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Mass Spectra of Complexes of 8-Quinolinol and 2-Methyl-8-quinolinol with Divalent Metals

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The mass spectra of $M(ox)_2$ (oxH = 8-quinolinol; M = Co, Ni, Cu, Zn, Pd, Cd, Pt) show intense molecular ions $[M(ox)_2]^+$ which fragment by loss of ligand radicals to give $[M(ox)]^+$ and by loss of ligand fragments such as $H^•$, $OH^•$, H_2O, CO and C_9H_7N. The subsequent fragmentation of the ions $[m(ox)]^+$ (M = Co, Ni, Cu, Pd, Pt) involves loss of CO followed by elimination of C_2H_2. In contrast the ions $[Zn(ox)]^+$ and $[Cd(ox)]^+$ show loss of metal to give $[ox]^+$. When M = Zn loss of ZnH from $[M(ox)_2]^+$ and loss of metal from $[M(ox)_2 - 17]^+$ are also observed. In each case the loss of the metal species is accompanied by the combination of two ligands and formation of complex metal-free ions. All the complexes show fairly intense doubly charged molecular ions. The spectra of $M(mox)_2$ (moxH = 2-methyl-8-quinolinol; M = Co, Ni, Cu, Zn) show similar features to those of the respective $M(ox)_2$ compounds.

Introduction

Previously we reported on the mass spectra of several complexes of 8-quinolinol with trivalent [1] and tetravalent [2, 3] metals. The main fragmentation pattern of these compounds depends primarily on the common oxidation states of the metals and is characterised by loss of intact ligand radicals. Decompositions involving loss of ligand fragments occurs to a very limited extent and only in complexes containing a transition metal. Another feature is the presence of doubly charged ions in the spectra of all the compounds. Here we report on the mass spectra of the complexes $M(ox)_2$ (oxH = 8-quinolinol, M = Co, Ni, Cu, Zn, Pd, Cd, Pt) and $M(mox)_2$ (moxH = 2-methyl-8-quinolinol, M = Co, Ni, Cu, Zn). The present work was undertaken to evaluate further the effect of the metal and/or ligand character (a) on the fragmentation pattern of metal chelates and (b) on the formation of doubly charged ions. The mass spectra of several complexes of 8-quinolinol with divalent metals have been reported earlier but their fragmentation patterns have not been discussed in detail and no reference to doubly charged ions has been made [4].

Experimental

The complexes were prepared as described in the literature [5]. The mass spectra were obtained on a Hitachi RMS–4 spectrometer operating at 80 eV, and by use of a direct insertion probe at *ca.* 250 °C. Exact mass measurements and enhanced metastable spectra were obtained on an AEI MS–9 instrument at the Physico–Chemical Measurements Unit, Harwell.

Results and Discussion

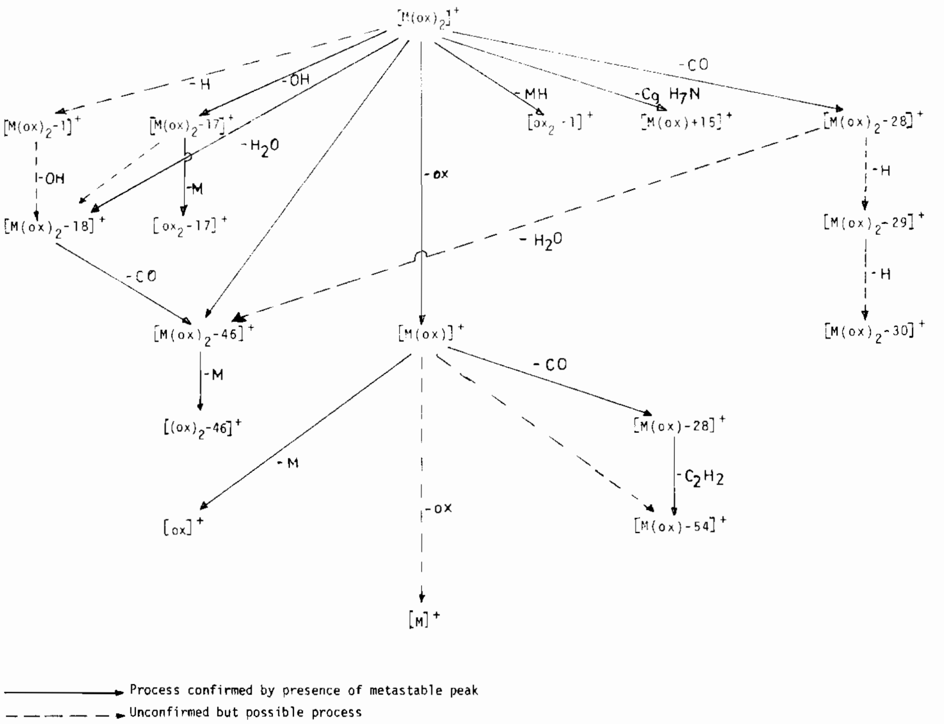
$M(ox)_2$ Compounds

The mass spectra of the compounds $M(ox)_2$ are given in Tables I to III. Non-metal ions with m/e values below 144 are not included. The most abundant of these ions had m/e values 117, 116, 90, 89, 63 and 39; the sum of their intensities was less than 10% of the total ion current. In all cases, except when M = Cu, the molecular ion $[M(ox)_2]^+$ is the most abundant ion. This ion fragments by loss of a ligand radical to give $[M(ox)]^+$ and by reactions involving elimination of ligand fragments (Scheme 1). The subsequent decomposition of the ions $[M(ox)]^+$ depends on the nature of the metal. When M = Co, Ni, Cu, Pd, or Pt the ion $[M(ox)]^+$ decomposes by loss of CO which is followed by loss of C_2H_2. These reactions parallel the decomposition of $[M(ox)]^+$ (M = Fe [1] or Ru [6]) and may proceed by a mechanism analogous to that suggested for $[Fe(ox)]^+$. However, they differ from the decomposition behaviour of the ions $[M(ox)]^+$ (M = Ti, Sn or Ge) which fragment by loss of HCO followed by CN [3]. The behaviour of the ions $[Zn(ox)]^+$ and $[Cd(ox)]^+$ is significantly different. These ions show neither loss of intact ligand radicals nor loss of ligand fragments but decompose by metastable supported loss of metal to give $[ox]^+$. Loss of a metal atom is also involved in the reaction $[Zn(ox)_2 - 17]^+ \xrightarrow{*} [(ox)_2 - 17]^+$ and several reactions of the $M(mox)_2$ complexes (see below). That metal atom loss takes place in the spectra of metal chelates is unusual. In the reaction $[Zn(ox)_2 - 17]^+ \longrightarrow [(ox)_2 - 17]^+$ the loss of metal is accompanied by another unusual

TABLE I. Ion Abundances[a] for $M(ox)_2$.

Ion[b,c]	M in $M(ox)_2$							Assignment
	Co m/e	Ni[d] m/e	Cu m/e	Zn m/e	Pd m/e	Cd[e] m/e	Pt[f] m/e	
$[M(ox)_2]^+$	347 56 (7)[g]	346 42 (6)	351 22 (13)	352 46 (15)	394 43 (6)	402 72 (8)	483 46 (22)	$C_{18}H_{12}N_2O_2M$
$[M(ox)_2 - 1]^+$	346 7	345 4	–	351 5	393 6	–	–	$C_{18}H_{11}N_2O_2M$
$[M(ox)_2 - 17]^+$	330 1	329 0.6	–	335 2	–	–	–	$C_{18}H_{11}N_2OM$
$[M(ox)_2 - 18]^+$	329 1	328 0.8	333 0.7	334 0.4	376 w[h]	384 0.2	–	$C_{18}H_{10}N_2OM$
$[M(ox)_2 - 28]^+$	319 0.3	318 1	–	324 0.3	366 w	–	–	$C_{17}H_{12}N_2OM$
$[M(ox)_2 - 29]^+$	318 0.6	–	–	323 0.3	–	–	–	$C_{17}H_{11}N_2OM$
$[M(ox)_2 - 30]^+$	317 0.5	–	–	–	–	–	453 2 (0.5)	$C_{17}H_{10}N_2OM$
$[M(ox)_2 - 46]^+$	301 0.3	–	–	–	–	–	–	$C_{17}H_{10}N_2M$
$[M(ox) + 15]^+$	218 2	217 8	222 1	–	265 3	–	–	$C_9H_5NO_2M$
$[M(ox)]^+$	203 13	202 15	207 39	208 11	250 21	258 11	339 1	C_9H_6NOM
$[M(ox) - 28]^+$	175 5	174 11	179 4	–	222 16	–	311 10	C_8H_6NM
$[M(ox) - 54]^+$	149 2	148 3	153 0.5	–	–	–	285 7	C_6H_4NM
$[M]^+$	59 3	58 4	63 10	–	106 5	–	–	
$[(ox)_2 - 1]^+$	–	–	–	287 1	–	–	–	$C_{18}H_{11}N_2O_2$
$[(ox)_2 - 17]^+$	–	–	–	271 0.5	–	–	–	$C_{18}H_{11}N_2O$
$[(ox)_2 - 46]^+$	242 1	242 0.4	–	–	–	–	–	$C_{17}H_{10}N_2$
[oxH]	145 2	145 10	145 21	145 7	145 5	145 5	145 3	C_9H_7NO
[ox]	144 w	144 w	144 1	144 7	144 w	144 11	144 1	C_9H_6NO

[a] Abundances are expressed as percentages of the total ion current due to metal-containing ions and metal-free ions with m/e > 144. All species are corrected for isotopic abundance. [b] Only metal-containing ions and metal-free ions with m/e > 144 are recorded. [c] m/e values are given for the ions containing ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{106}Pd, ^{114}Cd and ^{195}Pt. [d] A peak corresponding to a nickel-containing ion at m/e 298 (ab.0.6) is also present. [e] A peak corresponding to a cadmium-containing ion at m/e 352 (ab.2) is also present. [f] Peaks corresponding to platinum-containing ions at m/e 425 (ab.6), 396 (ab.1), 357 (ab.1), 321 (ab 1) and 298 (ab.1) are also present. [g] Figures in brackets indicate abundance of doubly charged species. [h] w = weak.



Scheme 1. Fragmentation scheme for $M(ox)_2$.

TABLE II. Metastable Ions in $M(ox)_2$.

Transition	M in $M(ox)_2$	m/e Values for Transition[a]	m* Found	m* Calcd	Neutral Fragment
$[M(ox)_2]^+ \longrightarrow M(ox)_2 - 17]^+$	Zn	352 → 335	319	318.82	OH
$[M(ox)_2]^+ \longrightarrow [M(ox)_2 - 18]^+$	Co	347 → 329	312	311.93	H_2O
	Ni	346 → 328	311	310.93	
	Cu	351 → 333	316	315.92	
	Cd	402 → 384	367	366.80	
$[M(ox)_2]^+ \longrightarrow [M(ox)_2 - 28]^+$	Co	347 → 319	293	293.26	CO
	Ni	346 → 318	292	292.26	
	Zn	352 → 324	299	298.23	
	Pd	394 → 366	340	339.99	
$[M(ox)_2 - 18]^+ \longrightarrow [M(ox)_2 - 46]^+$	Co	329 → 301	275	275.38	CO
$[M(ox)_2]^+ \longrightarrow [M(ox)_2 - 46]^+$	Co	347 → 301	261	261.10	H_2O + CO
$[M(ox)_2]^+ \longrightarrow [M(ox)]^+$	Co	347 → 203	119	118.76	ox
	Cu	351 → 207	122	122.08	
	Zn	352 → 208	123	122.90	
	Pd	394 → 250	158	158.63	
	Cd	402 → 258	165.5	165.80	
$[M(ox)_2]^+ \longrightarrow [(ox)_2 - 1]^+$	Zn	352 → 287	234	234.00	ZnH
$[M(ox)_2 - 17]^+ \longrightarrow [(ox)_2 - 17]^+$	Zn	335 → 271	219	219.23	Zn
$[M(ox)_2]^+ \longrightarrow [M(ox) + 15]^+$	Ni	346 → 217	136	136.10	C_9H_7N
	Pd	394 → 265	178	178.24	
$[M(ox)_2 - 46]^+ \longrightarrow [(ox)_2 - 46]^+$	Co	301 → 242	194	194.56	Co
$[M(ox)]^+ \longrightarrow [M(ox) - 28]^+$	Co	203 → 175	151	150.86	CO
	Ni	202 → 174	150	149.88	
	Cu	207 → 179	154	154.79	
$[M(ox) - 28]^+ \longrightarrow [M(ox) - 54]^+$	Ni	174 → 148	126	125.88	CN
$[M(ox)]^+ \longrightarrow [ox]^+$	Zn	208 → 144	100	99.69	Zn
	Cd	258 → 144	80.5	80.40	Cd

[a] Only transitions involving ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{106}Pd and ^{114}Cd are given.

TABLE III. Accurate Mass Measurements on Selected Peaks for $M(ox)_2$.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
$Co(ox)_2$	347	347.0233	$C_{18}H_{12}N_2O_2Co$	374.0231
	346	346.0155	$C_{18}H_{11}N_2O_2Co$	346.0152
	330	330.0200	$C_{18}H_{11}N_2OCo$	330.0203
	329	329.0128	$C_{18}H_{10}N_2OCo$	329.0125
	218	217.9653	$C_9H_5NO_2Co$	217.9652
	149	148.9673	C_6H_4NCo	148.9676
$Ni(ox)_2$	217	216.9671	$C_9H_5NO_2{}^{58}Ni$	216.9673
$Cu(ox)_2$	351	351.0168	$C_{18}H_{12}N_2O_2{}^{63}Cu$	351.0194
	333	333.0086	$C_{18}H_{10}N_2O^{63}Cu$	333.0089
	222	221.9616	$C_9H_5NO_2{}^{63}Cu$	221.9616
	179	178.9805	$C_8H_6N^{63}Cu$	178.9796
$Zn(ox)_2$	352	352.0187	$C_{18}H_{12}N_2O_2{}^{64}Zn$	352.0190
	351	351.0105	$C_{18}H_{11}N_2O_2{}^{64}Zn$	351.0111
	335	335.0165	$C_{18}H_{11}N_2O^{64}Zn$	335.0162
	334	334.0087	$C_{18}H_{10}N_2O^{64}Zn$	334.0084
$Pd(ox)_2$	394	393.9949	$C_{18}H_{12}N_2O_2{}^{106}Pd$	393.9955

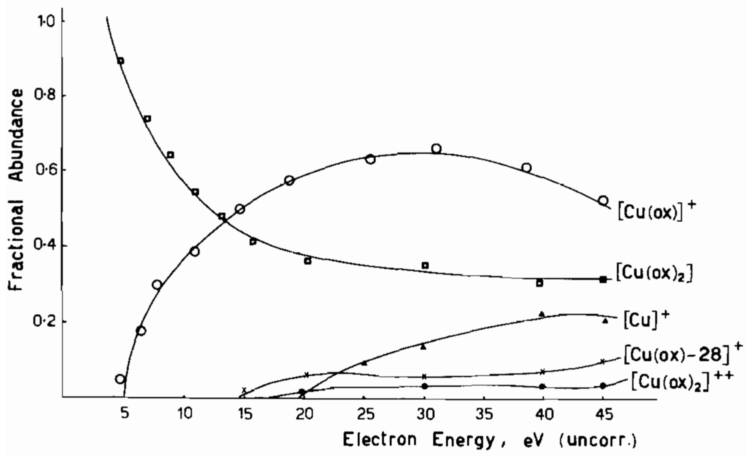
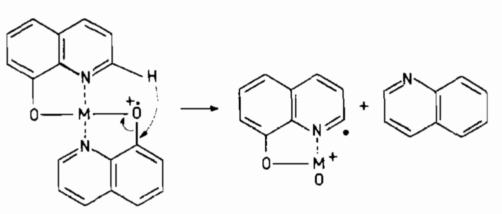


Fig. 1. Ionisation efficiency curves.

feature. Whatever the structure of $[(ox)_2 - 17]^+$ its formation suggests combination of two ox ligands or of two partially fragmented ox ligands in its precursor ions. Loss of a metal atom accompanied by combination of two ligands has been observed in the spectra of several hydrocarbon complexes of transition metals [7–9] but there are not reports of such reactions in metal chelates. Loss of metal is also observed in the case of the cobalt and nickel compounds which exhibit the reaction $[M(ox)_2 - 46]^+ \longrightarrow [(ox)_2 - 46]^+$. When M = Co the reaction is metastable supported. A related reaction which is observed in the spectrum of $Zn(ox)_2$ is $[Zn(ox)_2]^+ \xrightarrow{*} [ox_2 - 1]^+$. Here the combination of two ligands accompanies the loss of the neutral metal species ZnH. Several examples of this type of reaction are shown by the $M(mox)_2$ compounds.

In contrast to the behaviour of the $M(ox)_3$ compounds which exhibit ligand fragmentation only when the metal is a transition metal, in the compounds $M(ox)_2$ fragmentation of the ligand is observed for both transition and non-transition metals. Reactions involving loss of $H^\bullet$, $OH^\bullet$ and H_2O species from $[M(ox)_2]^+$ are observed in most cases. When M = Co, Ni, Zn and Pd loss of CO from $[M(ox)_2]^+$ is also observed. These reactions are often metastable supported and are analogous to reactions of other 8-quinolinolato complexes for which appropriate mechanisms have been proposed [1, 3]. Some of the compounds exhibit loss of $HCO^\bullet$ and/or CH_2O species from $[M(ox)_2]^+$ or from $[M(ox)_2 - 28]^+$. These reactions are generally weak except in the case of the platinum compound. A reaction which is shown by several of the compounds is $[M(ox)_2]^+ \longrightarrow [M(ox) + 15]^+$. When M = Ni or Pd the reaction is metastable supported and exact mass measurements on $[Ni(ox) + 15]^+$ indicate that its formula is $C_9H_5NNiO_2$. It is possible that the ion $[M(ox) + 15]^+$ arises from $[M(ox)_2]^+$ by elimination of quinoline. A possible mechanism is



A common feature of all the $M(ox)_2$ compounds studied in the presence of intense doubly charged molecular ions. When M = Zn or Pt these ions are present in higher abundance than any singly charged fragment ion and when M = Pt there are also two doubly charged fragment ions. Ionisation efficiency curves indicate that the doubly charged molecular ions appear at energies comparable to those required for the appearance of the secondary fragment ion $[M(ox - 28]^+$ (Figure).

M(mox)$_2$ Compounds

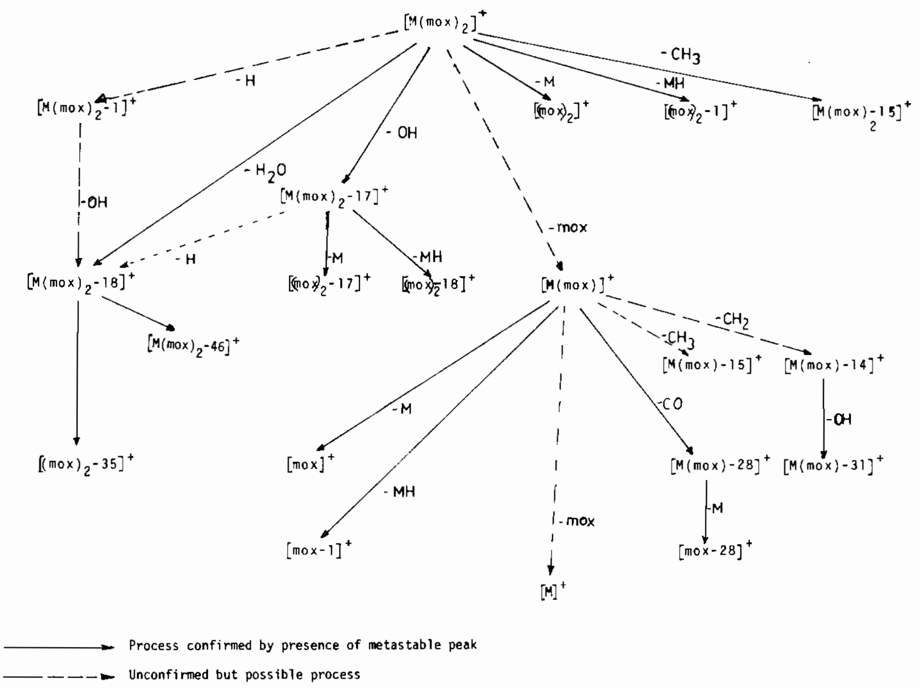
The spectra of the compounds $M(mox)_2$ are given in Tables IV to VI. Non-metal ions with m/e values below 159 are not included. The sum of the intensities of these ions was less than 10% of the total ion current and the most abundant of these had m/e values 158, 131, 130, 103, 78, 77, 63, 52, 51, 50 and 39.

The spectra of the compounds $M(mox)_2$ have several similar features to those of the corresponding $M(ox)_2$ compounds. Thus, in all cases the molecular ion $[M(mox)_2]^+$ is the most abundant ion and is accompanied by a fairly intense doubly charged molecular ion. The molecular ion $[M(mox)_2]^+$ fragments by reactions involving elimination of the ligand fragments $H^\bullet$, $OH^\bullet$, H_2O and CO (Scheme 2). These reactions are not only prominent but are also often metastable supported. In addition, but not unex-

TABLE IV. Ion Abundances[a] for $M(mox)_2$.

Ion[b,c]	M in $M(mox)_2$				Assignment
	Co m/e	Ni m/e	Cu m/e	Zn m/e	
$[M(mox)_2]^+$	375 44 (3)[d]	374 27 (4)	379 35 (1)	380 69 (7)	$C_{20}H_{16}N_2O_2M$
$[M(mox)_2 - 1]^+$	374 2	373 2	378 0.5	–	$C_{20}H_{15}N_2O_2M$
$[M(mox)_2 - 15]^+$	360 20 (1)	359 35	364 0.2	365 8 (1)	$C_{19}H_{12}N_2O_2M$
$[M(mox)_2 - 17]^+$	358 3 (0.3)	357 3		363 3 (0.3)	$C_{20}H_{15}N_2OM$
$[M(mox)_2 - 18]^+$	357 10 (0.4)	356 5	361 0.6	362 7 (0.4)	$C_{20}H_{14}N_2OM$
$[M(mox)_2 - 46]^+$	329 0.6 (0 3)	328 5	333 1	–	$C_{19}H_{14}N_2M$
$[M(mox)]^+$	217 6	216 5	221 29	222 2	$C_{10}H_8NOM$
$[M(mox) - 1]^+$	216 3	215 7	220 25	–	$C_{10}H_7NOM$
$[M(mox) - 14]^+$	203 0.2	–	–	–	C_9H_6NOM
$[M(mox) - 15]^+$	202 0.2	–	206 0.1	–	C_9H_6NOM
$[M(mox) - 28]^+$	189 2	188 4	193 1	–	C_9H_8NM
$[M(mox) - 31]^+$	186 1	–	–	–	C_9H_5NM
$[M]^+$	59 2	58 1	63 2	64 0.3	
$[(mox)_2]$	–	–	–	316 0.5	$C_{20}H_{16}N_2O_2$
$[(mox)_2 - 1]$	–	–	–	315 0.7	$C_{20}H_{15}N_2O_2$
$[(mox)_2 - 17]$	–	–	–	299 1	$C_{20}H_{15}N_2O$
$[(mox)_2 - 18]$	–	–	–	298 1	$C_{20}H_{14}N_2O$
$[(mox)_2 - 35]$	281 0.3	–	–	–	$C_{20}H_{13}N_2$
[mox]	–	–	–	158 3	$C_{10}H_8NO$
[mox – 1]	–	–	–	157 2	$C_{10}H_7NO$
[mox – 28]	130 1	–	–		C_9H_8N

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions and metal-free ions with m/e ⩾ 158. All species are corrected for isotopic abundance. [b] Only metal-containing ions and metal-free ions with m/e ⩾ 158 are recorded. [c] m/e values are given for the ions containing ^{58}Ni, ^{63}Cu and ^{64}Zn. [d] Figures in brackets indicate abundance of doubly charged species.



Scheme 2. Fragmentation scheme for $M(mox)_2$.

TABLE V. Metastable Ions in $M(mox)_2$.

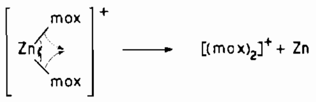
Transition	M in $M(mox)_2$	m/e Values for Transition[a]	m^*		Neutral Fragment
			Found	Calcd	
$[M(mox)_2]^+ \longrightarrow [M(mox)_2 - 15]^+$	Co	$375 \longrightarrow 360$	345.5	345.5	CH_3
	Ni	$374 \longrightarrow 359$	345	344.16	
	Cu	$379 \longrightarrow 364$	344	343.85	
	Zn	$380 \longrightarrow 365$	350.5	350.59	
$[M(mox)_2]^+ \longrightarrow [M(mox)_2 - 17]^+$	Zn	$380 \longrightarrow 363$	347	346.76	OH
$[M(mox)_2]^+ \longrightarrow [M(mox)_2 - 18]^+$	Co	$375 \longrightarrow 357$	340	339.8	H_2O
$[M(mox)_2]^+ \longrightarrow [(mox)_2]^+$	Zn	$380 \longrightarrow 316$	262(br)[b]	262.7	Zn
$[M(mox)_2]^+ \longrightarrow [(mox)_2 - 1]^+$	Zn	$380 \longrightarrow 315$	261(br)	261.1	ZnH
$[M(mox)_2 - 17]^+ \longrightarrow [(mox)_2 - 17]^+$	Zn	$363 \longrightarrow 299$	246(br)	246.2	Zn
$[M(mox)_2 - 17]^+ \longrightarrow [(mox)_2 - 18]^+$	Zn	$363 \longrightarrow 298$	245(br)	244.6	ZnH
$[M(mox)_2 - 18]^+ \longrightarrow [M(mox)_2 - 46]^+$	Co	$357 \longrightarrow 329$	303	303.19	CO
$[M(mox)_2 - 18]^+ \longrightarrow [(mox)_2 - 35]^+$	Co	$357 \longrightarrow 281$	222	221.2	CoOH
$[M(mox)]^+ \longrightarrow [M(mox) - 28]^+$	Co	$217 \longrightarrow 189$	164.5	164.6	CO
	Cu	$221 \longrightarrow 193$	169	168.55	
$[M(mox) - 14]^+ \longrightarrow [M(mox) - 31]^+$	Co	$203 \longrightarrow 186$	170.5	170.4	OH
$[M(mox)]^+ \longrightarrow [(mox)]^+$	Zn	$222 \longrightarrow 158$	112.5	112.4	Zn
$[M(mox)]^+ \longrightarrow [(mox) - 1]^+$	Zn	$222 \longrightarrow 157$	111	111	ZnH
$[M(mox) - 28]^+ \longrightarrow [(mox) - 28]^+$	Co	$189 \longrightarrow 130$	89.5	89.4	Co

[a] Only transitions involving ^{58}Ni, ^{63}Cu and ^{64}Zn are given. [b] br = broad.

TABLE VI. Accurate Mass Measurement on Selected Peaks for $M(mox)_2$.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
$Co(mox)_2$	375	375.0560	$C_{20}H_{16}N_2O_2Co$	375.0544
	328	328.0409	$C_{19}H_{13}N_2Co$	328.0411
	281	281.1076	$C_{20}H_{13}N_2$	281.1079
	202	202.9783	C_9H_6NOCo	202.9781
$Ni(mox)_2$	374	374.0576	$C_{20}H_{16}N_2O_2{}^{58}Ni$	374.0579
$Cu(mox)_2$	379	379.0495	$C_{20}H_{16}N_2O_2{}^{63}Cu$	379.0508

pectedly, the ions $[M(mox)_2]^+$ exhibit reactions involving loss of $CH_3^{\bullet}$ radicals. When M = Zn loss of metal from the molecular ion occurs whereby the two ligands combine



to give the ion $[(mox)_2]^+$. The ion $[Zn(mox)_2]^+$ also exhibits loss of ZnH to give the ion $[(mox)_2 - 1]^+$. A broad band of overlapping metastable peaks at m/e 261 is associated with these reactions. Another broad band of overlapping metastable peaks is associated with the loss of Zn and ZnH from $[Zn(mox)_2 - 17]^+$. Loss of metal-containing species is also observed in the case of the cobalt compounds which exhibits the metastable supported elimination of the species CoOH from $[Co(mox)_2 - 18]^+$.

The ion $[M(mox)]^+$ is present in the spectra of all the $M(mox)_2$ compounds and in close similarity to the compounds $M(ox)_2$ it is most abundant when M = Cu. The copper compound also exhibits the ion $[M(mox) - H]^+$ in high abundance. The further fragmentation of the ions $[M(mox)]^+$ (M = Co, Ni, Cu) proceeds by loss of CO and $CH_3^{\bullet}$ radicals. When M = Zn the ion $[M(mox)]^+$ does not exhibit these reactions but fragments by the metastable supported loss of a zinc atom and ZnH to give $[mox]^+$ and $[mox - 1]^+$ respectively. Loss of a metal atom is observed in the case of the cobalt compound which exhibits the metastable supported reaction $[M(mox) - 28]^+ \longrightarrow [(mox) - 28]^+$.

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