limited, and if it depends only on the energy difference[13,40,48] between donor and acceptor.[38] Both the relative constancy of $k_{q,X}$ and the relatively small magnitude of these constants argue that the magnitude of the gap between the energies of donor and acceptor states is not the sole nor always the most important factor determining the rate of triplet-to-triplet energy transfer.

The rates of $Ru(bipy)_3^{2+}$ sensitized excitation of CTTM states in $Co(HEDTA)X^-$ complexes vary by about 10^2 as the ligand X is changed from Br to O_2CR (*i.e.*, for $Co(EDTA)^-$); the variation is about tenfold on changing X from Br to Cl. This sensitivity of $k_{q,Co}$ to X is about the magnitude expected if the CTTM triplet acceptor states vary in their energies in about the same way as do the CTTM spectroscopic ($X^- \rightarrow Co(III)$; see section A above) states through the series of four compounds. Yet in each instance, the products of sensitized CTTM excitation correspond to oxidation of carboxylate ligands, not X^-. The sensitivity to X of $k_{q,Co}$ for a process yielding carboxylate oxidation can be reconciled if the electronic manifolds for the $X^- \rightarrow Co(III)$ and the $RCO_2^- \rightarrow Co(III)$ CTTM triplet states are strongly interacting and, in a limiting case, if the latter state has a lower dissociation energy than the former as illustrated in Figure 4.

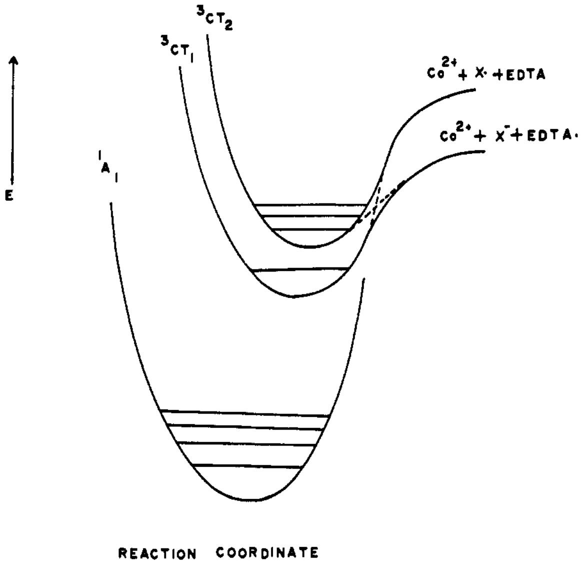

Figure 4. Hypothetical potential energy surfaces for CTTM excited states of triplet spin multiplicity. Charge transfer to metal triplet excited states correspond to $X^- \rightarrow Co^{III}(^3CT_1)$ and $RCO_2^- \rightarrow Co^{III}(^3CT_2)$.

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[48] D. A. Buckingham and A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 6.

Mass Spectrometric Study of Polydentate Schiff Base Coordination Compounds. I. Cobalt(II), Nickel(II), and Copper(II) Complexes of Salen[1] and Oaben[2]

William C. Gilbert, Larry T. Taylor, and John G. Dillard*

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.

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Abstract: Positive and negative ion mass spectra have been measured for the cobalt(II), nickel(II), and copper(II) neutral complexes with Salen and Oaben. Parent ion clusters are detected in both the positive and negative ion mass spectra. Polymeric positive ions containing two metal ions and a single ligand are detected in low abundance for all compounds. Ionization potentials of the compounds have been measured. Fragmentation patterns for the metal-containing ions are presented and discussed. The fragmentation patterns suggested are supported by metastable transitions.

Metal coordination compounds play an important role in biological energy transfer systems.[3] Schiff base metal complexes may show some utility as model compounds for describing energy transfer for certain of these biological molecules. Ionization data and appearance potential information may be of importance to an understanding of the energy levels in these complexes and the application of theoretical models to describe the levels. A systematic study of neutral coordination compounds of polydentate Schiff base ligands with the first-row transition metals has been initiated.

The mass spectra of metal chelates including β-diketones as ligands have been investigated.[4-12] In

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[1] Salen = bis(salicylidene)ethylenediamine.

[2] Oaben = bis(*o*-aminobenzylidene)ethylenediamine.

[3] "Bioinorganic Chemistry," *Advan. Chem. Ser.*, No. **100** (1972).

[4] C. G. MacDonald and J. S. Shannon, *Aust. J. Chem.*, **19**, 1545 (1966).

[5] C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967).

[6] G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, **7**, 870 (1968).

[7] G. M. Bancroft, C. Reichert, J. B. Westmore, and H. D. Gesser, *ibid.*, **8**, 474 (1969).

[8] H. F. Holtzclaw, R. L. Lintvedt, H. E. Baumgarten, R. G. Parker, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **91**, 3774 (1969).

[9] P. Haake and S. H. Mastin, *ibid.*, **93**, 6823 (1971).

[10] L. E. Warren, M. M. Bursey, and W. E. Hatfield, *Org. Mass Spectrom.*, **5**, 15 (1971).

[11] E. P. Dudek and M. Barber, *Inorg. Chem.*, **5**, 375 (1966).

[12] E. P. Dudek and G. O. Dudek, *Inorg. Nucl. Chem. Lett.*, **2**, 53 (1966).

Table I. Mass Spectra of Schiff Base–Metal Complexes (70 eV)

		M(Salen)								M(Oaben)					
		Co		Ni		Cu				Co		Ni		Cu	
	A	RA	*m/e*	RA	*m/e*	RA	*m/e*		B	RA	*m/e*	RA	*m/e*	RA	*m/e*
a	$M(C_{16}H_{14}N_2O_2)^+$	100	325	100	324	100	329	l	$M(C_{16}H_{16}N_4)^+$	100	323	100	322	100	327
b	$M(C_{14}H_{10}N_2O_2)^+$	10.1	297	1.3	296	1.7[a]	300	m	$M(C_{14}H_{12}N_4)^+$	1.0	295	~0.5	294	2.3[a]	298
c	$M(C_9H_9N_2O)^+$			0.1	219	6.4[a]	223	n	$M(C_9H_{10}N_3)^+$	0.2	219	<0.5	218	2.3[a]	222
d	$M(C_9H_9NO)^+$	2.1	206	1.9	205	8.0	210	o	$M(C_9H_{10}N_2)^+$	1.6	205	2.0	204	7.3	209
e	$M(C_8H_7NO)^+$	5.1	192	26.6	191	53.2	196	p	$M(C_8H_8N_2)^+$	2.3	191	7.3	190	2.8	195
f	$M(C_7H_7NO)^+$	13.0	180	4.6	179	10.1	184	q	$M(C_8H_6N_2)^+$	3.6	189	4.1	188	3.6	193
g	$M(C_7H_5NO)^+$	8.3	178	6.7	177	7.8	182	r	$M(C_7H_6N_2)^+$	14.1	177	15.7	176	[b]	[b]
h	$M(C_7H_6O)^+$	17.3	165	18.3	164	18.4	169	s	$M(C_7H_7N)^+$	11.4	164	6.9	163	2.1	168
i	M^+	17.7	59	11.3	58	11.9	63	t	M^+	7.9	59	9.5	58	19.3	63
j	$M(C_{16}H_{14}N_2O_2)^{2+}$	13.3	162.5	12.0	162	8.5	164.5	u	$M(C_{16}H_{16}N_4)^{2+}$	9.6	161.5	11.0	161.0	5.8	163.5
k	$M_2(C_{16}H_{14}N_2O_2)^+$	1.1	384	1.3	382	1.7	392	v	$M_2(C_{16}H_{16}N_4)^+$	0.07	382	0.6	380	0.08	390

[a] Contains one less hydrogen than fragment listed. [b] Fragment masked by other fragments.

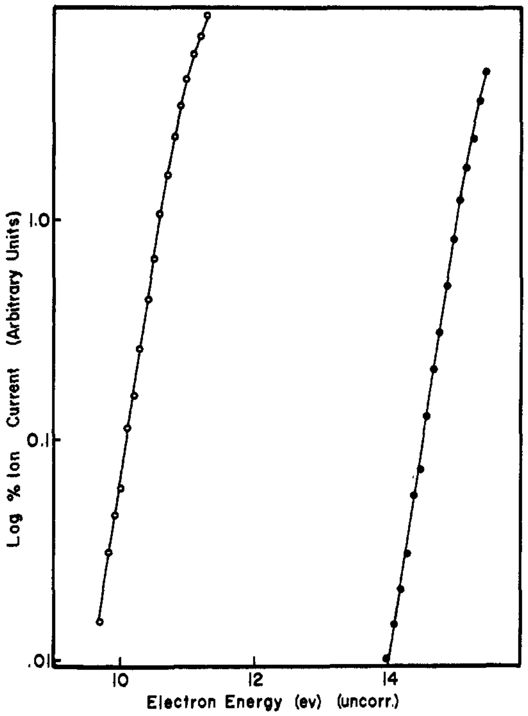

Figure 1. Semilog ionization efficiency curves for Ni(Salen)$^+$ (○) and Xe$^+$ (●) *vs.* uncorrected electron energy.

some instances[5–8,13–15] ionization potentials have been measured. Mass spectra of Schiff base complexes have not been extensively explored. In cases where mass spectra have been cited,[16–19] it has been primarily to assign molecular weights to species in the gas phase and to examine the fragmentation patterns for use in structure elucidations. Fragmentation patterns were recently postulated for bis(benzoylisopropylidene)-ethylenediamine[18] and *N*,*N*-bis(salicylidene)-1,1-(dimethyl)ethylenediamine and their metal chelates along with *N*,*N*-bis(salicylidene)ethylenediamine (Salen) and its nickel(II) complex.[20] In none of these cases was any energetic measurement reported. In this paper the results of an investigation of the positive and negative ion mass spectra and measurements of the ionization potentials of the neutral complexes of nickel(II), cobalt(II), and copper(II) with Salen[1] and Oaben[2] are reported.

Experimental Section

Mass spectra and ionization potentials for positive ions and resonance capture appearance potentials for negative ions were obtained using an Hitachi Perkin-Elmer RMU-7 mass spectrometer described earlier.[21] Data acquisition for the energetic measurements was accomplished using the MADCAP IV data acquisition program and a Digital PDP8/I computer. The electron energy scales were calibrated with Xe and Kr for positive ions (ionization potentials = 12.13 and 13.99 eV, respectively)[22] and SF$_6$ for negative ions (0.08 eV).[23] Mass calibration at 70 eV and at other electron energies was accomplished using perfluorokerosene.[21]

Ionization efficiency curves for the Salen complexes were interpreted using the semilogarithmic method[24] and extrapolated voltage difference technique.[25] With the semilogarithmic method the ionization curves were very closely parallel to those for the calibrant, and this method was the primary choice for the Salen complexes and the only method used for the Oaben complexes. A typical semilog ionization efficiency curve for Ni(Salen)$^+$ is shown in Figure 1. The standard deviations reported represent the precision for all determinations made over the past 12 months. It is anticipated that the accuracy of the ionization potentials is at least 0.5 eV. The vertical ionization potential measured here would deviate from the true adiabatic value if the potential energy representation for the neutral complex, ML, and the singly charged complex ion, ML$^+$, differ significantly. In such an instance the measured electron impact value would represent the formation of ML$^+$ in an excited electronic state.

All the complexes were prepared by conventional methods.[26] Two molecular equivalents of the appropriate aldehyde and 1 mol equiv of ethylenediamine were dissolved in ethanol and refluxed with stirring for 1 hr. In some cases the tetradentate ligand precipitated during this period. One molecular equivalent of the metal acetate, previously dissolved or suspended in ethanol, was then slowly added to the ligand solution. There was an immediate change in the color and 1 hr later a highly crystalline product was observed in the flask. After refluxing an additional hour, the solution was cooled and filtered. The product was washed with excess cold ethanol and dried *in vacuo* at 100° for 12 hr.

The Oaben complexes showed little or no detectable impurities as determined from the low-voltage mass spectrum of each compound.

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(13) D. D. Lloyd, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 500 (1971).

(14) S. M. Shildcrout, R. G. Pearson, and F. E. Stafford, *J. Amer. Chem. Soc.*, **90**, 4006 (1968).

(15) M. M. Bursey and P. F. Rogerson, *Inorg. Chem.*, **9**, 676 (1970).

(16) A. van den Bergen, K. S. Murray, M. J. O'Connor, and B. O. West, *Aust. J. Chem.*, **22**, 39 (1969).

(17) L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 1072 (1969).

(18) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, and J. S. Shannon, *Aust. J. Chem.*, **18**, 1539 (1965).

(19) E. P. Dudek, E. Chaffee, and G. Dudek, *Inorg. Chem.*, **7**, 1257 (1968).

(20) K. S. Patel, K. L. Rinehart, and J. C. Bailar, *Org. Mass Spectrom.*, **4**, 441 (1970).

(21) J. G. Dillard, *Inorg. Chem.*, **8**, 2148 (1969).

(22) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxal, and F. H. Field, NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

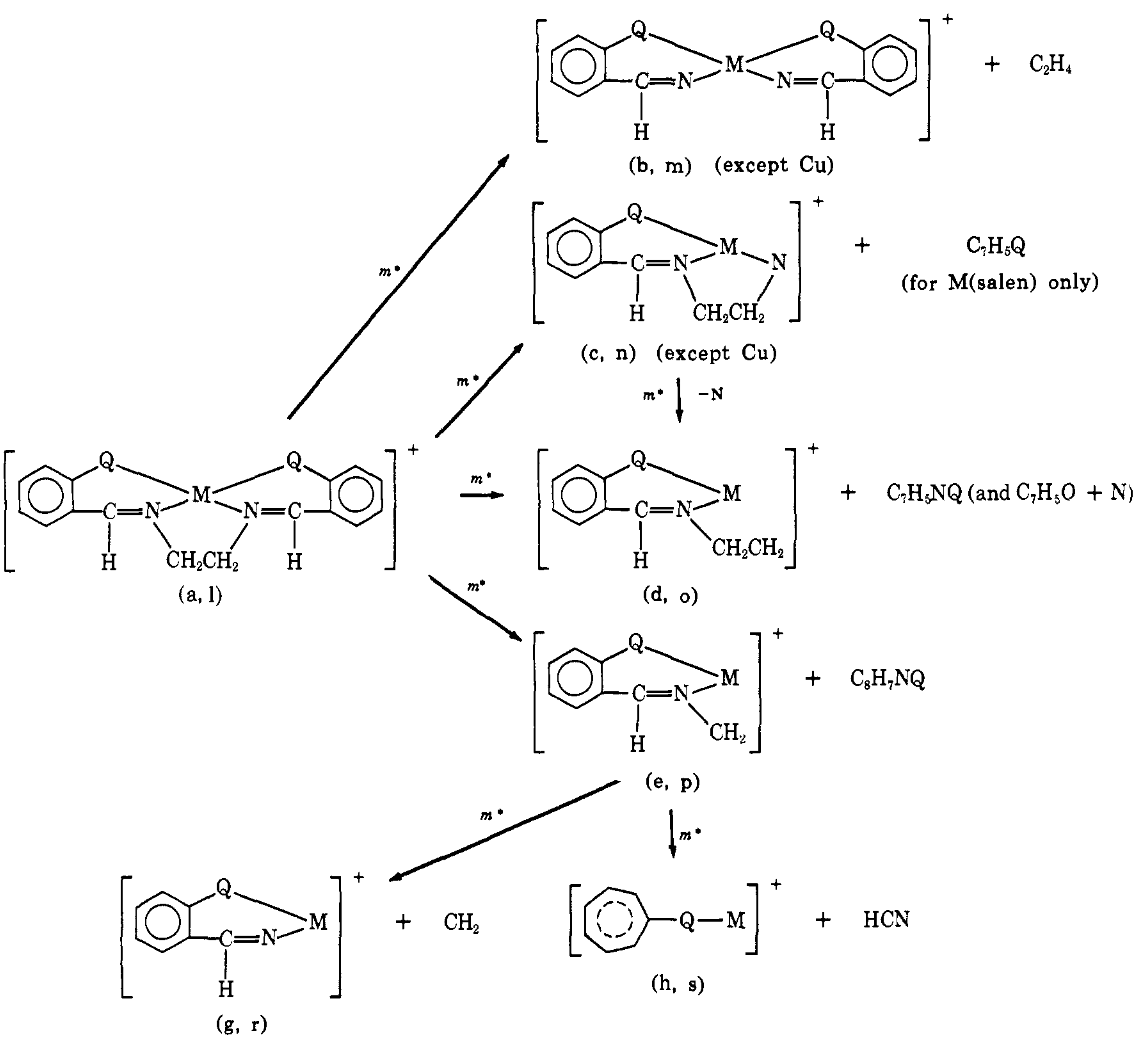
(23) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

(24) F. P. Lossing, A. W. Tickner, and W. A. Brice, *ibid.*, **19**, 1254 (1951).

(25) J. W. Warren, *Nature (London)*, **165**, 810 (1950).

(26) R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 82 (1966).

Scheme I. Unimolecular Decomposition Scheme: M(Salen) (a–h), Q = O, and M(Oaben) (l–s), Q = NH



The Salen complexes, however, showed a minor but persistent impurity with a cluster of ions beginning at *m/e* 322. The impurity increased in abundance as the temperature was increased to above 250°. From the calculated and experimental isotopic abundance measurements the ion appeared to be the parent ion of an Fe–Salen complex. This observation is similar to that reported earlier[8] where iron from the stainless steel in the ion source replaced the copper ion in coordination compounds with β-diketone ligands. In order to avoid this troublesome annoyance the mass spectra and appearance potentials were measured at less than 200°. In most cases the ion source temperature was 175°. The molecular, dimer, and fragment ion currents were first order in measured analyzer tube pressure.

Results and Discussion

I. General Spectra. Positive Ions. The major metal-containing fragment ions for the six complexes with the corresponding monoisotopic relative abundances are listed in Table I. Part A lists the important fragment ions of the Salen complexes while part B presents those for the Oaben complexes. A proposed molecular formula is given for each ion as is the mass at which the most abundant metal-containing ion appears. From the low-resolution data presented here it is not possible to distinguish between loss of nitrogen atoms and CH_2 from the fragment ions. In the fragmentation scheme simple bond cleavage processes are suggested rather than rearrangement ions where there is a question about the loss of atomic nitrogen or CH_2 groups. For example, formation of the ion at *m/e* 205 in Ni(Salen) is assumed to arise from the molecular ion by loss of C_7H_5NO rather than loss of C_8H_7O (see metastable data). On the other hand the fragmentation of ion (c) by loss of atomic nitrogen to produce (d) is suggested for Ni(Salen) and Co(Salen) (see Scheme I). The spectrum reported here for Ni(Salen) is in excellent agreement with the spectrum reported by Patel, *et al.*[20] In an attempt to discover the details of the fragmentation process a careful study of the metastable ions was carried out. A summary of the data is presented in Table II where calculated and measured metastable ion transitions are given. The calculated values are based on the most abundant metal-containing ion using the *m/e* values given in Table I for the molecular and fragment ions.

The positive ion spectra of nickel(II)–, cobalt(II)–, and copper(II)–Salen and –Oaben complexes are strikingly similar. The spectrum of each complex is characterized by an intense molecular ion which is the most abundant ion in the spectrum. This abundance coupled with the relatively abundant doubly charged molecular ions and the dominance of metal-containing fragment ions demonstrates the high stability of the molecular ions.

Although the fragmentation patterns for all of these complexes are very similar, there are some very important differences in the relative abundances of the fragments. One major fragmentation pathway with

Table II. Metastable Transitions Observed in M(Salen) (a–k) and M(Oaben) (l–s)

	m^*			m^*			m^*	
Cobalt	Calcd	Obsd	Nickel	Calcd	Obsd	Copper	Calcd	Obsd
a → b 325 → 297	271.41	271.5	a → b 324 → 296	270.42	270.3			
l → m 323 → 295	269.43	269.5	l → m 322 → 294	268.44	268.5			
			a → c 324 → 219	148.03	148.0			
l → n 323 → 219	148.49		l → n 322 → 218	147.59	147.5			
a → e 325 → 192	113.42	113.4	a → e 324 → 191	112.60	112.5	a → e 329 → 196	116.77	116.7
l → o 323 → 205	130.11	130.0	l → o 322 → 204	129.4		l → o 327 → 209	133.58	133.7
a → d 325 → 206	130.57	130.6	a → d 324 → 205	129.71	129.5	a → d 329 → 210	134.04	134.0
l → p 323 → 191	112.95	112.8	l → p 322 → 190	112.11	112.3	l → p 327 → 195	116.28	116.5
			c → d 219 → 205	191.9	191.8			
e → g 192 → 178	165.02	165.1	e → g 191 → 177	164.03		e → g 196 → 182	169.0	169.1
p → r 191 → 177	164.03	164.1	p → r 190 → 176	163.03	163.1			
e → h 192 → 165	141.8	141.8	e → h 191 → 164	140.82	140.9	e → h 196 → 169	145.72	
p → s 191 → 164	140.82	140.9	p → s 190 → 163	139.84	139.7	p → s 195 → 168	144.73	144.6

the Salen ligand is the cleavage about the central carbon–carbon bond of the parent to yield fragment (e). This pathway seems to be especially favored for nickel(II) and copper(II). The same pathway exists for the Oaben complexes to yield fragment (p), but (p) is not as abundant.

Mass spectra were scanned above the parent ion isotopic cluster for each complex in order to determine if polymeric fragments were present and stable enough to be detected. Earlier Dudek, *et al.*,[19] had observed peaks in the mass spectrum of nickel(II) complexes of Schiff bases derived from salicylaldehyde and N-substituted ethylenediamines which correspond to two nickel ions and two tridentate ligands. Relatively intense polymeric isotopic clusters (see Table I) were observed in each M(Salen) spectrum. That these ions are most accurately represented as $[M_2(Salen)]^+$ was confirmed by comparing calculated and experimentally measured relative isotopic abundances. The mass spectra of the M(Oaben) complexes also showed distinct isotopic clusters at higher *m*/*e* indicative of the dinuclear species $[M_2(Oaben)]^+$. In Cu(Oaben) and Ni(Oaben) other metal-containing ions were detected in very low abundance $<0.1\%$ in addition to some species which appeared to be purely ligand in nature. Due to the low abundance of the ligand and some of the metal-containing ions, it was not possible to assign an elemental composition based on isotopic abundance measurements. The important polymeric ion in each spectrum was the $[M_2(Oaben)]^+$ ion.

The presence of these polymeric species in the gas phase suggests the presence of polymeric molecules in the gas phase. However, no important ions indicative of a molecular ion dimer or dimer fragment other than $[M_2(Salen)]^+$ and $[M_2(Oaben)]^+$ were observed regardless of the electron energy. It is known that several M(Salen) complexes exist as dimers in the solid state. X-Ray structure data on Cu(Salen) indicate that dimers are formed by intermolecular copper–oxygen bonds resulting in weakly pentacoordinate copper(II).[27] Although not isomorphous, a similar dimeric structure has been indicated for Ni(Salen).[26] A dimeric structure for the oxygen inactive form of Co(Salen) has been suggested[28a] in which square-pyramidal coordination of cobalt atoms is achieved through the bridging of an oxygen atom from a second Co(Salen) molecule. An oxygen active form contains pairs of nearly planar Co(Salen) molecules.[28b] No significant metal–metal interaction is believed to exist in this form. In contrast to the M(Salen) complex, M(Oaben) compounds are reported to have little or no tendency for dimer formation.[29] The observation of the dinuclear species in the gas phase might cast some doubt on these conclusions. On the other hand the absence of significant polymeric ions other than the M_2L^+ (L = Salen or Oaben) in the mass spectra makes it impossible from this work to confirm the presence of dimers. It is possible that the M_2L^+ ions may be formed *via* a solid–solid reaction on the direct insertion probe or in the sublimation process and thus are not indicative of polymeric species in the gas phase.

Negative Ions. The 50-eV negative ion spectrum was measured for each complex. With the exception of Ni(Oaben) the most abundant ion in the spectrum was the parent ion. The major negative ion in the spectrum of Ni(Oaben) was the parent ion minus two hydrogens. The 50-eV spectra indicated the presence of additional fragment ions. A relatively weak metal-containing fragment was detected at 106 mass units below the parent for Ni(Salen) and Cu(Salen) corresponding to the loss of C_7H_6O. A fragment ion at 105 mass units

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(27) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

(28) (a) S. Bruckner, M. Colligaris, G. Nardin, and L. Randaccio, *Acta Crystallogr., Sect. B*, **25**, 1671 (1969); (b) W. P. Schaefer and R. E. Marsh, *ibid.*, **25**, 1675 (1969).

(29) B. M. Higson and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 269 (1972).

was noted in the spectrum of Cu(Oaben) associated with the loss of C_7H_7N. The negative ion spectra of Co(Salen), Ni(Oaben), and Co(Oaben) revealed no abundant fragment negative ions.

The Cu(Oaben) negative ion spectrum was unique in that several metal-containing fragments appeared, in addition to those mentioned above. The metal-containing ions were the negative ion analogs of the positive fragment ions (n), (o), (p), (q), and (r) listed in Table IB. The negative ions in Salen or Oaben were not investigated.

II. Energetics. The measured ionization potentials (IP's) for the free ligands and the six metal complexes, including Mn(Salen), are presented in Table III. The difference in the IP's for the Salen and Oaben free ligands is as expected[22] resulting from the replacement of a phenol OH group in Salen with a NH_2 group in Oaben.

Table III. Ionization Potentials (eV)

Salen	8.53 ± 0.07	Oaben	7.83 ± 0.04
Mn(Salen)	7.77 ± 0.08	Co(Oaben)	6.98 ± 0.10
Co(Salen)	7.52 ± 0.06	Ni(Oaben)	6.84 ± 0.08
Ni(Salen)	7.57 ± 0.09	Cu(Oaben)	7.15 ± 0.11
Cu(Salen)	7.69 ± 0.09		

The ionization energies of the complexes are all lower than that of the free ligand and slightly lower than the values for the free metals. The decrease in ionization energy upon complexation is related to the presence of the metal ion in the compound. It is suggested that the electron removed in the ionization process must be from an orbital where the metal ion makes a significant contribution. If the electron were lost from the ligand, an increase in the ionization energy would be expected due to reduced electron density on the ligand upon coordination. In addition there is a slight increase in the ionization potential in the M(Salen) series Co–Ni–Cu although the uncertainty in the measurements yields overlap in the values in some cases. In the M(Oaben) compounds copper has the highest ionization potential while the cobalt and nickel values are in the reversed order compared to M(Salen). For the M(Salen) compounds the trend parallels the variation in the second and third ionization energies for the free metals.

Additional evidence for the removal of the electron from the metal is provided by the value measured for Mn(Salen). The ionization potential is higher than the values in the other M(Salen) complexes. The electronic structure of Mn(II) is $4s^03d^5$. This half-filled d shell should be quite stable so that removal of a metal electron would require more energy than its neighbors in the transition series.

For the M(Salen) and the M(Oaben) complexes the ionization potentials of the free ligands and the complexes differ by less than 1.0 eV and it is conceivable that coordination could lower the ionization potential of the ligand by as much as 1.0 eV. However, the variation of the ionization potential with the metal ion is suggestive of removal of an electron from an orbital possessing some metal character. Furthermore replacing Salen on the metal with the much better donor Oaben[30] is predicted to increase electron density on the metal resulting in a lower ionization potential. From an inspection of Table III this trend is exactly that which is observed for all three metals.

Binding energy measurements of the metal core electron levels, $2p_{1/2}$, and $2p_{3/2}$ on cobalt in Co(Salen) and in Co(Oaben) *via* X-ray photoelectron spectroscopy[31] indicate that the binding energy is lower for Co(Oaben) than for Co(Salen) by 0.5 eV. Surprisingly this difference is almost exactly equal to the difference in the values of the valence ionization potentials measured in the gas phase. This result supports the notion that the electron removed upon ionization is localized on the metal.

Recently, Lloyd[13] has shown that the ionization process for metal β-diketone complexes involves removal of an electron from an orbital with a significant contribution by the metal. Lloyd's photoelectron result is in contrast to the previous suggestion of Reichert, *et al.*,[6,7] that the electron was removed from the ligand.

An energy level diagram has recently been suggested for Ni(Salen) and Ni(Oaben) as obtained from molecular orbital calculations.[32] The theoretical model indicates that the highest occupied molecular orbital is in both cases predominantly a ligand π orbital. However, lying just below the ligand orbital is a group of closely spaced metal d orbitals. It is reported that the highest occupied molecular orbital in Ni(Oaben) is at higher energy than the corresponding orbital in Ni(Salen) in agreement with the present results. Likewise the highest occupied metal orbital appears at higher energy in Ni(Oaben). These theoretical results suggest that the electron removed comes from the ligand. However, the comparison of the valence ionization potentials reported here and the measured X-ray photoelectron binding energies for the metal core electrons suggest that the increased electron density on the metal is responsible for the lowering of the ionization potentials in the complexes. In this situation then the electron would necessarily be removed from a predominantly metal orbital. It is expected that measurements of the ionization potentials of other coordination compounds and their derivatives may help answer this question.

Energetic measurements were performed on all negative parent ions except Ni(Oaben) and some fragment negative ions in the copper complexes. Negative ions may be formed from a compound through resonance electron capture or an ion pair process. Appearance potentials for the major negative ions are presented in Table IV. All complexes, except Ni(Oaben), formed parent molecular ions by direct resonance capture processes. No secondary electron processes were noted. Only the fragment ions in the copper complexes were of sufficient intensity at low energies for appearance potential measurements.

Figure 2 is a plot of the ionization efficiency curve for the formation of $[\mathrm{Ni(Salen)}]^-$. The solid curve is the capture curve for SF_6^- which was used for the energy calibration. The width of the peak yields the electron energy distribution. The distribution is approximately Maxwellian as expected and less than 0.5

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(30) M. Green and P. A. Tasker, *J. Chem. Soc. A*, 3105 (1970).

(31) J. Burness, J. G. Dillard, and L. T. Taylor, ACS–CIC Inorganic Summer Symposium, Buffalo, N. Y., June 1972.

(32) G. De Alti, V. Galasso, and A. Bigotto, *Inorg. Chim. Acta*, **6**, 153 (1972).

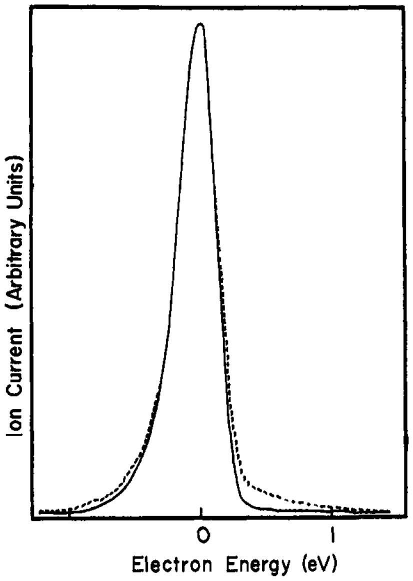

Figure 2. Resonance capture curve for Ni(Salen)$^-$ (-----) and SF_6^- (——) (corrected energy scale).

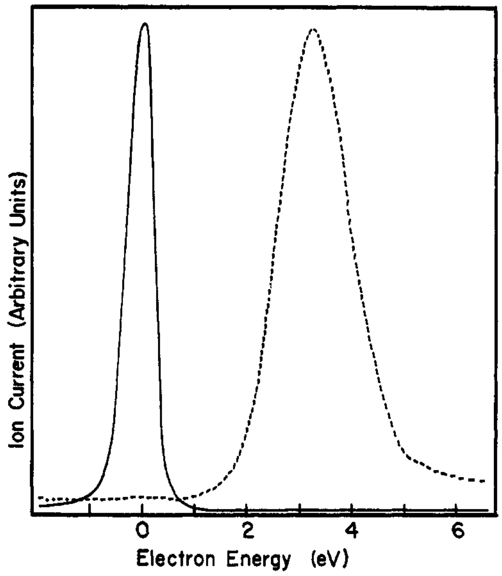

Figure 3. Resonance capture curves for Cu(Oaben)$^-$ (——) and $Cu(C_9H_{10}N_8)^-$ (-----) (corrected energy scale).

Table IV. Negative Ions in M(Salen) and M(Oaben) at Low Energies

Metal	Ion	Resonance potential
	M(Salen)	
Co	Co(Salen)$^-$	0.08
Ni	Ni(Salen)$^-$	0.08
Cu	Cu(Salen)$^-$	0.08
	Cu(Salen-106)$^-$	3.2
	M(Oaben)	
Co	Co(Oaben)$^-$	0.08
Ni		
Cu	Cu(Oaben)$^-$	0.08
	Cu(Oaben-105)$^-$	3.2
	Cu(Oaben-106)$^-$	3.8

eV wide at half-height. The ion currents for SF_6^- and [Ni(Salen)]$^-$ are scaled to the same height by the data manipulation and plotting process. The actual abundance of the metal complex ion is at least a factor of 10 less than that for SF_6^-. Similar ionization efficiency curves were obtained for [Cu(Salen)]$^-$, [Co(Salen)]$^-$, [Cu(Oaben)]$^-$, and [Co(Oaben)]$^-$. All ions were formed by direct capture of a thermal electron.

In the 50-eV negative ion spectrum of Ni(Oaben) only the parent ion minus two hydrogens was noted. No resonance capture processes were detected in Ni(Oaben). If the electron is captured by the metal in the resonance process, then the failure to observed the [Ni(Oaben)]$^-$ ion may not be too surprising since the Ni(I) species formed would be unstable. The fact that [Ni(Salen)]$^-$ was detected while [Ni(Oaben)]$^-$ was not may be due to the increased electron density on the metal as a result of coordination with the stronger Oaben ligand. Such an increase in electron density would render the Ni(I) state in [Ni(Oaben)]$^-$ unattainable. The failure to detect [Ni(Oaben)]$^-$ is not believed due to differences in autoionization lifetimes since in these molecules the lifetimes for the negative ions are expected to be approximately equal. Thus if the foregoing arguments are valid, additional evidence is provided for electron capture by the metal rather than the ligand.

Dissociative capture processes were observed at low energies in the copper compounds. The resonance capture curve for the formation of the $[Cu(C_9H_{10}N_8)]^-$ ion is presented in Figure 3, where [Cu(Oaben)]$^-$ is used as the internal energy calibrant. Similar dissociative capture processes were observed in the other complexes as summarized in Table IV.