Inorganica Chimica Acta, 18 (1976) L11 - L12

Acid–Base Chemistry in the Gas Phase; Interaction of Divalent Transition Metal Hexafluoroacetylacetonates with Pyridine under Chemical Ionization Mass Spectrometric Conditions

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Received February 24, 1976

We present results of a systematic study of the gas-phase interaction of a number of divalent transition metal derivatives of the ligand 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hexafluoroacetylacetone; LH) with pyridine (py) as reagent gas, under chemical ionization mass spectrometric conditions.

It is well known that anhydrous neutral complexes of the type Metal(ligand)$_2$, where the metal is divalent and the ligand bidentate, can function as highly reactive Lewis acids and form base adducts, thereby increasing the coordination number of the metal.[1,2] Such studies have, of necessity, been confined to the solution phase. Recently, reports[3-5] have indicated the potential of isobutane chemical ionization mass spectrometry in the study of organometallics as well as lanthanide perfluorinated β-diketonates. It is now recognised[6,7] that a variety of reagent gases conducive to various reaction types, such as acid–base and charge-transfer, are available for chemical ionization mass spectrometric studies. We now report results obtained from the interaction of pyridine, maintained at a pressure of 0.6 Torr, with a number of divalent metal hexafluoroacetylacetonates, maintained at ion source pressures of *ca.* 5 × 10^{-6} Torr and temperatures of between 100–150 °C, with sample temperatures of 35–85 °C.

Table I lists the significant ions formed in the C.I. mass spectra of these compounds, using pyridine as reagent gas. The spectra were all well resolved and, more importantly, completely devoid of positive ions of the types reported[8,9] for the 70 eV electron impact fragmentations of the same metal complexes. Thus, the most common significant ions for all metals were of the type [Metal·L·py$_2$]$^+$, [Metal·L·py$_3$]$^+$, [Metal·L$_2$·py$_2$]$^+$, in which displacement of one hexafluoroacetylacetonate ligand has been effected in the first two ions. In the latter ion pyridine has formed a possible six-coordinate species whose stability as an ion is apparently influenced by the $3d^n$ configuration of the metal. The first two species are unknown in the solution phase. One novel ion identified was [Ni·L·py$_4$]$^+$. The high relative abundance of the species [Cu·py$_2$]$^+$ is attributed to the formation of this ion from two precursor ions, *viz.*, Cu·L·py$_2^+$ and Cu·py$_3^+$. The most significant ions formed by pyridine itself under these pressure conditions were [pyH]$^+$ and [py$_2$H]$^+$, and similar ions are known to form from ammonia under comparable conditions.[6,7] Thus, the ions formulated as [Metal·L$_2$py$_3$ + H]$^+$ may be regarded as solvated [Metal·L$_2$py$_2$H]$^+$ species.

TABLE I. Relative intensities (%) of Significant Ions Formed by the Interaction of Pyridine as Reagent Gas with Divalent Metal Hexafluoroacetylacetonates, (Metal·L$_2$),[a] under Chemical Ionization Conditions.

Ions	Mn	Co	Ni	Cu	Zn
[Metal·py$_2$]$^+$	–	–	2	100	–
[Metal·py$_3$]$^+$	–	–	5	7	–
[Metal·L·py]$^+$	10	4	8	2	21
[Metal·L·py$_2$]$^+$	77	98	100	21	100
[Metal·L·py$_3$]$^+$	89	84	89	12	27
[Metal·L·py$_4$]$^+$	–	–	8	–	–
[Metal·L$_2$·py–F]$^+$	–	–	–	< 1	–
[Metal·L$_2$·py]$^+$	38	1	< 1	–	–
[Metal·L$_2$·py$_2$–F]$^+$	4	3	1	2	1
[Metal·L$_2$·py$_2$]$^+$	100	100	19	< 1	–
[Metal·L$_2$·py$_3$–F]$^+$	3	2	1	–	–
[Metal·L$_2$·py$_3$ + H]$^+$	1	17	45	–	–

[a] L = $CF_3COCHCOCF_3^-$; intensities are averaged from several spectra run under similar conditions. All species are corrected for isotopic abundance.

Table II lists metastable peaks observed for the main transitions involving loss of pyridine; that is, for the processes [Metal·L$_2$·py$_2$]$^+$ → [Metal·L$_2$·py]$^+$, [Metal·L·py$_3$]$^+$ → [Metal·L·py$_2$]$^+$ and [Metal·L·py$_2$]$^+$ → [Metal·L·py]$^+$, which is evidence, at least in part, for the reversibility of pyridine addition to these metal chelates. Thermal removal of pyridine from the various adduct species can be effected by the use of much higher ion source temperatures, that is, 200 °C or greater. The interaction of the metal chelates with pyridine is also affected by variations in sample pressures and also the use of other reagent gases such as alkyl-substituted pyridines.

The spectra were obtained on an AEI MS 902 mass spectrometer fitted with an SRI chemical ionization source, under conditions as described, with all metal chelates being characterized by both positive and negative[10] E.I. mass spectrometry before use in this study.

TABLE II. Metastable Ion Peaks[a] for Various Metal–Ligand–[b]Pyridine Species Decompositions.

Process		Mn	Co	Ni	Cu	Zn
$[\mathrm{Metal{\cdot}L_2{\cdot}py_2}]^+ \rightarrow [\mathrm{Metal{\cdot}L_2{\cdot}py}]^+$	obs.	479.0	483.0	c	487.0	–
	calc.	479.0	482.9	481.9	486.8	–
$[\mathrm{Metal{\cdot}L{\cdot}py_3}]^+ \rightarrow [\mathrm{Metal{\cdot}L{\cdot}py_2}]^+$	obs.	353.6	357.5	356.5	361.3	362.2
	calc.	353.5	357.4	356.4	361.3	362.3
$[\mathrm{Metal{\cdot}L{\cdot}py_2}]^+ \rightarrow [\mathrm{Metal{\cdot}L{\cdot}py}]^+$	obs.	276.8	280.6	280.0	284.6	285.5
	calc.	276.9	280.7	279.8	284.6	285.6
$[\mathrm{Metal{\cdot}L{\cdot}py_2}]^+ \rightarrow [\mathrm{Metal{\cdot}py_2}]^+$	obs.	–	–	c	114.2	–
	calc.	–	–	110.3	114.1	–

[a] The peaks were resolved in terms of ^{55}Mn, ^{59}Co, ^{58}Ni, ^{63}Cu, ^{64}Zn. [b] Ligand = L = $\mathrm{CF_3COCHCOCF_3^-}$. [c] Not observed.

Acknowledgement

We express thanks to the Australian Research Grants Committee for their support.

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