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Mass Spectra of Tetracobalt(II) and Tetrazinc(II) μ_4-Oxo-hexa-μ-carboxylates (Basic Cobalt and Zinc Carboxylates)

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The mass spectra of the compounds $M_4O(RCO_2)_6$ (M = Co or Zn; R = Me, Et, n-Pr. M = Co; R = i-Pr) show the presence of tetrametallic molecular ions $[M_4O(RCO_2)_6]^{+\cdot}$ which are very intense when M = Co but are weak when M = Zn. In all cases the main decomposition pathways involve initial loss of a ligand radical from the molecular ion followed by elimination of the even-electron species $M(RCO_2)_2$ and $(RCO_2)_2O$. The ions $[M_4O(RCO_2)_4]^{+\cdot}$ arising by successive loss of two ligand radicals from the molecular ion are very weak but the corresponding doubly charged ions $[M_4O(RCO_2)_4]^{2+}$ are present in considerable abundance. The mode of fragmentation of the trimetallic ions $[M_3O(RCO_2)_3]^+$, which are present in high abundance in all cases, depends markedly on the nature of M and R. When M = Zn these ions fragment by loss of even-electron species only but when M = Co loss of odd-electron species is also observed. This behaviour is rationalized in terms of the ability of cobalt, but not of zinc, to change oxidation state.

Introduction

Several mass spectrometric studies of metal carboxylates have been reported recently. By far most of the attention has been placed on copper carboxylates[1–3] but reports on thallium(III) carboxylates,[4] the carboxylates $M_4O(RCO_2)_6$ (M = $Be^{5,6}$ or Zn^7) and the dimetallic carboxylates $MM'(MeCO_2)_4$ (M = Mo; M' = Mo or $Cr)^{8,9}$ have also appeared. We now report a study of the carboxylates $M_4O(RCO_2)_6$ (M = Co or Zn; R = Me, Et, n-Pr. M = Co; R = i-Pr). This investigation relates to our studies of the effect of the metal on the fragmentation of metal-containing ions.[10, 11]

The X-ray crystal structure of $Zn_4O(MeCO_2)_6$ shows that the four metal atoms lie at the corners of a tetrahedron with six bidentate carboxylate groups bridging each pair of metals along an edge.[12] An oxygen atom is at the centre of the tetrahedron and is bonded to each metal atom. An analogous structure is indicated for the other complexes by their mass spectrometric behaviour and by other studies.[13]

Experimental

The compound $Zn_4O(MeCO_2)_6$ was prepared as described in the literature.[12] The preparation of the other compounds will be described in a later paper.*

The mass spectra were obtained on a Hitachi RMS-4 spectrometer operating at 80eV, 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

The mass spectra of the compounds $M_4O(RCO_2)_6$ are given in Tables I to III. Only the metal-containing species are recorded; in the case of the zinc compounds these are easily identified because of the isotope pattern due to the naturally occurring isotopes of zinc. The spectra also showed the presence of non-metal species arising from the carboxylato groups of the compounds; the intensities of these ions was less than 15% of the total ion current.

All the compounds studied showed molecular ions $[M_4O(RCO_2)_6]^{+\cdot}$ In the case of the zinc compounds these ions are of low abundance but in contrast the molecular ions of the cobalt compounds are very intense. This difference can be related to ligand→metal π electron donation which is possible when M = Co, due to the presence of empty *d* orbitals, but not when M = Zn. The difference can also be related to the oxidation state characteristics of these metals. Since the pioneering work of Shannon *et al.*[14] many features of the mass spectra of metal compounds have been rationalised in terms of the ability of the metal to change oxidation state.[1, 9, 11] In the case of the cobalt compounds electron transfer from ligand to metal $[Co^{II}_4O(RCO_2)_6]^{+\cdot} \rightarrow [Co^{II}_3Co^IO(RCO_2)_6]^+$ or metal to ligand $[Co^{II}_4O(RCO_2)_6]^{+\cdot} \rightarrow [Co^{II}_3Co^{III}O(RCO_2)_6]^+$ gives even-electron character to the molecular ion which is thus expected to be more stable.

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* J. Charalambous, D. E. Shaw, unpublished results

TABLE I. Ion Abundances[a] for $M_4O(RCO_2)_6$.

Ion[b]	M/R in $M_4O(RCO_2)_6$													
	Co/CH_3		Co/C_2H_5		Co/$CH_3CH_2CH_2$		Co/$(CH_3)_2CH$		Zn/CH_3[c]		Zn/C_2H_5[c]		Zn/$CH_3CH_2CH_2$[c]	
	m/e		m/e		m/e		m/e		m/e[c] d		m/e		m/e	
$[M_4O(RCO_2)_6]^+$	606	22.3	690	8.2	774	13.1	774	6.5	626	w	710	1.3	794	1.5
$[M_4O(RCO_2)_5]^+$	547	32.9(1.3)[e]	617	48.3(0.6)	687	32.0(0.2)	687	58.0(0.2)	567	26.9	637	36.6	707	61.0
$[M_4O(RCO_2)_5-CH_2]^+$	533	0.3	603	2.0	673	0.5	673	0.1		–		–	693	4.0
$[M_4O(RCO_2)_5-C_2H_4]^+$		–		–	659	1.4		–		–		–	679	3.1
$[M_4O_2(RCO_2)_4]^+$	504	0.6	560	0.2	616	0.4	616	0.4	524	0.3	580	0.7	636	1.9
$[M_4O(RCO_2)_4]^+$	488	w(3.7)	544	0.4(4.0)	600	0.8(1.4)	600	0.5(1.6)	508	0.4(3.4)	564	1.4(3.5)	620	1.8(10.2)
$[M_4O_2(RCO_2)_3]^+$	445	1.3(0.4)	487	1.6	529	3.3	529	1.5	465	6.9(1.7)[f]	507	4.6	549	1.6
$[M_4O_2(OH)(RCO_2)_2]^+$		–		–		–		–	423	4.7		–		–
$[M_3O_2(RCO_2)_3]^+$	386	1.0		–		–		–		–		–		–
$[M_3O(RCO_2)_3]^+$	370	24.2	412	26.1	454	31.0	454	21.0	385	22.9	427	11.5	469	8.1
$[M_3O(RCO_2)_3-2]^+$		–	410	0.6	452	1.5	452	0.9		–		–		–
$[M_3O(RCO_2)_3-3]^+$		–	409	1.0	451	1.5	451	w		–		–		–
$[M_3O(RCO_2)_3-4]^+$		–	408	0.7	450	1.3	450	w		–		–		–
$[M_4O_3(RCO_2)]^+$		–		–		–		–	363	3.0		–		–
$[M_3O(OH)(RCO_2)_2]^+$	328	0.4	356	1.6	384	1.5	384	1.0		–		–		–
$[M_3O_2(RCO_2)_2]^+$	327	0.2		–		–		–		–		–		–
$[M_3O(R)(RCO_2)_2]^+$	326	w		–		–		–	341	4.0		–		–
$[M_3O(R)(RCO_2)_2-H_2O]^+$		–		–		–		–	323	2.0[g]		–		–
$[M_3O(H)(RCO_2)_2]^+$		–	340	2.0	368	1.3	368	0.8		–		–		–
$[M_3O(RCO_2)_2]^+$	311	6.7	339	0.8	367	2.3	367	1.0		–		–		–
$[M_3O(R)(OH)(RCO_2)]^+$		–		–		–		–	299	5.5		–		–
$[M_3O(H_2O)(RCO_2)]^+$		–		–	298	1.8	298	1.1		–		–		–
$[M_3O(OH)(RCO_2)]^+$	269	1.1	283	1.2	297	1.0	297	1.5		–		–		–
$[M_3O_2(RCO_2)]^+$	268	1.0	282	0.7	296	1.0	296	1.0	283	7.6		–		–
$[M_3O(H)(RCO_2)]^+$		–		–	281	0.1	281	0.2		–		–		–
$[M_3O(RCO_2)]^+$		–		–	280	0.1	280	0.4		–		–		–
$[M_2(RCO_2)_2]^+$	236	0.4		–		–		–		–		–		–
$[M_2O(RCO_2)]^+$	193	0.8	207	0.1	221	w	221	w	203	3.8		–		–
$[M(CO_2)(RCO_2)]^+$	162	0.7	176	w	190	w	190	w		–	181	5.8	195	1.8
$[M(R)(RCO_2)]^+$		–		–		–		–		–	166	1.1		–
$[M(C_2H_4)(RCO_2)]^+$		–		–	174	2.2	174	w		–		–	179	1.6
$[M(RCO_2)]^+$	118	0.3	132	0.2	146	2.2	146	2.5	123	0.8	137	24.4	151	3.0
$[MR]^+$		–		–		–		–	79	2.0	93	3.6	107	0.8
$[M]^+$	59	w	59	0.2	59	w	59	w	64	1.9	64	3.4	64	0.5

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions. All species are corrected for isotopic abundance. [b] Only metal-containing ions are recorded. [c] m/e values are given for the ions containing ^{64}Zn. [e] Figures in brackets indicate abundance of doubly charged species. [d] The spectrum also contains peaks corresponding to zinc-containing ions at m/e 187 (ab. 0.6) and 159/161 (ab. 1.4). [f] Combined abundance of $[M_4O(RCO_2)_3]^{2+}$ and $[M_4O_2(RCO_2)_3 + H]^{2+}$. [g] Combined abundance of ions at m/e 323 and 321.

TABLE II. Metastable Ions in $M_4O(RCO_2)_6$.

Transition	M/R in $M_4O(RCO_2)_6$	m/e Values for Transition	m*		Neutral Fragment
			Found[a]	Calcd.	
$[M_4O(RCO_2)_6]^+ \rightarrow [M_4O(RCO_2)_5]^+$	Co/Me	606→547	494	493.7	RCO_2
	Co/Et	690→617	552	551.7	
	Co/n-Pr	774→687	610	609.8	
	Co/i-Pr	774→687	610	609.8	
$[M_4O(RCO_2)_5]^+ \rightarrow [M_4O(RCO_2)_4]^+$	Co/n-Pr	687→600	524	524.0	RCO_2
	Co/i-Pr	687→600	524	524.0	
$[M_4O(RCO_2)_5]^+ \rightarrow [M_4O_2(RCO_2)_3]^+$	Co/Me	547→445	362	362.0	$(RCO)_2O$
	Co/Et	617→487	384	384.4	
$[M_4O(RCO_2)_5]^+ \rightarrow [M_3O(RCO_2)_3]^+$	Co/Et	617→412	275	275.1	$M(RCO_2)_2$
	Co/n-Pr	687→454	300	300.0	
	Co/i-Pr	687→454	300	300.0	
	Zn/Me	567→385	262	261.4	
	Zn/Et	637→427	285	286.2	
$[M_3O(RCO_2)_3]^+ \rightarrow [M_3O(RCO_2)_2]^+$	Co/Me	370→311	262	261.4	RCO_2
	Co/Et	412→339	279	278.9	
$[M_3O(RCO_2)_3]^+ \rightarrow [M_3O(OH)(RCO_2)_2]^+$	Co/Et	412→356	307	307.6	R CH=CO
	Co/n-Pr	454→384	325	324.8	
	Co/i-Pr	454→384	325	324.8	
$[M_3O(RCO_2)_2]^+ \rightarrow [M_3O(OH)(RCO_2)]^+$	Co/Me	311→269	233	232.7	R CH=CO
	Co/Et	339→283	236	236.2	
	Co/n-Pr	367→297	240 br.[b]	240.3	
	Co/i-Pr	367→297	240 br.	240.3	
$[M_4O_2(RCO_2)_3]^+ \rightarrow [M_3O(RCO_2)_2]^+$	Co/Me	445→311	218	217.3	$MO(RCO_2)$
	Co/Et	487→339	236	236.0	
$[M_3O(RCO_2)_3]^+ \rightarrow [M_3O(R)(RCO_2)_2]^+$	Co/Me	370→326	287	287.2	CO_2
	Zn/Me	385→341	302	302.0	
$[M_3O(H_2O)(RCO_2)]^+ \rightarrow [M_3O(RCO_2)]$	Co/n-Pr	298→280	263	263.1	H_2O
	Co/i-Pr	298→280	263	263.1	
$[M(CO_2)(RCO_2)]^+ \rightarrow [M(RCO_2)]^+$	Zn/Et	181→137	103	103.7	CO_2

[a] For the zinc compounds only transition involving ^{64}Zn are given. [b] Broad.

TABLE III. Accurate Mass Measurements on Selected Peaks.

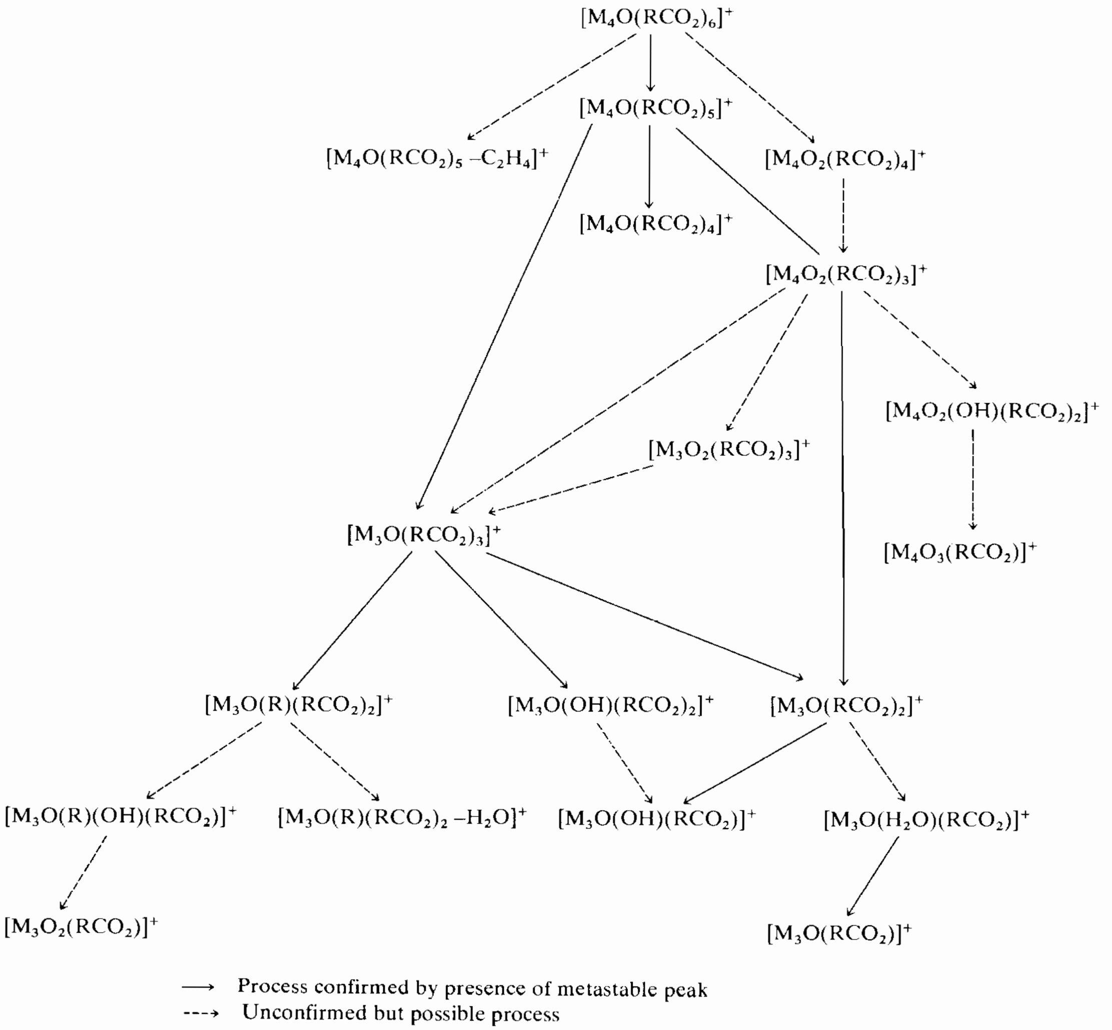
Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
$Co_4O(MeCO_2)_6$	445	444.7624	$C_6H_9O_8Co_4$	444.7620
	370	369.8339	$C_6H_9O_7Co_3$	369.8339
	311	310.8208	$C_4H_6O_5Co_3$	310.8213
	269	268.8102	$C_2H_4O_4Co_3$	268.8104
	268	267.8022	$C_2H_3O_4Co_3$	267.8024
	193	192.8746	$C_2H_3O_3Co_2$	192.8744
$Co_4O(EtCO_2)_6$	690	689.9023	$C_{18}H_{30}O_{13}Co_4$	689.9013
$Co_4O(n\text{-}PrCO_2)_6$	774	773.9928	$C_{24}H_{42}O_{13}Co_4$	773.9948
$Zn_4O(MeCO_2)_6$	465	464.7468	$C_6H_9O_8{}^{64}Zn_4$	464.7460
	423	422.7410	$C_4H_7O_7{}^{64}Zn_4$	422.7412
	363	362.7257	$C_2H_3O_5{}^{64}Zn_4$	362.7258
	341	340.8323	$C_5H_9O_5{}^{64}Zn_3$	340.8322
	203	202.8668	$C_2H_3O_3{}^{64}Zn_2$	202.8664
$Zn_4O(EtCO_2)_6$	710	709.8857	$C_{18}H_{30}O_{13}{}^{64}Zn_4$	709.8849
	637	636.8552	$C_{15}H_{25}O_{11}{}^{64}Zn_4$	636.8559
	707	706.9350	$C_{20}H_{35}O_{11}{}^{64}Zn_4$	706.9342
$Zn_4O(n\text{-}PrCO_2)_6$	195	194.9635	$C_5H_7O_4{}^{64}Zn$	194.9635
	179	179.0035	$C_6H_{11}O_2{}^{64}Zn$	179.0050
	151	150.9736	$C_4H_7O_2{}^{64}Zn$	150.9737

In all cases studied the initial fragmentation step involves loss of an $RCO_2\cdot$ radical from the molecular ion to give the ion $[M_4O(RCO_2)_5]^+$ which is the most intense ion in each spectrum (Scheme). Further fragmentation proceeds mainly by loss of the even-electron species $M(RCO_2)_2$ and $(RCO)_2O$. These processes are metastable supported in most of the compounds and are analogous to decomposition processes shown by the corresponding beryllium species.[5] In some compounds loss of the radicals $RCO\cdot$ and $RCO_2\cdot$ and of the even-electron species CH_2 and C_2H_4 from the ion $[M_4O(RCO_2)_5]^+$ is also observed. However, except for a few cases, these processes are not metastable supported and the daughter ions are of low intensity. The elimination of C_2H_4 is observed only when R = n-Pr and presumably arises by a McLafferty type of rearrangement.

Loss of a ligand radical from the even-electron ion $[M_4O(RCO_2)_5]^+$ leads to the odd-electron ion $[M_4O(RCO_2)_4]^{+\cdot}$. This ion is generally of low intensity but strikingly the corresponding doubly charged ion is invariably present in considerably higher abundance. For example when M = Zn and R = n-Pr the ion $[M_4O(RCO_2)_4]^{2+}$ is the second most abundant ion and carries 10% of the metal-containing current. The high stability of these doubly charged ions may be related to their even-electron character. A metastable transition involving the ion $[Zn_4O(MeCO_2)_4]^{2+}$ was reported earlier[7] but this or analogous transitions for the other compounds were not observed during this study.

Loss of an $M(RCO_2)_2$ species from $[M_4O(RCO_2)_5]^+$ leads to the ion $[M_3O(RCO_2)_3]^+$. This process is strongly metastable supported and the ion $[M_3O$

SCHEME. Fragmentation Scheme for $M_4O(RCO_2)_6$.



$(RCO_2)_3]^+$ is a very pronounced feature in the spectrum of each compound. The ion $[M_3O(RCO_2)_3]^+$ could also arise from $[M_4O_2(RCO_2)_4]^+$ *via* the ions $[M_4O(RCO_2)_3]^+$ and/or $[M_4O_2(RCO_2)_3]^+$. The high stability of the ion $[M_3O(RCO_2)_3]^+$ can be rationalized by postulating a planar structure for it. Such a structure allows extensive delocalization of charge between the out-of-plane orbitals of the metals and the oxo and carboxylato ligands. Although this rationalization of the stability of $[M_3O(RCO_2)_3]^+$ is regarded as speculative it should be noted that in the ions $[M_3O(MeCO_2)_6]^+$ (M = Cr or Fe)[15, 16] X-ray studies indicate that the M_3O core is planar and the oxygen atom is at the centre of the triangle of the metal atoms.

The fragmentation of the even-electron ions $[M_3O(RCO_2)_3]^+$ depends markedly on the nature of M and R. When M = Co the ions $[M_3O(RCO_2)_3]^+$ show a variety of decomposition reactions which involve loss of odd- and even-electron neutral species. These reactions are often metastable supported and lead to ions in which the trimetallic M_3O core is retained. In the case of the zinc compounds two types of behaviour are observed. When R = Me, the ion $[Zn_3O(RCO_2)_3]^+$ fragments exclusively by initial loss of carbon dioxide which is followed by further elimination of even-electron neutral species to give several trimetallic ions. When R = Et or n-Pr trimetallic ions, other than $[Zn_3O(RCO_2)_3]^+$, are absent. However, these compounds as well as $Zn_4O(MeCO_2)_6$, show several dimetallic and monometallic ions which are considerably more abundant than the analogous cobalt-containing ions. The reactions leading to these ions are obscured by the absence of relevant metastable transitions.

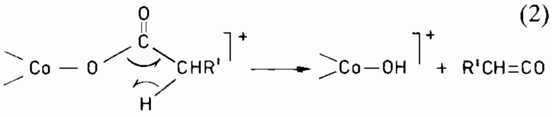
Decarboxylation of $[M_3O(RCO_2)_3]^+$ is observed for both metals but only when R = Me. This reaction is metastable supported and may result in the formation of metal–methyl species by migration


(1)

of the methyl group. The higher abundance of $[Zn_3O(Me)(MeCO_2)]^+$ compared with the abundance of $[Co_3O(Me)(MeCO_2)_2]^+$ and the tendency of the former ion only to retain the methyl group in subsequent decomposition reactions (Scheme), parallel the known greater stability of alkyl-zinc compounds compared with alkyl–cobalt compounds and support methyl migration to the metal. Further evidence for alkyl migration is provided by the ions $[MR]^+$. These ions are present only when M = Zn reflecting again the stability of alkyl–zinc compounds.

The main decomposition reactions of the ions $[Co_3O(RCO_2)_3]^+$ involve loss of ketene to give $[Co_3O(OH)(RCO_2)_2]^+$ or loss of a ligand radical to give $[Co_3O(RCO_2)_2]^+$. In addition all the cobalt compounds, except when R = CH_3, show weak ions corresponding to $[Co_3O(RCO_2)_3\text{–}nH]^+$ (n = 2,3 or 4) which may arise from $[Co_3O(RCO_2)]^+$.

The elimination of ketene from $[Co_3O(RCO_2)_3]^+$ can be attributed to a rearrangement of the following type:

(2)


The involvement of a hydrogen atom attached on the α-carbon atom is suggested because the reaction is significant when R = CH_3 as well as in all other cases. Loss of ketene is also observed in the decomposition of $[Co_3O(RCO_2)_2]^+$ and from the ions $[M_4O_2RCO_2)_3]^+$ (M = Zn or Co).

The elimination of a ligand radical from the even-electron ion $[M_3O(RCO_2)_3]^+$ occurs only when M = Co. This can be correlated with the ability of cobalt to change oxidation state by assuming that the reaction is accompanied by the reduction of the metal and that in the daughter ion one of the metal atoms has oxidation state +I (3):

$$[M^{II}{}_3O(RCO_2)_3]^+ \rightarrow [M^{II}{}_2M^{I}O(RCO_2)_2]^+ + RCO_2\cdot \quad (3)$$

This ability is also reflected in the elimination of a ligand radical from $[M_3O(RCO_2)_2]^+$ and in reaction (4), both of which are observed when M = Co but not when M = Zn:

$$[M_4O(RCO_2)_3]^+ \rightarrow [M_3O(RCO_2)_2]^+ + MO(RCO_2) \quad (4)$$

Reaction (4) is metastable supported when R = Me or Et and in the former case the composition of the eliminated species is indicated by exact mass measurements. If the species $MO(RCO_2)$, in which the metal has oxidation state +III, is eliminated in a single step then reaction (4) provides strong evidence for oxidation state changes in the spectra of the cobalt compounds. Several instances of elimination of neutral species containing the metal atom in a lower oxidation state than in the precursor molecule have been reported earlier.[14] The elimination of $MO(RCO_2)$, however, is the first example of elimination of a neutral species containing the metal in a higher oxidation state than in the precursor molecule.

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