Stepwise Ligand Dissociation and Multiple Changes in Oxidation State in the Fast Atom Bombardment Mass Spectra of Cyanometalate Complexes of Transition Metals *

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Both positive- and negative-ion fast atom bombardment (f.a.b.) mass spectra of cyanometalate complexes (metal = Fe, Cr, Mn, Ni, Mo, or W in various oxidation states) show considerable fragmentation, especially when the counter ion is an alkali metal. Analysis of the spectra reveals the existence of several families of ions from each complex, each family being characterised by the number of cations associated with the complex ion. Each family of ions give long sequences of peaks which indicate the sequential loss of neutral CN and possibly $(CN)_2$ fragments, a conclusion confirmed by searching for the precursors of a given daughter ion. As each CN fragment is lost, the oxidation state of the metal decreases by one, leading eventually to very low oxidation states and co-ordination numbers. These sequential processes have implications for the mechanism of f.a.b., which is viewed as a gas-phase rather than a matrix process.

Fast atom bombardment (f.a.b.) mass spectrometry [1] was developed initially for studies of involatile organic compounds but, more recently, a number of applications of the technique to organometallic compounds (such as carbonyl,[2] triphenylphosphine,[2c,2f] and alkene [2e] complexes of transition metals, including clusters [2f]) have been described. Bojesen [3] has investigated the f.a.b. mass spectra of a series of co-ordination compounds featuring mono- and poly-dentate *N*-donor ligands. Aqueous solutions of $[PtX(PEt_3)_3]^+$ ions also yield good f.a.b. spectra (X = Cl or H).[4] A recent investigation [5] dealt with positive- and negative-ion f.a.b.–m.s. (fast atom bombardment–mass spectrometry) of very large polyoxoanions such as $[H_2Si_2W_{18}Nb_6O_{77}]^{6-}$; the negative-ion spectra showed sequential loss of WO_3 fragments and of O atoms, while the positive-ion spectra showed much less fragmentation. Phthalocyanines give very little or no fragmentation [6] while various Cu^I and Cu^{II} chelates yield the intact cation.[7]

Noting the sequential loss of CO from neutral and charged carbonyl–metal species, and the isoelectronic identity of CO and CN^- ligands, we have investigated the processes undergone by a series of cyanometalate complexes, $[A^+]_n[M'(CN)_x]^{n-}$ (A = cation) during both positive and negative f.a.b.–m.s. A preliminary note relating to part of this work has appeared.[8]

Experimental

The mass spectra were obtained on an MS 80 mass spectrometer fitted with a f.a.b. gun (Kratos Analytical Instruments) and data were analysed using a DS 55 data system. The primary xenon beam energy was 8 keV with a gun current of 1 mA and all spectra were recorded using an unheated sample probe at a resolution of *ca.* 1000.

Matrices for alkali-metal salts were either a glycerol–water mixture or a 5:1 mixture of dithiothreitol and dithioerythritol [diastereoisomers of $HSCH_2CH(OH)CH(OH)CH_2SH$]. These were equally effective, but it so happened that the former was used for potassium and caesium salts and the latter for sodium salts. Tetra-n-alkylammonium, tetraphenylphosphonium, and bipyridinium salts were examined in a matrix of 3-nitrobenzyl alcohol (nba).

Table 1. R.m.m. values of complexes studied, including principal isotopic patterns

Complex	R.m.m.
$K_3[Cr(CN)_6]$	325,* 326
$K_3[Mn(CN)_5(NO)]$	332
$K_3[Fe(CN)_6]$	329
$K_4[Fe(CN)_6]$	368
$K_2[Ni(CN)_4]$	240,* 242
$K_4[Mo(CN)_8]$	456, 458, 459, 460, 461, 462,* 464
$[\{Mo(CN)_8\}(H_3O)(Hbipy)_3]$	791, 793, 794, 795, 796, 797,* 799
$[NBu_4]_4[Mo(CN)_8]$	1 270, 1 272, 1 273, 1 274, 1 275, 1 276,* 1 278
$Na_3[W(CN)_8]$	459, 460, 461,* 463
$Na_4[W(CN)_8]$	482, 483, 484,* 486
$K_3[W(CN)_8]$	507, 508, 509,* 511
$K_4[W(CN)_8]$	546, 547, 548,* 550
$Cs_3[W(CN)_8]$	789, 790, 791,* 793

* Major isotopic species.

Cyanometalate complexes were either obtained from commercial suppliers or were prepared by standard techniques; several of the latter complexes were gifts from colleagues of B. S. at the Jagiellonian University, Cracow.

Results and Discussion

Both positive and negative f.a.b.–m.s. of a variety of cyanometalates $[A^+]_n[M'(CN)_x]^{n-}$ (Table 1) gave highly structured spectra (Figures 1 and 2) indicating the loss of one to six CN ligands. The nature of A was significant: where A was an alkali metal (Na, K, or Cs) both positive- and negative-ion spectra were obtained, although the latter generally contained more intense background peaks. 'Cleaner' negative-ion spectra were obtained when A was an organic cation such as $[NBu^n{}_4]^+$ or $[PPh_4]^+$, but these salts gave no positive-ion spectra. Accordingly, discussion is in terms of positive and negative species.

Positive-ion Spectra of Cyanometalates.—These are exemplified in Figures 1 and 2 and summarised in Table 2. Where M′ consists of several isotopes the r.m.m. (relative molecular mass) referred to in the discussion of a particular fragment is that of

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* *Non-S.I. units employed:* eV = 1.602×10^{-19} J, a.m.u. = 1.66×10^{-27} kg.

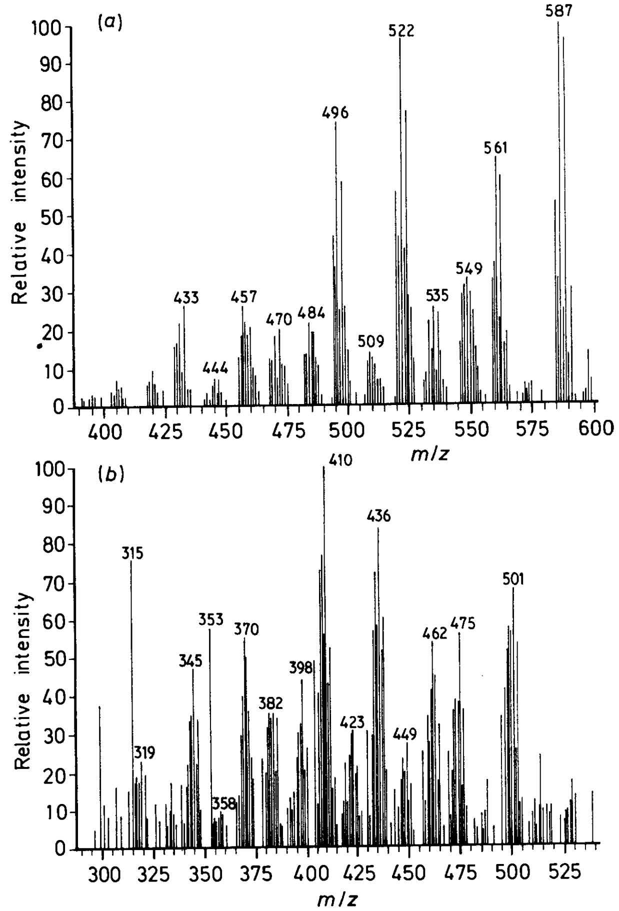


Figure 1. Positive-ion f.a.b.–m.s. spectra of $K_4[M(CN)_8]$ salts in a glycerol–water matrix: (a) M = W; (b) M = Mo

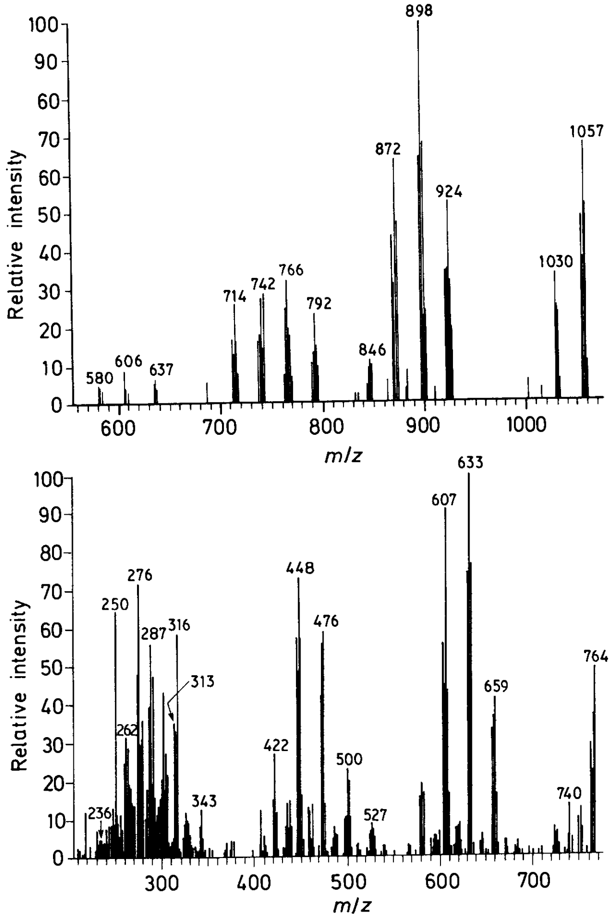
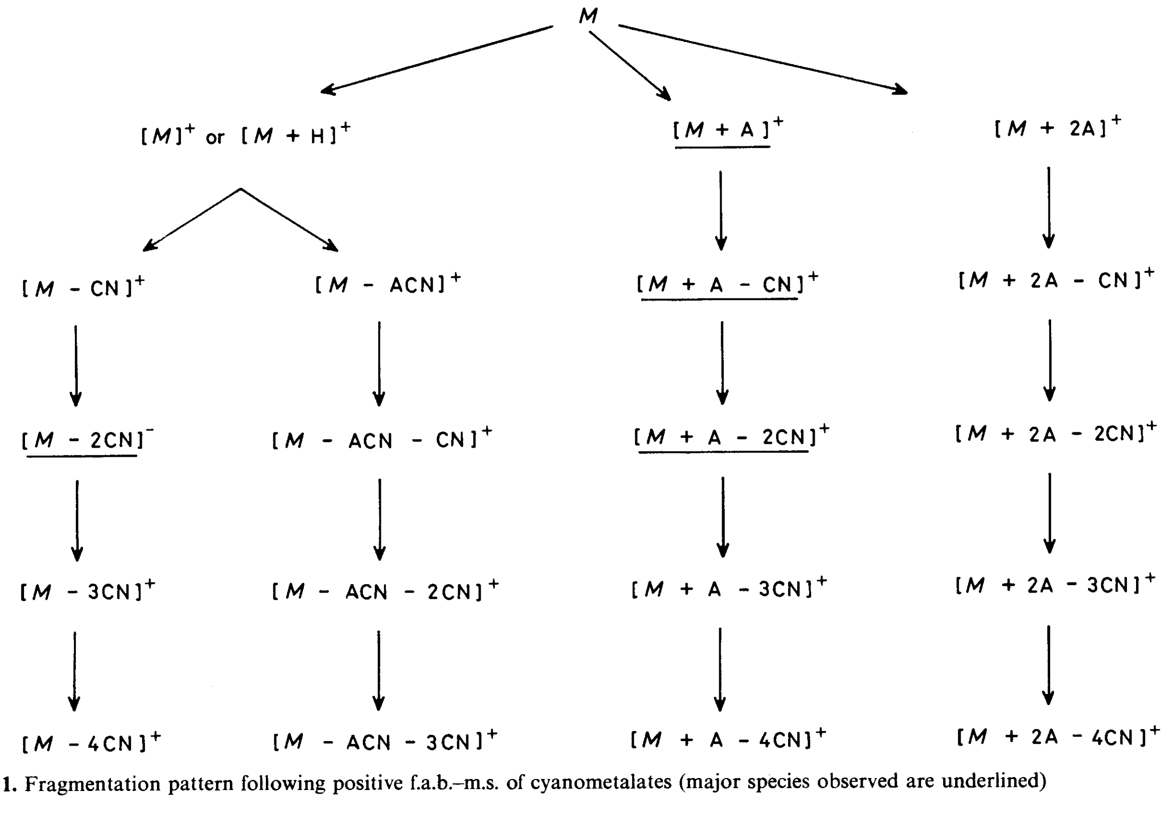


Figure 2. F.a.b.–m.s. spectra of $Cs_3[W(CN)_8]$ in a glycerol–water matrix. (a) Positive-ion spectrum; (b) negative-ion spectrum



Scheme 1. Fragmentation pattern following positive f.a.b.–m.s. of cyanometalates (major species observed are underlined)

Table 2. Masses and percentage relative abundances (normalised to highest sample peak) observed in the positive f.a.b.–mass spectra of complex cyanides

Ions observed	$K_3[Cr(CN)_6]$	$K_3[Fe(CN)_6]$	$K_4[Fe(CN)_6]$	$K_2[Ni(CN)_4]$	$K_4[Mo(CN)_8]$
$[M + 2A]^+$		407 (58)		317 (20)	
$[M + 2A - CN]^+$		380 (17)		292 (4)	
$[M + 2A - 2CN]^+$		353 (20)		266 (6)	
$[M + 2A - 3CN]^+$		330^a (37)			
$[M + 2A - 4CN]^+$					
		368 (61)			
$[M + A]^+$	364 (93)	342 (66)	407 (100)	279 (100)	501 (67)
$[M + A - CN]^+$	338 (36)	315 (47)	380 (19)	253 (31)	475 (56)
$[M + A - 2CN]^+$	311 (93)	293 (16)	353 (26)	227 (6)	449 (27)
$[M + A - 3CN]^+$			331 (28)		423 (30)
$[M + A - 4CN]^+$			303^a (12)		398^a (44)
$[M]^+$ or $[M + H]^+$(*)	*326 (7)	*330^a (37)	*369 (74)	*241 (11)	462 (54)
$[M - CN]^+$	299 (27)	303 (26)	342 (74)	214 (13)	436 (83)
$[M - 2CN]^+$	273 (100)	277 (100)	315 (47)	188 (75)	410 (100)
$[M - 3CN]^+$	247 (13)	250 (27)			382 (35)
$[M - 4CN]^+$			261 (58)		358 (10)
$[M - ACN]^+$		261 (36)	303^a (12)		398^a (44)
$[M - ACN - CN]^+$	234 (27)	234 (20)	277 (87)	150 (5)	370 (55)
$[M - ACN - 2CN]^+$	207 (38)	212 (64)	251 (23)		345 (47)
$[M - ACN - 3CN]^+$			225 (20)		319 (23)

Ions observed	$Na_3[W(CN)_8]$	$Na_4[W(CN)_8]$	$K_3[W(CN)_8]$	$K_4[W(CN)_8]$	$Cs_3[W(CN)_8]$
$[M + 2A]^+$	507 (64)		589 (63)		1 057 (68)
$[M + 2A - CN]^+$	481 (16)		561 (42)		1 030 (26)
$[M + 2A - 2CN]^+$	456 (76)		535 (24)		
$[M + 2A - 3CN]^+$	430 (35)		510 (13)		
$[M + 2A - 4CN]^+$	405 (8)		484^a (18)		
$[M + A]^+$	484 (64)	507 (44)	548 (39)	587 (100)	924 (52)
$[M + A - CN]^+$	460 (100)	484^a (94)	524 (100)	561 (63)	898 (100)
$[M + A - 2CN]^+$	434^a (51)	458^a (100)	498 (69)	535 (26)	872 (64)
$[M + A - 3CN]^+$	408^a (31)	430 (44)	470 (17)	509 (14)	846 (11)
$[M + A - 2CN]^+$	381 (19)		445^a (6)	484^a (22)	
$[M]^+$ or $[M + H]^+$(*)	*463 (23)	484^a (94)	510 (13)	*549 (32)	*792 (24)
$[M - CN]^+$	434^a (51)	458^a (100)	484^a (18)	522 (93)	766 (32)
$[M - 2CN]^+$	408^a (31)	434 (65)	457 (24)	496 (72)	742 (29)
$[M - 3CN]^+$	383 (17)	408^a (23)	433 (32)	470 (20)^b	714 (26)
$[M - 4CN]^+$	359 (6)	381^a (23)	405 (6)	444 (8)	
$[M - ACN]^+$	411 (28)	435 (50)	445^a (6)	484^a (22)	637 (7)
$[M - ACN - CN]^+$	385 (13)	408^a (23)	419 (9)	457 (26)	606 (9)
$[M - ACN - 2CN]^+$	361 (9)	381^a (23)		433 (27)	580 (5)
$[M - ACN - 3CN]^+$	331 (29)		366 (8)		

[a] Pairs of overlapping peaks at a particular mass number. [b] $K_4[W(CN)_8]$ also shows a strong cluster at 490; we ascribe this tentatively to $[M - 3CN + H_2O]^+$ or $[M - 3CN + OH]^+$. This peak is also present to a lesser extent in the spectrum of $K_3[W(CN)_8]$.

the most abundant isotope; in certain cases, *e.g.* tungsten with ^{182}W (26.41%), ^{184}W (30.64%), and ^{186}W (28.41%), there can be ambiguity over which is the major peak of a cluster, especially if there is statistical variation of ion current and small sample concentration variation. All spectra contain peaks due to many fragment ions, indicating ready loss of one or more CN ligands to give a series of fragments of sufficient stability to provide good levels of detection. If one denotes the principal r.m.m. of the complex as *M*, the peaks observed fall into four series as summarised in Scheme 1 (A = metal cation).

The higher r.m.m. species in each series deserves comment. $[M + 2A]^+$ refers to the original complex clustered with two cations but bearing a charge of +1, *i.e.* the metal centre M′ has been subject to one-electron reduction. In $[M + A]^+$ or $[M + H]^+$ the oxidation state of M′ is unchanged, while in $[M]^+$ the oxidation level of the metal centre M′ is increased by +1 unit. Within a series, as CN ligands are lost without change either in the total charge of +1 or the number of cations in the cluster, the formal oxidation state of the metal is reduced by one for each CN ligand lost, as exemplified by the sequence of oxidation states observed in the fragment ions given by $K_4[Fe(CN)_6]$ as follows:

Ion observed (abbreviated form)	Ion observed (molecular formula)	Oxidation state of Fe
$[M + H]^+$	$\{K_4H[Fe(CN)_6]\}^+$	+2
$[M - CN]^+$	$\{K_4[Fe(CN)_5]\}^+$	+2
$[M - 2CN]^+$	$\{K_4[Fe(CN)_4]\}^+$	+1
$[M - 3CN]^+$	$\{K_4[Fe(CN)_3]\}^+$	0
$[M - 4CN]^+$	$\{K_4[Fe(CN)_2]\}^+$	−1

The cyanoferrate moieties display oxidation states well known in carbonyl–metal species, such as $[Mn(CO)_6]^+$, $Fe(CO)_5$, $[V(CO)_6]^-$, $[Fe(CO)_4]^{2-}$, $Ni(CO)_3$,[9] and $[Ni(CO)_3]^-$.[10] The stabilising effect of cyanide ligands on low oxidation states is evident from the observation of Co^I in

Table 3. Masses and percentage relative abundances (normalised to highest sample peak) in the negative f.a.b.–mass spectra of complex cyanides containing alkali-metal cations

Ions observed	$K_3[Fe(CN)_6]$	$K_4[Fe(CN)_6]$	$K_3[W(CN)_8]$	$K_4[W(CN)_8]$	$Cs_3[W(CN)_8]$
$[M]^-$	329 (85)	367 (39)	507 (11)	548 (4)	
$[M - \text{CN}]^-$	302 (44)	340 (30)	481 (7)	523 (59)	764 (30)
$[M - 2\text{CN}]^-$		318 (9)			740 (13)
$[M - \text{A}]^-$	290 (41)	329 (93)		507 (6)	659 (41)
$[M - \text{A} - \text{CN}]^-$	264 (100)	302 (57)	445 (56)	483 (5)	633 (100)
$[M - \text{A} - 2\text{CN}]^-$	237 (33)	275 (27)	419 (100)	461 (17)	607 (90)
$[M - 2\text{A}]^-$	252 (6)	291 (49)	434 (7)	473 (10)^a	527 (8)
$[M - 2\text{A} - \text{CN}]^-$	225 (13)	264 (100)	407 (16)	445 (39)	500 (22)
$[M - 2\text{A} - 2\text{CN}]^-$	199 (70)	237 (41)	379 (61)	419 (100)	474 (56)
$[M - 2\text{A} - 3\text{CN}]^-$	172 (89)	212^b (15)	353 (84)		448 (73)
$[M - 2\text{A} - 4\text{CN}]^-$	147 (12)	187^b (38)	327 (48)		422 (26)
$[M - 2\text{A} - 5\text{CN}]^-$	121 (7)	161^b (20)	302 (69)		
$[M - 2\text{A} - 6\text{CN}]^-$			276 (73)		
$[M - 2\text{A} - 7\text{CN}]^-$			250 (30)		343^b (13)
$[M - 3\text{A}]^-$		253 (14)	392 (29)	432 (3)	
$[M - 3\text{A} - \text{CN}]^-$		223 (11)	367 (21)	407 (13)	
$[M - 3\text{A} - 2\text{CN}]^-$	160 (11)	199 (73)	341 (27)	379 (38)	341^b (8)
$[M - 3\text{A} - 3\text{CN}]^-$		173 (66)	314 (44)	355 (65)	313 (35)
$[M - 3\text{A} - 4\text{CN}]^-$		147 (29)	288 (96)	327 (37)	287 (39)
$[M - 3\text{A} - 5\text{CN}]^-$		121 (13)	262 (65)	302 (35)	262 (31)
$[M - 3\text{A} - 6\text{CN}]^-$			236 (10)	276 (46)	236 (5)
$[M - 3\text{A} - 7\text{CN}]^-$				250 (25)	
$[M - 4\text{A}]^-$		212^b (15)		393 (33)	
$[M - 4\text{A} - \text{CN}]^-$		187^b (38)		365 (10)	
$[M - 4\text{A} - 2\text{CN}]^-$		161^b (20)		341 (19)	
$[M - 4\text{A} - 3\text{CN}]^-$				314 (20)	
$[M - 4\text{A} - 4\text{CN}]^-$				288 (49)	
$[M - 4\text{A} - 5\text{CN}]^-$				262 (38)	
$[M - 4\text{A} - 6\text{CN}]^-$				236 (7)	

[a] A peak at 490 (67) is not attributable to any non-solvated species. The water solvate of $[M - 2\text{A}]^-$ has $m/z = 488$. The glycerol solvate of $[M - 4\text{A}]^-$ has $m/z = 485$. $\{K_3[W(CN)_8]$ shows a strong peak at $m/z = 522$ (67) attributable to $[(M - 2\text{A})\text{glycerol}]^-$ with $m/z = 526\}$. [b] Pairs of overlapping peaks.

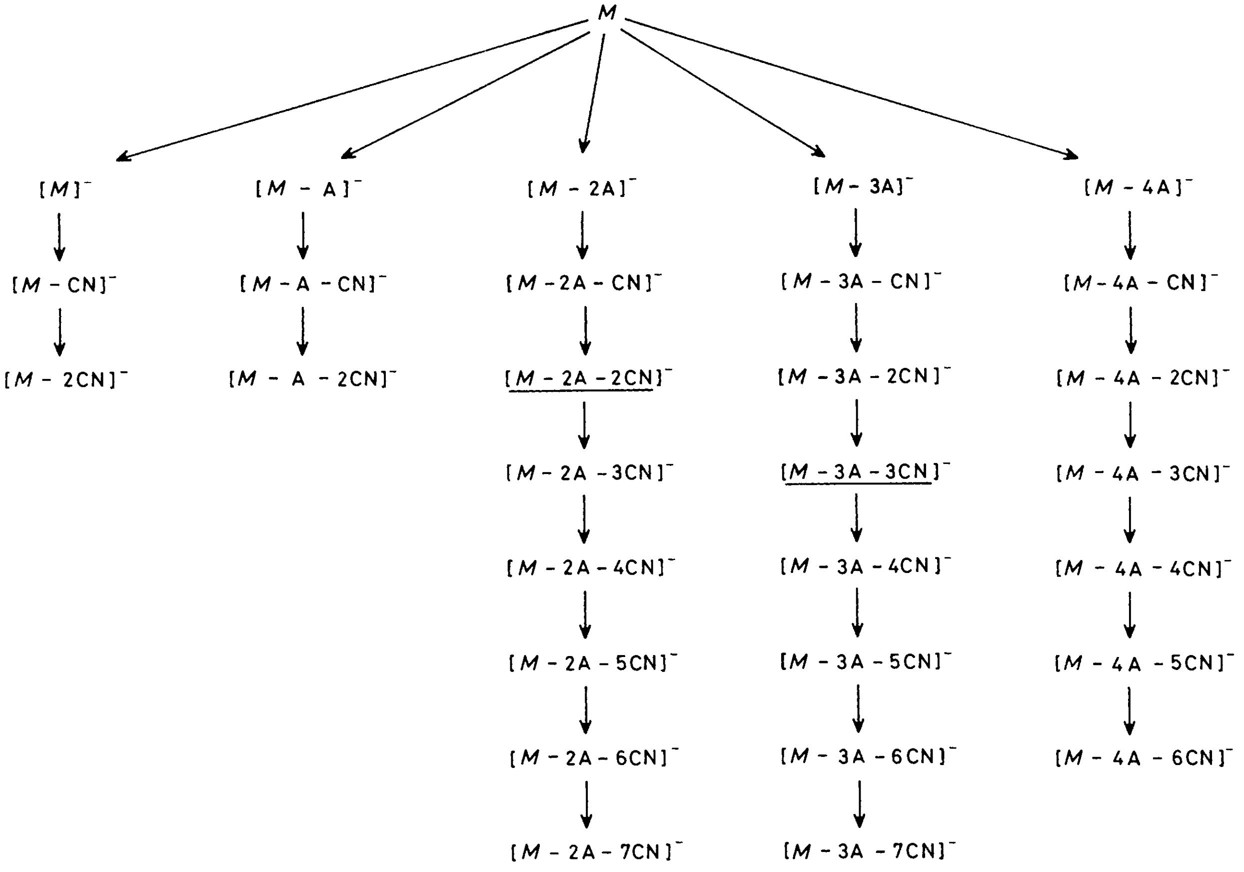
Table 4. Masses and percentage relative abundances (normalised to highest sample peak) of peaks observed in the negative f.a.b.–mass spectra of complex cyanides containing organic cations (matrix = nba)

Ions observed	Complex		
	$[NBu_4]_4[Mo(CN)_8]$	$[NBu_4]_3[W(CN)_8]$	$[PPh_4]_3[W(CN)_8]$
$[M - \text{A}]^-$	1 031 (9)	877 (21)	1 070 (38)
$[M - \text{A} - \text{CN}]^-$		850 (3)	1 044 (9)
$[M - 2\text{A}]^-$	785 (48)	634 (6)	733 (25)
$[M - 2\text{A} - \text{CN}]^-$	762 (16)	608 (37)	706 (62)
$[M - 2\text{A} - 2\text{CN}]^-$	735 (15)	582 (26)	680 (40)
$[M - 2\text{A} - 3\text{CN}]^-$		556 (7)	654 (5)
$[M - 3\text{A}]^-$	546 (6)	394 (2)	392 (9)
$[M - 3\text{A} - \text{CN}]^-$	522 (8)	366 (3)	366 (12)
$[M - 3\text{A} - 2\text{CN}]^-$	495 (79)	340 (53)	340 (39)
$[M - 3\text{A} - 3\text{CN}]^-$	469 (100)	314 (100)	314 (100)
$[M - 3\text{A} - 4\text{CN}]^-$	443 (7)	287 (58)	288 (49)

$[Co(CN)_5]^{4-}$ obtained on reduction of $[Co(CN)_5]^{3-}$ by $e^-(aq)$[11] and in such ions[12,13] as $[W(CN)_7]^{5-}$, $[Mo(CN)_7]^{4-}$, $[V(CN)_7]^{4-}$, and $[Re(CN)_7]^{4-}$. The hydrated electron, $e^-(aq)$, does not reduce $[Fe(CN)_6]^{4-}$ in aqueous solution, however, and it is clear that the attainment of such low oxidation states in the gas phase is associated with a concomitant loss of CN or $(CN)_2$ which is not achieved in solution. The alternative formulation of regarding the excess of electrons as situated on the ligands, *i.e.* formally as $[CN]^{2-}$, is much less attractive: aqueous cyanide ion shows immeasurably low reactivity towards solvated electrons,[14] with k_2 for $e^-(aq) + CN^- < 10^6$ dm^3 mol^{-1} s^{-1}.

The low co-ordination numbers achieved after loss of several CN groups also find their analogues in metal–carbonyl chemistry and photochemistry in rigid matrices at low temperatures, *e.g.* in $Fe(CO)_4$,[15] $Ni(CO)_3$,[8,16] and $Ta(CO)_n$ (n = 1—6).[16]

Although the spectra may be rationalised by assuming that successive loss of CN radicals occurs, one cannot rule out the more energetically favourable loss of $(CN)_2$ as a single entity. In



Scheme 2. Fragmentation pattern following negative f.a.b.–m.s. of cyanometalates (major species observed are underlined)

the positive f.a.b. mass spectrum of $K_4[W(CN)_8]$, precursors of the daughter ion, $m/z = 496$, were shown to be the ions of $m/z = 522$ and 548 by scanning the accelerating voltage at constant electric and magnetic field strengths. The loss of 56 a.m.u. (atomic mass unit) could be due to loss of $(CN)_2$ or to the rapid successive loss of two CN radicals in the field-free region between the ion source and electric sector. (We thank a referee for suggesting this experiment.) The multiple loss of CN radicals in the first field-free region finds an analogue in that of CO loss from $[Cr(\eta^6\text{-}PhCH_3)(CO)_3]^{\cdot +}$ which occurs both singly and multiply,[17a] and also from various ions $[Cr(CO)_n]^{\cdot +}$ derived from $Cr(CO)_6$.[17b]

Negative-ion Spectra.—These are illustrated by Figure 2(*b*) and summarised in Tables 3 and 4. Rich fragmentation patterns are evident, which are summarised in Scheme 2. Loss of up to six CN groups occurs only with alkali-metal cation salts. In the case of salts of organic cations, the loss of *n* CN groups is accompanied by loss of *n* or *n* − 1 cations and the very low oxidation states achieved in positive-ion f.a.b. are not found. The alkali-metal salts yield both very high and very low oxidation states, *e.g.* in the following sequence for $K_4[W(CN)_8]$:

Ion observed (abbreviated form)	Ion observed (molecular formula)	Oxidation state of W
$[M - 4A]^-$	$[W(CN)_8]^-$	+7
$[M - 4A - CN]^-$	$[W(CN)_7]^-$	+6
$[M - 4A - 2CN]^-$	$[W(CN)_6]^-$	+5
$[M - 4A - 3CN]^-$	$[W(CN)_5]^-$	+4
$[M - 4A - 4CN]^-$	$[W(CN)_4]^-$	+3
$[M - 4A - 5CN]^-$	$[W(CN)_3]^-$	+2
$[M - 4A - 6CN]^-$	$[W(CN)_2]^-$	+1

The final member of the $[M - 3A]^-$ family from $K_4[W(CN)_8]$ is, at m/z 250, $[M - 3A - 7CN]^-$, *i.e.* $\{K[W(CN)]\}^-$ containing W^0. Also striking is the $[M - 4A]^-$ species from $K_4[Fe(CN)_6]$, *i.e.* $[Fe(CN)_6]^-$ containing Fe^V and its CN radical-loss product $[Fe(CN)_5]^{\cdot -}$. The ultimate members of the $[M - 2A]^-$ sequence derived from $K_3[Fe(CN)_6]$ are m/z 147 (12) and 121 (7) attributed to $[M - 2A - 4CN]^-$ and $[M - 2A - 5CN]^-$ respectively, *i.e.* $\{K[Fe(CN)_2]\}^-$ (Fe is as Fe^0) and $\{KFe(CN)\}^-$ (Fe is as Fe^{1-}). The appearance of high oxidation states, *e.g.* Fe^V, Fe^{IV}, and Fe^{III} from $[Fe(CN)_6]^{4-}$ and W^{VII}, W^{VI}, and W^V from $[W(CN)_8]^{4-}$ is surprising in a *negative* f.a.b. experiment. It appears to be associated with the loss of several cations from the ion cluster without simultaneous loss of CN^- ions; these are lost subsequently, certainly singly and possibly pair-wise, to give the sequences shown in Scheme 2. The entropy gain from fragmentation of the ion cluster more than compensates for the gas-phase free energy of oxidation of the metal centre.

The other general feature of the negative-ion spectra is the lower background of those obtained from salts of organic cations: those from the alkali-metal salts show extensive background with minor peaks at virtually every mass number. However, the vast majority of species described in Table 3 give a relatively low intensity background spectrum.

Mixed Ligand Complex.—Tripotassium pentacyanonitrosylmanganate(II) gave a positive-ion f.a.b. spectrum indicating loss either of one cyano group or the nitrosyl group, or both, but multiple loss of cyano groups did not occur (Table 5).

Mixed Cation Complex.—$[\{Mo(CN)_8\}(H_3O)(Hbipy)_3]$ (bipy = 2,2′-bipyridyl)[18] gave a negative-ion f.a.b. spectrum

Table 5. Positive f.a.b.–m.s. of $K_3[Mn(CN)_5(NO)]$: principal peaks (normalised to highest sample peak) and assignments (dithiothreitol–dithioerythritol matrix)

m/z	Assignment
371 (100)	$[M + K]^+$
345 (28)	$[M + K - CN]^+$
341 (12)	$[M + K - NO]^+$
333 (75)	$[M + H]^+$
313 (18)	$[M + K - CN - NO]^+$
306 (30)	$[M - CN]^+$
302 (30)	$[M - NO]^+$
276 (79)	$[M - CN - NO]^+$

Table 6. Negative f.a.b.–m.s. of $[\{Mo(CN)_8\}(H_3O)(Hbipy)_3]$: principal peaks (normalised to highest sample peak) and assignments (nba matrix)

m/z	Assignment
774 (37)	$[M - H_3O]^-$
746 (20)	$[M - H_3O - CN]^-$
636 (16)	$[M - Hbipy]^-$
615 (25)	$[M - H_3O - Hbipy]^-$
590 (25)	$[M - H_3O - Hbipy - CN]^-$
563 (25)	$[M - H_3O - Hbipy - 2CN]^-$
461 (100)	$[M - H_3O - 2Hbipy]^-$
411 (25)	$[M - H_3O - 2Hbipy - 2CN]^-$

indicating the prior loss of one, two, or three cations with H_3O^+ loss featuring in every fragment except for $[M - (Hbipy)]^-$. Either 0, 1, or 2 cyano groups were lost (Table 6).

General Comments.—While both the alkali-metal and organic salts of the cyanometalates give negative f.a.b. spectra, the organic salts fail to yield positive species. It appears that the necessary aggregation of positive ions around the negative central ion does not occur, probably due to weaker coulombic forces inherent in the ion clusters of the large cations, and steric effects must be significant in species such as $[A_6\{M'(CN)_x\}]^+$ and $[A_5\{M'(CN)_x\}]^+$.

The processes occurring in the positive and negative f.a.b. spectra of the cyanometalates are closely similar: a series of neutral CN radicals and possibly $(CN)_2$ molecules are expelled from the complex ion leaving it with the same overall charge but with the oxidation state of the metal centre reduced by one unit for each CN radical lost. The difference between the species encountered in positive and negative f.a.b. rests in most instances merely on the number of cations in the ion cluster, although the highest oxidation states are unique to negative f.a.b. What is not clear is whether the departure of CN is consequent upon receipt of sufficient excitation, reaction (1), or whether it occurs following secondary electron capture, reaction (2) [in positive f.a.b. $n - (x - z) = 1$ while in negative f.a.b. $n - (x - z) = -1$].

$$\{[A^+]_n[M'^z(CN)_x]^{(x-z)-}\}^{\pm} \xrightarrow{Xe^*} \{[A^+]_n[M'^{z-1}(CN)_{x-1}]^{(x-z)-}\}^{\pm} + CN \quad (1)$$

$$e^- + \{[A^+]_n[M'^z(CN)_x]^{(x-z)-}\}^{\pm} \longrightarrow \{[A^+]_n[M'^{z-1}(CN)_x]^{(x-z-1)-}\}^{0}_{2-} \longrightarrow CN^- + \{[A^+]_n[M'^{z-1}(CN)_{x-1}]^{(x-z)-}\}^{\pm} \quad (2)$$

One-electron reduction products have been detected by Williams *et al.*[19] in the f.a.b.–mass spectra of neutral organic molecules and by Pelzer *et al.*[20] in the f.a.b.–mass spectra of aqueous solutions of salts of simple aqua cations. However, there is no account of multiple electron capture and accordingly we favour reaction (1) as the most likely pathway. The driving force for reaction (1) is the entropic release of a small fragment of reasonable stability, which more than compensates for the electrochemical potentials associated with access to some of the extreme oxidation states encountered. In respect of the latter, the effect of cyanide ion in stabilising low oxidation states as in $[Co^I(CN)_5]^{4-}$ and $[W(CN)_7]^{5-}$ should be noted.[11,12]

As regards the general implications of these results for f.a.b.–m.s., it appears that although this 'soft' ionisation process is normally associated with the appearance of rather simple spectra, particularly of HM^+ and a few fragments derived therefrom, extending it to most co-ordination compounds examined hitherto, the presence of groups such as CO, PPh_3, and CN^- in numbers can lead to multiple dissociation processes and, in the case of the cyanometalates, to simultaneous multiple changes in the oxidation state of the central metal atom. It seems unlikely that sufficient energy can be taken up by the cyanometalate ion cluster in a single step to effect elimination of many ligands simultaneously, and a sequential process is more probable, possibly in some instances involving the loss of $(CN)_2$ molecules, although one can only speculate about the overall thermochemistry of processes described by reaction (1). Many of the intermediates we describe are unknown in solution chemistry, which implies that, at least for this range of compounds, the f.a.b. process is occurring in the gas phase and not in the bulk or the surface of the matrix. This is in agreement with the proposal of Schröder *et al.*[21] that the ionisation is a gas-phase process aided by the evaporated matrix molecules which function as (single molecule) agents for chemical ionisation.

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