Negative-ion Mass Spectra of Metal Complexes; Fluorinated β-Diketonates of Various Metals

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Summary A systematic negative-ion mass spectrometric study of a number of bi- and tri-valent derivatives of the ligand 1,1,1,5,5,5-hexafluoropentane-2,4-dione is reported; the results indicate that negative ion formation by secondary electron capture processes is potentially an extremely valuable technique for the characterization of inorganic complexes.

WE present a systematic negative-ion mass spectrometric study of a number of bi- and tri-valent metal derivatives of the ligand 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hexafluoroacetylacetone; LH).

A recent report[1] indicated the relative complexity of the negative-ion mass spectra of several metal-containing compounds. In contrast, the negative-ion spectra of complexes reported here, run at 70 eV, are much less complex than the corresponding positive ion spectra.[2–4] Molecular anions and ligand ions, in general, predominate, with fragments formed as a result of fluorine migrations and rearrangements also evident, usually only in low abundance. Metastable peaks in the spectra are characteristically very broad and of low intensity, in contrast to the metastable peaks found in 70 eV negative-ion spectra of organic compounds.[5]

It is known[5] that a wide range of organic compounds will accept an electron to produce molecular anions which then may fragment by simple cleavage processes or rearrangements, and evidence[5,6] has been presented suggesting that secondary electrons are captured to give molecular anions.

TABLE

Negative-ion mass spectra of metal hexafluoroacetylacetonates. Relative abundances (%)[a]

ML_3 Complexes

Ions	V	Cr	Mn	Fe	Co	Al
$[ML_3]^-$	100	7·4	0·6	7·6	1·4	100
$[ML_2F]^-$	3·8	<0·1	—	—	—	7·3
$[ML_2]^-$	0·3	—	2·2	2·2	32·1	2·4
$[ML_2-138]^-$	—	—	—	—	1·5	—
$[MLF_2]^-$	1·8	—	100	1·0	14·0	4·8
$[MLF]^-$	0·2	<0·1	2·4	1·1	27·2	1·5
$[L]^-$	87·0	100	6·3	100	100	41·9
$[F]^-$	6·4	1·2	7·0	0·9	0·8	2·2

ML_2 Complexes

Ions	Mn	Fe	Co	Ni	Cu	Zn	Mg
$[ML_2]^-$	1·1	2·7	100	34·4	100	100	8·5
$[ML_2-138]^-$	—	—	6·7	24·5	0·8[b]	—	2·4
$[MLF_2]^-$	100	2·1	68·2	—	—	90·5	100
$[MLF]^-$	1·7	2·5	99·1	16·1	1·0	67·8	—
$[L]^-$	24·2	100	22·7	100	80·5	87·1	22·5
$[F]^-$	1·8	—	—	—	1·0	26·2	9·2
$[MF_3]^-$	3·3	—	—	—	—	23·2	3·9

[a] Includes all metal-containing peaks. [b] Deuteriation showed this to be $[CuL.CF_3]^-$.

We propose that a similar secondary electron capture process may be operative for the formation of the molecular anions of metal complexes discussed here.

The Table shows the significant ions formed in the 70 eV negative-ion mass spectra of tris(hexafluoroacetylacetonates) of various metals. The chromium(III) and iron(III) chelates exhibit the simplest spectra and metastable peaks have been resolved for the transitions $[ML_3]^- \rightarrow [L]^-$ for them. Neutral fragments thus lost correspond to the stoicheiometry ML_2 where the metal may be inferred to be reduced to a lower oxidation state, *i.e.* +2. There are clear similarities in the spectra of the V^{III} and Al^{III} complexes; again changes of metal oxidation states are evident for the metals in the fragment ions.

Also in the Table are listed the significant ions formed in the 70 eV negative-ion mass spectra of bis(hexafluoroacetylacetones) of various metals. Intense molecular anions are formed by the Co^{II}, Cu^{II}, and Zn^{II} chelates and the fragment ions $[MLF_2]^-$, $[MLF]^-$ are also significant. Metastable peaks supporting fluorine migration processes were most readily observed for the Co^{II} chelate for the following transitions: $[CoL_2]^- \rightarrow [CoLF_2]^-$; $[CoL_2]^- \rightarrow [CoLF]^-$; $[CoLF_2]^- \rightarrow [L]^-$. Significantly, of all the metal chelates studied, the Co^{II} compound gave the highest ratio (1:3) of negative to positive ions in the ion source. The similarity in the spectra of the Mn^{II} and Mg^{II} chelates, particularly in the formation of the $[MLF_2]^-$ ion, the metastable transition $[MLF_2]^- \rightarrow [L]^-$ for the Mn^{II} compound, as well as the typical metallic behaviour for magnesium, indicate that they retain the oxidation state +2.

The spectra were obtained with a modified[7] Hitachi–Perkin-Elmer RMU-6L single-focussing mass spectrometer, under similar conditions to those previously described.[5]

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