH]^+$	2 (65)	2 (68)		2 (56)			2 (60)			2 (65)
$[Met]^{\bullet+}$	24 (64)	23 (67)	31 (52)	10 (55)	5 (91)	8 (56)	18 (59)	20 (58)	18 (63)	2 (64)
$[C_9H_8NO]^+$ (146)				2				*g*	2	2
$[C_8H_7NO]^{\bullet+}$ (133)				6		2				11
$[C_8H_6NO]^+$ (132)				7		3		4	23	8
$[C_7H_7N]^{\bullet+}$ (105)				3		2				5
$[C_7H_7]^+$ (91)	2			2					2	3
$[C_6H_6]^{\bullet+}$ (78)				3		2			2	5
$[C_6H_5]^+$ (77)	2	2		4		4	2	2	4	4
$[C_4H_3]^+$ (51)	2	4	2	2		4	2	2	2	4
$[C_3H_3]^+$ (39)	2			2		3	2		2	3

[a] See footnote *a*, Table 1. Abundances <2% are not shown. [b] Also $[M - O]^{\bullet+}$ at 2% (*m/z* 314)[g] and $[TiO_2H]^+$ at 2% (*m/z* 81). [c] From ClCr(salen). Also $[ClCr\,(salen)]^{\bullet+}$ at 3% (*m/z* 353)[g] and $[ClCr\,(salen) - H_2Cl]^{\bullet+}$ or $[M - H_2]^{\bullet+}$ at 3% (*m/z* 316).[g] [d] Also $[C_8H_8NO]^+$ at 3% (*m/z* 134). [e] From ClFe (salen). Also $[FeC_8H_6NO]^+$ at 3% (*m/z* 188). [f] Also $[CoC_6H_5]^+$ at 4% (*m/z* 136). [g] These relative abundances are greater at 18 eV than at 70 eV. [h] See $[MetC_7H_6O]^+$. [i] Not distinguished from M^{2+}.

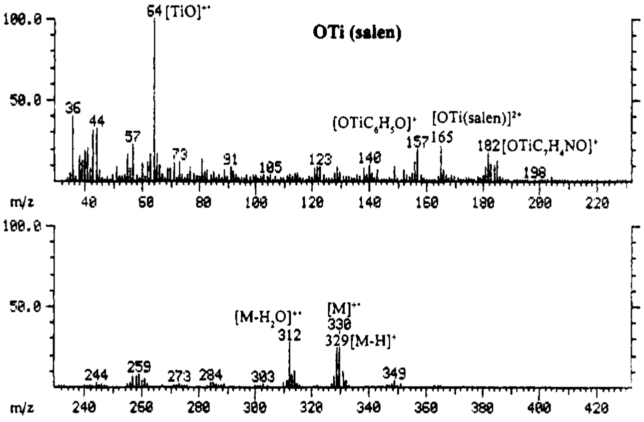


Figure 1. Mass spectrum of OTi(salen) at 70 eV EI.

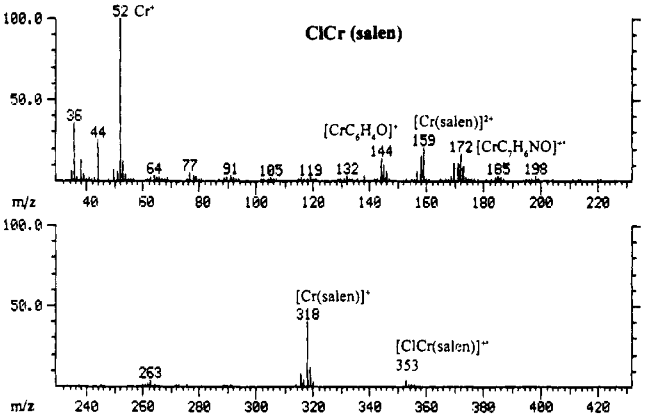


Figure 2. Mass spectrum of ClCr(salen) at 70 eV EI.

structures of the complexes and on agreement of observed and calculated natural isotopolog abundances.[3] The *m/z* values refer to the principal isotopolog. Some of these assignments have been given in the literature. Lacey *et al.*[13] include EI data for H_2(salen) and Cu(salen) with deuterium labeling at the four ethylene-bridge positions. For Cu(salen) they propose an interesting elimination of neutral CuH (or CuD from the labeled complex) to explain the strong peak at *m/z* 132 (or 133), which we confirm as stronger for the Cu complex than for any other considered here. A few assignments are tentative as indicated. Fragment-ion types that are significant for only one complex are noted but are not included in the bodies of the tables.

Under EI, ClCr(salen) gives a weak molecular ion, but for comparison in Table 2 its fragments are listed under Met = Cr, rather than Met = CrCl, since there are no identifiable fragment ions containing Cl. On the other hand, fragments of ClFe(salen)

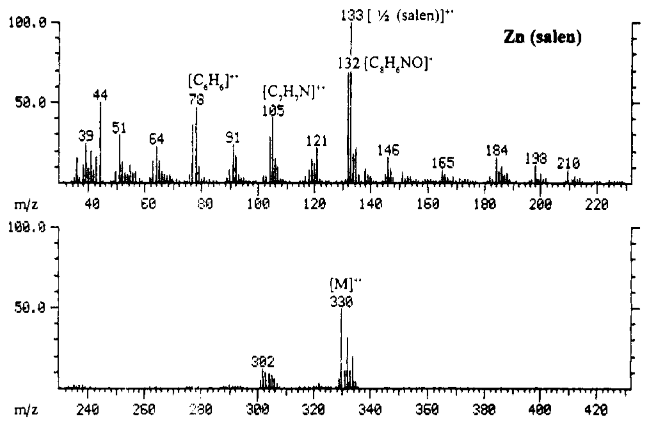


Figure 3. Mass spectrum of Zn(salen) at 70 eV EI.

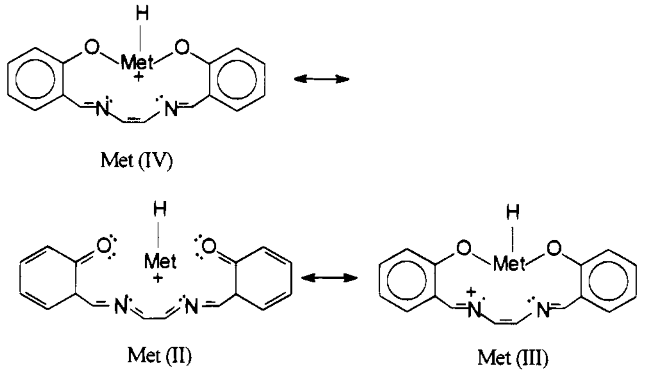
are listed under both Met = FeCl and Fe since it gives some ions retaining Fe with Cl and others retaining Fe without Cl. Only the two oxo complexes show loss of O atom or of H_2O, while their other fragments evidently involve retention of the oxo ligand.

Discussion

Chemical Ionization. If protonation by the methane plasma occurred at the metal atom in these complexes, the metal would undergo a formal two-electron oxidation, which would result in unusual oxidation states for most metals here. The most basic site in these complexes seems more likely to be on the salen group. All complexes and H_2(salen) give similar relative abundances of $[M + H]^+$, except for the two chloro complexes where this abundance is much lower because of facile loss of HCl or Cl$^\bullet$ by the protonated molecule. Loss of HCl from $[M + H]^+$ maintains the original oxidation states (+3) of the metals of ClCr(salen) and ClFe(salen), and loss of Cl$^\bullet$ occurs from $[M + H]^+$ of ClCr(salen) to give reduction to Cr(II). The chloro complexes also show uncommonly low $[M + C_2H_5]^+$, apparently because loss of chloroethane or of ethylene and HCl from this adduct ion gives also the stable $[\mathrm{Cr(salen)}]^{\bullet+}$ and $[\mathrm{Fe(salen)}]^{\bullet+}$ containing Cr(III) and Fe(III), respectively.

The molecular ion, $[M]^{\bullet+}$, is considered to form primarily by charge exchange with the methane plasma, although there may be small contributions directly from EI under imperfect CI conditions. This ion's relative abundance is greatest for complexes of VO, Mn, Co, Ni, and Cu. These correspond respectively to V(V) and metal(III) for the others if the electron is lost from the metal. This is to be expected if these complexes have lower ionization energies than H_2(salen). In fact the values reported for the salen complexes of Mn, Co, Ni, and Cu are all within 0.4 eV of each other, and their average is about 0.9 eV lower than that of H_2(salen).[12] The complexes of TiO and Zn, respectively d^0 and d^{10}, show $[M]^{\bullet+}$ abundances close to that of H_2(salen). Their ionization energies would be correspondingly larger if electron loss is from the salen ligand, because loss from the metal site is disfavored. The oxo ligand should make ionization at the metal difficult, but the accessible V(V) state and the impossible Ti(V) state explain why OV(salen) produces much more abundant $[M]^{\bullet+}$ than OTi(salen) does. For Zn(salen) the low abundance of $[M]^{\bullet+}$ is consistent with electron loss from the salen ligand because of the unfavorability of formation of Zn(III). Also, $[M]^{\bullet+}$ is not highly abundant for ClCr(salen) or ClFe(salen). In these cases, loss of Cl$^\bullet$ is observed in the EI spectra, although the molecular ions are in greater relative abundance at low energy. Even at 70 eV, however, the molecular ion gives the base peak for ClFe(salen). This argues that this different fragmentation (Cl atom loss) of the molecular ions is not primarily responsible for their low abundance in the CI spectra, and a mechanism involving ionization of the ligand also operates in the chlorometal complexes.

The ion $[M - H]^+$ forms from M by hydride abstraction. This ion is strongest for Mn(salen), from which the common Mn(IV) state would be formed if the metal is ultimately oxidized. We suggest a hydride loss from the ethylene bridge with a second hydride transferred to the metal.[19] This would give a completely conjugated ligand[20] and a possible increase of +2 in oxidation number for Met, which is most reasonable for Met = Mn. Alternatively, with charge still localized at the metal, the +2 oxidation state with a structure showing dative Met−O bonding could be formulated, whereas the metal would have the +3 oxidation state if the charge and the radical site were positioned on the salen ligand, as promoted by the now unsaturated bridge. These possibilities are illustrated below. Such delocalization would be favorable for Mn, which supports all three oxidation states shown.



Extending the mechanism for the Mn complex to OTi(salen), which also shows significant hydride abstraction, could involve a hydride transfer to the oxo ligand rather than to the metal. The resulting hydroxo complex with charge on the metal would restore the favored Ti(IV) state.

The CI fragments involving loss of HCl or Cl$^\bullet$ from the chloro complexes have already been considered. ClFe(salen) also shows an ion corresponding to loss of HCl and C_3H_3N, likely acrylonitrile, from the protonated molecule. This ion may be (phenolato)(salicylideneaminato)iron(III).

Minor untabulated fragments (1−2% each) from H_2(salen) include *m/z* 148 $[C_9H_{10}NO]^+$ by protonation at a nitrogen with heterolysis of the adjacent C−N single bond. A similar protonation with homolysis and hydrogen migration would give *m/z* 147 $[C_9H_9NO]^{\bullet+}$. The half-molecular ion $[C_8H_8NO]^+$ at *m/z* 134 would form by protonation at nitrogen with α-heterolysis of the central C−C bond to yield the charge-delocalized ion and a resonance-stabilized neutral ylide[21] (eq 1) or, with hydrogen migration and cyclization, dihydro-1,3-benzoxazine. Hydrogen migration or incorporation of the new proton into the ion must accompany formation of *m/z* 107 $[C_7H_7O]^+$ and *m/z* 91 $[C_7H_7]^+$, possibly hydroxytropylium and tropylium ions, respectively. The former corresponds to elimination of HCN by the ion at *m/z* 134. Similar results are reported in a recent

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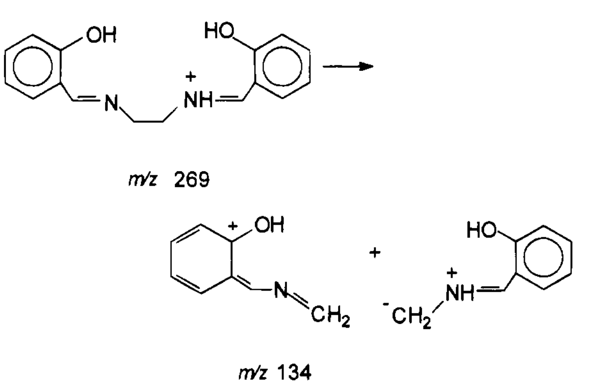
(19) In a series of tricyclic amines, we have found enhanced hydride abstractions and hydride shifts under methane CI when such an ethylene bridge is present: Schildcrout, S. M.; Geidner, R. M. *Org. Mass Spectrom.* **1989**, *24*, 241.

(20) (a) Thermal dehydrogenation at a saturated two-carbon bridge has been noted for Schiff-base metal complexes: Dilli, S.; Maitra, A. M.; Patsalides, E. *Inorg. Chem.* **1982**, *21*, 2832. (b) A negative-ion CI study of some Met(salen) complexes also reports evidence for such a dehydrogenation: Dillow, G. W.; Gregor, I. K. *Inorg. Chim. Acta* **1989**, *155*, 221.

(21) An analogous process in 1,2-dicarbazolylethane gives the principal ion in its methane CI spectrum.[17]



(1)

study of some ring-substituted derivatives of H_2(salen), where cleavages at the diimine chain dominate the fragmentation of the protonated molecules produced by fast-atom bombardment.[22]

Electron Ionization. We shall consider the principal ion types where relative abundances show significant dependence on the metal. Relative abundances of $[M]^{\bullet+}$ at 70 eV (Table 2) are largest for Met = VO, Mn, Co, and Ni. All these complexes, as well as that of Cu, also show highest abundances for $[M]^{\bullet+}$ under CI, which is attributed to their ionization at the metal site rather than the ligand, as already discussed. The abundance of $[M]^{\bullet+}$ under EI depends on the availability of facile fragmentation pathways. This implies that those complexes that ionize at the metal site tend to undergo EI fragmentation less extensively than those that ionize at the ligand. The anomalously low EI abundance of $[M]^{\bullet+}$ for Cu(salen) is a result of the high abundance of its fragment at m/z 132, whose origin is considered below.

The detection of the doubly charged molecular ions $[M]^{2+}$ reflects the high stability of the molecular structure of these chelates. These abundances are only estimates since the present instrument operates at unit resolution and shows abundances of ions with half-integral m/z values at either or both of the neighboring integral values. Because Mn is monoisotopic, the abundance of $[Mn(salen)]^{2+}$ at m/z 160.5 is not distinguishable from that of $[MnC_7H_6O]^{\bullet+}$ at m/z 161.

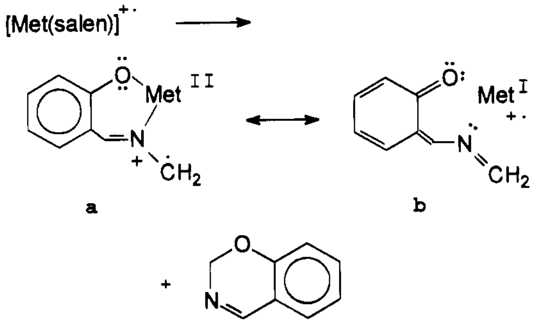
Hydrogen atom loss in EI gives the same product ion as hydride abstraction in CI. Both processes are most significant for OTi(salen) and Mn(salen). The rationale for this being so has been discussed for the CI process and applies as well to EI. What is listed in Table 2 as $[M - H]^+$ from Fe(salen) is in fact HCl loss from ClFe(salen). The analogous process is observed for ClCr(salen), but with very low abundance. In both of these cases, the ion becomes relatively stronger at 18 eV than at 70 eV, indicating a low-energy process. We hypothesize, by analogy with the CI hydride-loss mechanism, one hydrogen atom from the saturated bridge incorporating into the eliminated HCl and the other transferring as hydride to the metal.

Dehydrogenation, evidently at the ethylene bridge, gives $[M - H_2]^{\bullet+}$, detected with very low abundances at 70 eV from Met = TiO, Mn, and Co. Results at 18 eV show this to be a low-energy process at least for Met = TiO and Co. An analogous low-energy ion from ClCr(salen) at m/z 316 has 3% abundance at 70 eV but corresponds to loss of $Cl^\bullet$ and H_2.

Only the two oxo complexes show loss of H_2O, and at least for OTi(salen), this is a low-energy process as shown by the 18 eV results and as might be expected from the stability of the eliminated molecule. It evidently involves the oxo oxygen, and the salen ligand becomes completely conjugated if, again, both hydrogen atoms come from the saturated bridge carbons.[23] The charge on the resulting ion may reside on a Ti(III) or V(III) site, although the dehydrogenation also should make the salen ligand more capable of bearing a delocalized charge. The fragment $[M - O]^{\bullet+}$ is significant only for OTi(salen), for which it occurs at m/z 314 with 2% abundance at 70 eV, increasing at 18 eV. Loss of the oxo ligand here would also result in Ti(III), as with H_2O elimination.

Loss of 28 mass units has been attributed to elimination of C_2H_4 from the ethylene bridge, with the nitrogen atoms bonding to the metal, for Met = Co and Ni,[12] but this implies unlikely metal(V) states. The ion is now observed for Met = Mn, Co, and Zn (Table 2) and with very low abundances for Met = TiO, Cr, Fe, and Ni. We suggest that it may result from elimination of ethylene, or the elements of C_2H_4Cl from the chloro complexes, to give metal(III) with charge on the metal or to give metal(II) with charge and radical sites delocalized on the ligand, if a new N−N bond forms to make a highly conjugated ligand with possible dative bonding of the nitrogen atoms to the metal. The latter is especially likely for Met = Zn and Met = TiO, giving Ti(IV). $[M - 28]^+$ may alternatively arise from loss of the elements of $H_2CN^\bullet$ or of HCl + HCN from the chloro complexes.

The fragment $[MetC_8H_7NO]^{\bullet+}$ results from homolytic cleavage of the ethylene bridge of the molecular ion with elimination of C_8H_7NO or $^1/_2$(salen). It is most abundant for Met = Ni and Cu and moderately so for Met = FeCl. The 18 eV results for Cu(salen) show the process to be a low-energy one, so cyclized 2*H*-1,3-benzoxazine seems the most reasonable structure for the eliminated molecule (eq 2). The proposed[12,13] ion structure **a** permits delocalization of the radical site over the ligand, but it places the charge on the N atom so the metal keeps the oxidation state it had in the original (unionized) molecule. We suggest a significant contribution from the resonance structure **b**, where dative bonding obviates a ligand radical site and places the charge more reasonably on the metal, giving the respective states Ni(I), Cu(I), and ClFe^{II} for these most abundant cases. The ion has also been taken as a parent of the fragments $[MetC_7H_6O]^{\bullet+}$, with elimination of HCN,[11,12] in sibling rivalry with $[C_8H_6NO]^+$ at m/z 132, with elimination of MetH.[13] This is now supported by CID of $[MetC_8H_7NO]^{\bullet+}$ at 30 eV for Met = Ni and Cu, where HCN loss is important for Met = Ni, but MetH loss is the dominant process for both Met = Ni and Cu. In both cases, $Met^{\bullet+}$ is also an abundant fragment, which would be accompanied by another C_8H_7NO molecule.



(2)

A related fragment $[FeC_8H_6NO]^+$ shows no detectable analog for other Met. Originating from ClFe(salen), it corresponds to elimination of HCl + $^1/_2$ (salen). An ion related to cyano(2-methylphenolato)iron(III), but with a hydrogen removed from

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[22] Catinella, S.; Traldi, P.; Guerriero, P.; Tamburini, S.; Vigato, P. A. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 111.

[23] This is supported by 70 eV EI results for the VO complex of *N,N'*-bis(salicylidene)-1,1-dimethylethylenediamine, which cannot undergo 1,2-dehydrogenation at the saturated bridge and shows very little H_2O loss: Patel, K. S.; Bailar, J. C., Jr. *J. Coord. Chem.* **1973**, *3*, 113.

the methyl group, would give Fe(II) with the charge delocalized over the hydrocarbon ring system.

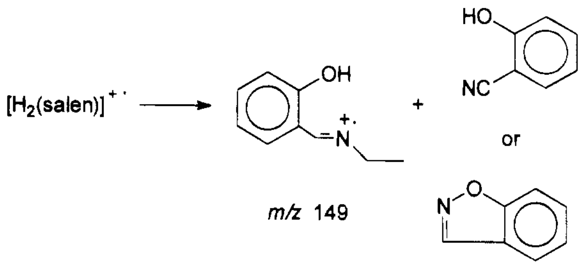
All of the complexes except those of Met = TiO and Zn show significant abundances of $[MetC_7H_6O]^{\bullet+}$. The greatest relative abundance occurs for Met = Ni. This is consistent with the just-mentioned ease of formation of its precursor ion for Met = Ni and Cu and the competing elimination of MetH, which is most favored for Met = Cu. The structure of the fragment resulting from HCN elimination has been proposed[11,12] to have a tropone ligand bonded to the metal ion. Such a structure permits delocalization of both the charge and radical sites over the ring as well as the metal, so the oxidation number of the metal is +1 or +2.

Loss of the elements of salen, evidently as two $^1/_2$(salen) molecules, to give $[Met]^{\bullet+}$ is observed at 70 eV for all complexes, although for ClCr(salen) this very abundant ion is $Cr^{\bullet+}$, corresponding to loss of HCl and $[salen - H]^{\bullet}$. This neutral radical should be especially stable if it involves dehydrogenation at the ethylene bridge with one hydrogen transferred to the Cl and the other to an O atom. Thus the radical site would be delocalized over both conjugated ring systems. An analogous process occurs to a lesser extent with ClFe(salen) to give $Fe^{\bullet+}$, and loss of salen leaves $[ClFe^{II}]^+$. The oxo complexes show abundant $[OTi^{III}]^{\bullet+}$ and $[OV^{III}]^{\bullet+}$. The relative abundance of $[Met]^{\bullet+}$ is exceptionally low for Zn(salen), for which, as already discussed, the charge seems to reside on the ligand rather the metal in the molecular ion. That it tends to remain on the ligand during fragmentation is evidenced by this low abundance of $Zn^{\bullet+}$ and the high abundances of the nonmetallic ions from Zn(salen) considered below.

The fragment $[C_8H_6NO]^+$ at *m/z* 132 in the spectrum of Cu(salen) was considered to arise by loss of CuH from $[CuC_8H_7NO]^{\bullet+}$. Labeling experiments showed the fragment ion retaining only one of the four ethylenic hydrogens, and it was taken to have an aromatic 1,3-benzoxazine structure.[13] Although this process was rationalized also by the favorable Cu(I) state in CuH, we now see also, with somewhat lower relative abundances, *m/z* 132 from other complexes, notably for Met = Mn and Zn. The mechanism may be analogous to that suggested for Met = Cu, but we find the presumed precursor $[MetC_8H_7NO]^{\bullet+}$ only at very low abundances for Met = Mn and Zn. For these cases, then, we suggest that *m/z* 132 may be accompanied by a single neutral $MetC_8H_8NO$. This must involve hydrogen migration and include either an organic radical site or a Met(I) or Met(III) state, the former more likely for Met = Zn and the latter for Mn.

Excepting *m/z* 132, among the other organic fragment ions from Met(salen), the abundance of each is at least as great for Met = Zn as for any other Met. Thus $[C_8H_7NO]^{\bullet+}$ or $[^1/_2(salen)]^{\bullet+}$ at *m/z* 133 is most abundant for Met = Zn, somewhat less so for Met = Mn, and weak or undetectable for all other cases. This ion is complementary to $[MetC_8H_7NO]^{\bullet+}$ already discussed, and the two ion types show nearly complementary abundances for the various Met. The already noted reluctance of the Zn atom to bear the charge accounts for the preferred elimination of the organic fragment ion when Met = Zn.

Several 70 eV EI studies of H_2(salen) have been reported.[11,13,14] Each of the CI fragments already discussed is observed also in EI. In agreement with the earlier work, we find the principal fragment at *m/z* 107. We also find that at 18 eV the relative abundances increase for the ions at *m/z* 149, 148, and 147, as well as for the molecular ion, suggesting low-energy paths for these fragmentations. At *m/z* 149, $[C_9H_{11}NO]^{\bullet+}$ would arise from C−N cleavage at the saturated bridge with hydrogen migration to the nascent ion and elimination of neutral C_7H_5NO, 2-hydroxybenzonitrile, or the bicyclic indoxazine (eq 3). Similar processes giving ions with a 2-methyl-1,3-benzoxazine ring system and neutrals with the indoxazine skeleton account for the fragments at *m/z* 148 and 147. The series of fragments at *m/z* 122, 121, and 120, which are not seen in CI, would then arise from complementary processes with charge retention by the indoxazine-type fragment accompanied by a neutral with the methylbenzoxazine skeleton. Fragment ions apparently analogous to those discussed here are reported in the EI spectrum of a ring-substituted derivative of H_2(salen), and although they were not hypothesized,[24] it seems that analogous bicyclic structures may pertain also to fragments of such compounds.



(3)

Conclusions

For the Met(salen) complexes studied, the relative-abundance trends among the positive ions from methane CI and those from high- and low-energy EI are rationalized in accord with two simplifying concepts. One is that the metal atom either acquires or retains a favorable oxidation state, often one expected from its condensed-phase chemistry. The other is that there is a localized charge in the molecular ion, produced by electron loss from either a metal or a ligand site. For Met = VO, Mn, Co, Ni, and Cu, the complexes ionize from the metallic site and, except for Cu(salen), undergo little EI fragmentation at 70 eV. For Met = TiO, CrCl, FeCl, and Zn, the complexes ionize from a ligand site and undergo more extensive EI fragmentation. CI processes include charge transfer and hydride abstraction as well as fragmentation of the plasma-ion adducts. Common to many of the CI and EI processes is loss or transfer of two hydrogen atoms from the saturated bridge of the ligand, producing conjugation between the aromatic rings.

The rationalization of ion chemistry from mass spectra should consider likely structures of the neutral fragments as well as the ions. We suggest some alternative mechanisms and structures, including cyclized structures, to explain the present results. The extensive fragmentation of Cu(salen) under 70 eV EI is due to the facile formation of $[C_8H_6NO]^+$, thought to involve elimination of CuH from $[CuC_8H_7NO]^{\bullet+}$, but the resulting ion is now seen to be significant also for Met = Mn and Zn with a different mechanism likely.

Acknowledgment. Support from the Ohio Board of Regents under the Research Challenge Program and from the CSU College of Graduate Studies and the YSU School of Graduate Studies is gratefully acknowledged. S.S. thanks the Government of India for a scholarship. The authors also thank NASA (Grant NCC 3-63) for the TSQ 45 and B. Winnick and D. Vrobel for technical assistance.

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(24) Guerriero, P.; Tamburini, S.; Vigato, P. A.; Seraglia, R.; Traldi, P. *Org. Mass Spectrom.* **1992**, *27*, 231.