Inorganica Chimica Acta, 141 (1988) 163–164

Stepwise Ligand Dissociation and Multiple Changes in Oxidation State in the Fast Atom Bombardment (FAB) of Cyanometallate Complexes

KEITH R. JENNINGS, TERENCE J. KEMP*,
and BARBARA SIEKLUCKA**

*Department of Chemistry, University of Warwick,
Coventry CV4 7AL, U.K.*

(Received July 9, 1987)

Fast Atom Bombardment (FAB) mass spectrometry [1] has proved invaluable in providing molecular weight information for polar samples. Since it is a 'soft' ionisation technique, only limited fragmentation is observed, giving rise to relatively simple mass spectra and structural information. For example, the FAB mass spectra of many inorganic complexes contain few peaks arising from fragment ions; phthalocyanines [2] give spectra consisting primarily of molecular ions $M^{+\bullet}$ and protonated molecular ions MH^+ whereas certain chelates of Cu^{II} give FAB spectra consisting of peaks arising from $M^{+\bullet}$ and MH^+ ions and others resulting from the loss of one or two ligands [3]. The negative ion FAB mass spectra of polyoxotungstates contain peaks due to ions formed by sequential loss of WO_3 fragments and O atoms, attributed [4] to attachment of solvated electrons followed by H atom abstraction, leading to weakened bonding in the cluster and hence to fragmentation. The corresponding positive ion spectra are much simpler and consist primarily of the MH^+ ion, the formation of which is attributed [4] to H atom abstraction from the matrix by the relatively stable, but undetected, radical cation $M^{+\bullet}$. Pelzer *et al.* have shown that one-electron reduction occurs during FAB ionisation of simple inorganic salts of Cu^{II}, Fe^{III}, Co^{III} etc., to an extent reflecting the reducibility of the metal centre [5]. The FAB mass spectra of neutral organometallic compounds indicate that the ions $M^{+\bullet}$ or $MH^{+\bullet}$ readily lose one or more ligands such as CO and PPh_3 [6].

We find that the positive ion FAB mass spectra of alkali metal salts of a series of cyanometallates (metal = W^V, W^{IV}, Mo^{IV}, Cr^{III}, Fe^{III}, Fe^{II}, Mn^{II}, Ni^{II}) contain peaks due to a large number of fragment ions (e.g. as for $K_4[Fe(CN)_6]$ in Fig. 1), indicating not only sequential loss of up to four CN ligands but also a change of no less than 4 or 5 in the formal oxidation state of the metal centre, e.g. from +2 to −2 for Fe, and from +5 to +1 for W. The pattern for $K_4[Fe(CN)_6]$ is typical (see Table I).

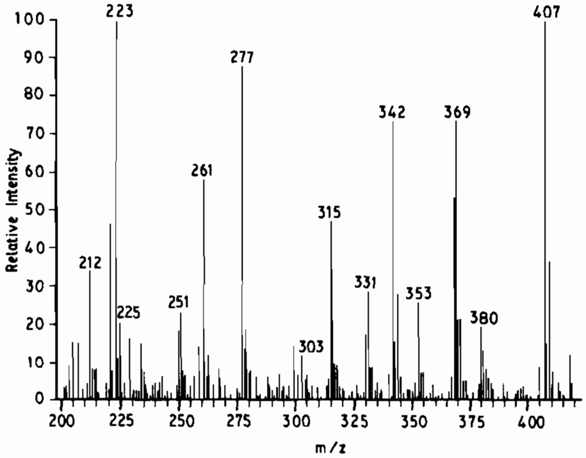

Fig. 1. Positive ion FAB mass spectrum of $K_4[Fe(CN)_6]$ (glycerol–water matrix). For assignments, see Table I.

TABLE I. Fragmentation Pattern in the Positive Ion FAB Mass Spectrum of $K_4[Fe(CN)]_6$

m/z	Molecular formula of fragment	Oxidation state of Fe
407(100)	$\{K_5[Fe(CN)_6]\}^+$	+2
380(19)	$\{K_5[Fe(CN)_5]\}^+$	+1
353(26)	$\{K_5[Fe(CN)_4]\}^+$	0
331(28)	$\{K_5[Fe(CN)_3]\}^+$	−1
303(12)	$\{K_5[Fe(CN)_2]\}^+$	−2
369(74)	$\{HK_4[Fe(CN)_6]\}^+$	+2
342(74)	$\{K_4[Fe(CN)_5]\}^+$	+2
315(47)	$\{K_4[Fe(CN)_4]\}^+$	+1
261(58)	$\{K_4[Fe(CN)_2]\}^+$	−1
303(12)	$\{K_3[Fe(CN)_5]\}^+$	+3
277(87)	$\{K_3[Fe(CN)_4]\}^+$	+2
251(23)	$\{K_3[Fe(CN)_3]\}^+$	+1
225(20)	$\{K_3[Fe(CN)_2]\}^+$	0

The formulation of the anionic components of the lower mass fragments is intriguing: solvated electrons show no tendency to add to free $[Fe(CN)_6]^{4-}$ ions in aqueous solution [7] but it may be that in gas phase ion clusters the lower oxidation states are more stable; certainly, the metals in the carbonylmetal species such as $[Mn(CO)_6]^+$, $[Fe(CO)_5]$, $[V(CO)_6]^-$ and $[Fe(CO)_4]^{2-}$ display very low oxidation states, and CO is isoelectronic with CN^-. Cyanometallates can feature metals in very low oxidation states [8, 9], e.g. $[Co(CN)_5]^{4-}$ and $[W(CN)_7]^{5-}$.

Negative ion FAB spectra of organic salts, (e.g. of PPh_4^+, $Bu_4{}^nN^+$) also display long fragment ion

---

*Author to whom correspondence should be addressed.

**On leave from Faculty of Chemistry, Jagiellonian University, Cracow, Poland.

0020-1693/88/$3.50

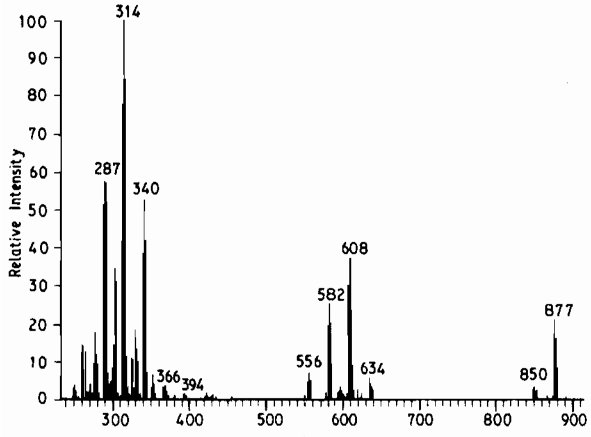

Fig. 2. Negative ion FAB mass spectrum of $(Bu_4{}^nN)_3[W(CN)_8]$ (3-nitrobenzyl alcohol matrix). For assignments, see text.

TABLE II. Fragmentation Pattern in the Negative Ion FAB Mass Spectrum of $(Bu_4{}^nN)_3[W(CN)_8]$

m/z	Molecular formula of fragment	Oxidation state of W
877(21)	$\{(Bu_4{}^nN)_2[W(CN)_8]\}^-$	+5
850(3)	$\{(Bu_4{}^nN)_2[W(CN)_7]\}^-$	+4
634(6)	$\{(Bu_4{}^nN)[W(CN)_8]\}^-$	+6
608(37)	$\{(Bu_4{}^nN)[W(CN)_7]\}^-$	+5
582(26)	$\{(Bu_4{}^nN)[W(CN)_6]\}^-$	+4
556(7)	$\{(Bu_4{}^nN)[W(CN)_5]\}^-$	+3
394(2)	$[W(CN)_8]^-$	+7
366(3)	$[W(CN)_7]^-$	+6
340(53)	$[W(CN)_6]^-$	+5
314(100)	$[W(CN)_5]^-$	+4
287(58)	$[W(CN)_4]^-$	+3

sequences, e.g. $(Bu_4{}^nN)_3[W(CN)_8]$ in Fig. 2, for which the formulae and oxidation states were assigned as in Table II. Although the abundance of the $[W(CN)_8]^-$ ion is low in this case, its relative abundance is increased several-fold in the mass spectrum of $(PPh_4)_3[W(CN)_8]$.

Clearly, the cyanometallates give rise to a range of fragment ions, in both positive and negative FAB mass spectra, indicating the stability in the gas phase of ions possessing unusual oxidation states and coordination numbers. The fragmentation patterns are reminiscent of the matrix photochemistry of metal carbonyls and reflect not only on the gas phase chemistry of coordination compounds but also give insight into the excitation processes involved in the FAB mass spectra of inorganic materials.

Acknowledgements

We thank the S.E.R.C. for funding the visit of Barbara Sieklucka to the U.K. through a Visiting Fellowship. Mr Inder Katyal is thanked for technical assistance with FAB measurements. Professor Alina Samotus is thanked for encouragement and for gifts of compounds.

References

1 M. Barber, R. S. Bordoli, R. D. Sedgwick and A. N. Tyler, *J. Chem. Soc., Chem. Commun.*, 325 (1981).
2 R. B. Freas and J. E. Campana, *Inorg. Chem.*, *23*, 4654 (1984).
3 R. L. Cerny, M. M. Bursey, D. L. Jameson, M. R. Malachowski and T. N. Sorrell, *Inorg. Chim. Acta*, *89*, 89 (1984).
4 K. S. Suslick, J. C. Cook, B. Rapko, M. W. Droege and R. G. Finke, *Inorg. Chem.*, *25*, 241 (1986).
5 G. Pelzer, E. De Pauw, D. V. Dung and J. Marien, *J. Phys. Chem.*, *88*, 5065 (1984).
6 R. Davis, I. F. Groves, J. L. A. Durrant, P. Brooks and I. Lewis, *J. Organomet. Chem.*, *241*, C27 (1983).
7 M. Anbar and E. J. Hart, unpublished data (quoted in M. Anbar and P. Neta, 'A compilation of rate constants of e^-_{aq}, H, and OH reactions with inorganic and organic compounds in aqueous solution', *Report 1A-1079*, Israel Atomic Energy Commission, Soreq Nuclear Research Centre, 1966, p. 8).
8 G. D. Venerable, II and J. Halpern, *J. Am. Chem. Soc.*, *93*, 2176 (1971).
9 A. M. Soares and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1886 (1981).