Studies on Transition-metal Cyano-complexes. Part I. Octacyanoniobates(III), -niobates(IV), -molybdates(V), and -tungstates(V)

By **Patrick M. Kiernan** and **William P. Griffith**,* Inorganic Chemistry Laboratories, Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

The preparation and properties of salts of $[Nb(CN)_8]^{n-}$ (n = 4 or 5) are described. E.p.r. spectra of $[Nb(CN)_8]^{4-}$ salts indicate a change in configuration from D_{2d} in the solid state to D_{4d} in solution. The vibrational and electronic spectra of these cyanoniobates are reported and support these structural changes. E.p.r. and vibrational spectra of $[M(CN)_8]^{3-}$ (M = Mo or W) salts in the solid state and in solution are also given.

WE recently briefly reported the isolation of $K_4[Nb(CN)_8]\cdot 2OH_2$ and some data on its e.p.r. spectrum.[1] We now give these results in full and describe the preparation of other salts of $[Nb(CN)_8]^{4-}$ and of $[Nb(CN)_8]^{5-}$. On the basis of their spectral properties, we discuss their configurations and also those of the d^1 complexes $[M(CN)_8]^{3-}$ (M = Mo or W) in the solid state and in solution.

RESULTS AND DISCUSSION

Preparation and Properties of Octacyanoniobates.—Previously reported cyanoniobates are $H[NbX_5(CN)]$ (X = Cl or Br), $[NbCl_4(CN)]\cdot OEt_2$,[2] and $[NbCl_3(CN)(NCMe)_2]$.[3] Earlier attempts to prepare unsubstituted cyanoniobates using halides as starting materials gave only oxo- or hydroxo-species.[2] We found that reaction of excess of aqueous potassium cyanide with an electrolytically reduced solution of niobium pentachloride in methanol yielded impure $K_5[Nb(CN)_8]$ (electrolytic reduction of ethanolic $NbCl_5$ is known to give a trivalent species).[4] The product is oxidised by air or hydrogen

---

[1] P. M. Kiernan, J. F. Gibson, and W. P. Griffith, *J.C.S. Chem. Comm.*, 1973, 816.

[2] G. Brauer and H. Walz, *Z. anorg. Chem.*, 1962, **319**, 236.

[3] D. J. Machin and J. F. Sullivan, *J. Less-Common Metals*, 1969, **19**, 413.

[4] R. Bosselaar, B. F. van der Hayden, and R. Mieras, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1199.

peroxide to $K_4[Nb(CN)_8]\cdot 2OH_2$ from which other octacyanoniobates(IV) can be obtained by metathetical procedures. Reduction of $[Nb(CN)_8]^{4-}$ with potassium amalgam gave $K_5[Nb(CN)_8]$.

Crystals of $K_4[Nb(CN)_8]\cdot 2OH_2$ are orange and air stable. Its aqueous solutions, though stable in the dark, disproportionate photolytically to give $K_5[Nb(CN)_8]$, niobium pentaoxide, and hydrocyanic acid as final products. In excess of cyanide photolysis still produces $K_5[Nb(CN)_8]$ but no Nb_2O_5, while in weakly acid solutions both oxidation and photolysis readily occur. With a large excess of acetic acid, aqueous solutions of the potassium salt yielded an unstable purple material, probably containing the $[Nb(CN)_7(OH_2)]^{3-}$ ion. The octacyanoniobates(III), $K_5[Nb(CN)_8]$ and the sodium salt, are deep red solids, oxidised in moist air. They are sparingly soluble in water to give solutions which are very sensitive to oxidation. Acid solutions decompose immediately to give unidentified cyanide-free hydrolysis products. We were unable to isolate any salts of $[Nb(CN)_8]^{5-}$ with organic cations, perhaps due to the difficulty of packing five such cations around the anion.

TABLE 1

E.p.r. data for octacyano-niobates, -molybdates, and -tungstates

	Phase	T/K	$g_{\parallel}$	$g_{\perp}$	$\langle g\rangle$ [a]	$A_{\parallel}$	$A_{\perp}$	$\langle A\rangle$ [a]
						cm^{-1} × 10^4		
(*a*) Octacyanoniobates(IV)								
$K_4[Nb(CN)_8]\cdot 2OH_2$	Powder	295			1.984			
	Solid soln.[b]	295	1.972	1.990	1.984	152	73	99
	Glycerol	360			1.985			97
	Glycerol	100	2.002 [c]	1.976		(67) [c]	112	
$[Pr^n_2H_2N][Nb(CN)_8]$	Solid soln.[d]	295	1.969	1.991	1.984	147	74	98
	CH_2Cl_2	295			1.985			96
	CH_2Cl_2	100	2.002 [c]	1.976		(60) [c]	114	
(*b*) Octacyanomolybdates(V)								
$K_3[Mo(CN)_8]$ [e]	Solid soln.[b]	298	1.978	1.988	1.985			
	Glycerol	77	1.998	1.989	1.992	14	39	31
$Na_3[Mo(CN)_8]\cdot 4OH_2$	Powder	295	1.996	1.986	1.989			
	Glycerol	100	1.998	1.990	1.993	(14) [c]	39	
$[Bu^n_4N]_3[Mo(CN)_8]$	Powder	295			1.992			
	Methanol	295			1.992			30
	Methanol	100	1.999	1.990	1.993	(12) [c]	39	
	CH_2Cl_2	295			1.992			30
	CH_2Cl_2	100	1.999	1.990	1.993	(12) [c]	39	
(*c*) Octacyanotungstates(V)								
$K_3[W(CN)_8]$ [e]	Solid soln.	298	1.942	1.973	1.963			
	Glycerol	77	1.982	1.968	1.972	19	69	
$Na_3[W(CN)_8]\cdot 4OH_2$	Powder	295	1.987	1.967	1.974			
	Glycerol	295			1.973			54
	Glycerol	100	1.982	1.969	1.973	(20) [c]	71	

[a] Calculated where parallel and perpendicular features were separable, otherwise measured. [b] 0.5% in $K_4[Mo(CN)_8]\cdot 2OH_2$ powder. [c] Calculated from perpendicular and isotropic values. [d] 0.5% in $[Pr^n_2H_2N]_4[Mo(CN)_8]$ powder. [e] Ref. 8.

The X-ray powder photographs of $K_4[Nb(CN)_8]\cdot 2OH_2$ and $K_4[Mo(CN)_8]\cdot 2OH_2$ show these salts to be isomorphous; the latter contains dodecahedral (D_{2d}) octacyanomolybdate[5] so it appears probable that $[Nb(CN)_8]^{4-}$ in the potassium salt also has this symmetry. All the salts of $[Nb(CN)_8]^{4-}$ are paramagnetic {*e.g.* $\mu_{\text{eff.}} = 1.69$ and 1.70 B.M. for the K^+ and $[Pr^n_2H_2N]^+$ salts at room temperature,* typical values[6] for eight-co-ordinate niobium(IV) complexes}. The $[Nb(CN)_8]^{5-}$ salts are all diamagnetic.

E.P.R. Spectra of $[Nb(CN)_8]^{4-}$ *and* $[M(CN)_8]^{3-}$ (M = Mo *or* W).—The salt $K_4[Nb(CN)_8]\cdot 2OH_2$ is particularly suitable for e.p.r. study since both the solid and its aqueous solutions are stable; it contains the 100% abundant ^{93}Nb isotope ($I = \frac{9}{2}$) and readily forms a solid solution with the isomorphous diamagnetic salt $K_4[Mo(CN)_8]\cdot 2OH_2$. The spectrum of such a powder at 295 K [Table 1, Figure 1(*a*)] was anisotropic with two well resolved sets of ten hyperfine features (^{13}C satellites can clearly be seen on the parallel features). Analysis of the spectrum using the procedure described by Vivien and Gibson,[7] which takes second-order effects and quadrupole interactions into account, yielded parameters with $g_{\perp} > g_{\parallel}$ and $A_{\parallel} > A_{\perp}$, as predicted[8] for a dodecahedral configuration for the anion. A similar ordering of g and hyperfine splitting constants was found for zircon ($Zr[SiO_4]$) doped with Nb^{IV}, where the metal is known to have a dodecahedral configuration,[9] and also in $K_3[M(CN)_8]$ dispersed in the non-isomorphous $K_4[M(CN)_8]\cdot 2OH_2$ host lattices. The spectrum of a dilute solid solution of $[Pr^n_2H_2N]_4[Nb(CN)_8]$ in the analogous molybdenum salt was identical in form to that found for $K_4[Nb(CN)_8]\cdot 2OH_2$ and gave the same ordering for the components of the g and A tensors. The spectrum of $Na_4[Nb(CN)_8]\cdot 4OH_2$ in a $Na_4[Mo(CN)_8]\cdot 4OH_2$ lattice was quite different, however, and suggests the presence of

---

* 1 B.M. ≈ 9.27×10^{-24} A m^2.

[5] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, 1968, **90**, 3177.

[6] R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2865.

[7] D. Vivien and J. F. Gibson, *J.C.S. Faraday II*, 1975, 1640.

[8] B. R. McGarvey, *Inorg. Chem.*, 1965, **5**, 476.

[9] V. M. Vinokurov, M. M. Zaripov, V. G. Stepanov, G. K. Chirkin, and L. Y. Shekun, *Soviet Phys. Solid State*, 1964, **5**, 1487.

two non-equivalent lattice sites. Studies on this system are still in progress.

A solution of $K_4[Nb(CN)_8]\cdot 2OH_2$ in a glycerol glass {and also of $[Pr^n{}_2H_2N]_4[Nb(CN)_8]$ in a dichloromethane glass} gave an e.p.r. spectrum [Figure 1(*b*)] quite different from that of the powder. Although the less intense parallel anisotropic features were partially obscured by the broad perpendicular features of the spectrum, we calculated $g_{\parallel}$ and $A_{\parallel}$ from the observed $g_{\perp}$ and $A_{\perp}$ values and the isotropic values observed in mobile glycerol solutions. Such calculated $g_{\parallel}$ and (particularly) $A_{\parallel}$ parameters are necessarily rather less accurate than directly measured values, but it is clear that $g_{\parallel} > g_{\perp}$ and $A_{\perp} > A_{\parallel}$. This is consistent with antiprismatic (D_{4d}) co-ordination for the anion, as is the proximity of $g_{\parallel}$ to the spin-only value of 2.002 3.[8,10]

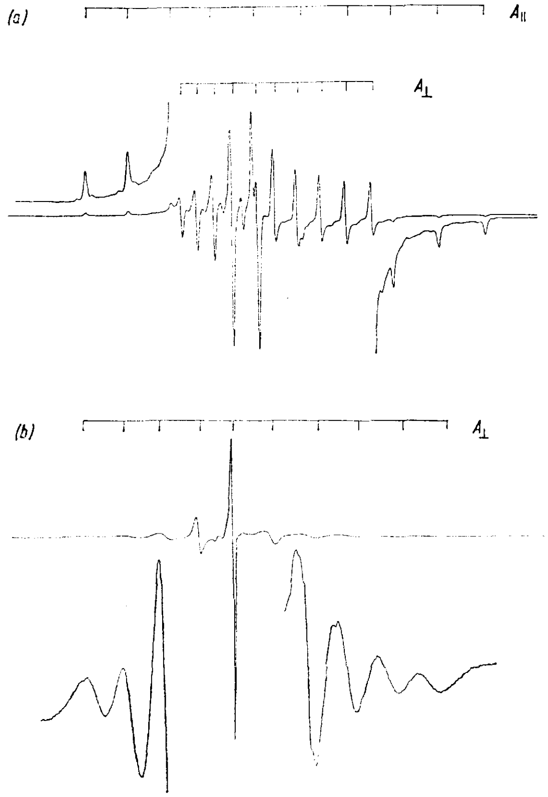

FIGURE 1 E.p.r. spectra of (*a*) $K_4[Nb(CN)_8]\cdot 2OH_2$ (0.5%) in $K_4[Mo(CN)_8]\cdot 2OH_2$ powder at 295 K, (*b*) $K_4[Nb(CN)_8]\cdot 2OH_2$ in a glycerol glass at 100 K

We conclude from these data that the configuration of $[Nb(CN)_8]^{4-}$ changes from D_{2d} in the dilute powder to D_{4d} in the glass for both the K^+ and $[Pr^n{}_2H_2N]^+$ salts. A similar configurational change has also been proposed for $K_3[M(CN)_8]$.[8] For these solid salts (M = Mo or W) in $K_4[M(CN)_8]\cdot 2OH_2$, however, the spectra are very weak.[8] This could be caused by the difficulty of introducing $K_3[M(CN)_8]$ into a lattice of totally different stoicheiometry; in order to overcome this incompatibility the anion may be forced to adopt D_{2d} symmetry to enter this otherwise alien environment. In contrast, the spectra of the Nb^{IV} solid solutions are very strong, demonstrating host–lattice compatibility. Work is now proceeding on the selection of a more suitable solid matrix for the $[M(CN)_8]^{3-}$ salts.

A check on the validity of e.p.r. criteria for determining the configuration of such octacyano-ions is provided by spectra of the isomorphous species $Na_3[M(CN)_8]\cdot 4OH_2$, since recent *X*-ray work has shown that the tungsten salt contains a D_{4d} anion.[11] The pure salts give anisotropic spectra similar to those of the glycerol glasses, in which $g_{\parallel} > g_{\perp}$ as expected for D_{4d} symmetry. During the course of our work, similar results and conclusions were drawn from the spectra of $Na_3[W(CN)_8]\cdot 3OH_2$.[12]

Despite the quite different $g_{\perp}$ and $g_{\parallel}$ values found for powders and glasses at low temperatures, isotropic *g* values are similar for $[Mo(CN)_8]^{3-}$ (ref. 8) and also for $[W(CN)_8]^{3-}$.[8,12] Our data for $[Nb(CN)_8]^{4-}$ also give similar isotropic *g* values for powders and glasses despite very different $g_{\perp}$ and $g_{\parallel}$ values (Table 1). Corden *et al.*[13] argued that, in the case of $[Bu^n{}_4N]_3[Mo(CN)_8]$, which was shown by *X*-ray studies to contain a D_{2d} anion, the almost identical isotropic *g* values at room temperature for this salt as a pure powder and in solution indicate that D_{2d} symmetry is retained in solution. Our work reinforces Pribush and Archer's argument[12] that comparison of isotropic *g* values is not a valid criterion for distinguishing between these configurations.

We have included data on $[Bu^n{}_4N]_3[Mo(CN)_8]$ since this salt displays clear resolution of the perpendicular and parallel features in a dichloromethane glass, unlike the spectra of this and other $[Mo(CN)_8]^{3-}$ salts in more polar glasses.

Vibrational Spectra of $[Nb(CN)_8]^{n-}$ *and* $[M(CN)_8]^{3-}$.—There have been many reports of the spectra of $[M(CN)_8]^{4-}$ salts (M = Mo or W) in the solid state and in solution, the most comprehensive being that of Long and Vernon[14] who concluded that the D_{2d} anions in $K_4[M(CN)_8]\cdot 2OH_2$ retain this configuration in aqueous solution. The only studies reported on $[M(CN)_8]^{3-}$ are of the solid $[Co(NH_3)_6]^{3+}$ salts over the range 2 000—2 200 cm^{-1}.[15] {An earlier attempted study[16] on $K_3[M(CN)_8]$ salts produced spectra which are clearly those of M^{IV} salts.}

In Table 2 we list the vibrational spectra of a number of salts of $[Nb(CN)_8]^{n-}$ (n = 4 or 5) and $[M(CN)_8]^{3-}$ over the range 200—2 200 cm^{-1}. Although the selection rules for D_{2d} and D_{4d} should distinguish between these two configurations for octacyano-complexes, solvent broadening, particularly in the i.r. spectra, rendered resolution of bands in the small spread of the cyanide-stretching region difficult. Below 600 cm^{-1} high solvent

---

[10] R. G. Hayes, *J. Chem. Phys.*, 1966, **44**, 2210.

[11] L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Acta Cryst.*, 1970, **B26**, 684.

[12] R. A. Pribush and R. D. Archer, *Inorg. Chem.*, 1974, **13**, 2556.

[13] B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, 1970, **9**, 356.

[14] T. V. Long and G. A. Vernon, *J. Amer. Chem. Soc.*, 1971, **93**, 1919.

[15] R. V. Parish, P. G. Simms, M. A. Wells, and L. A. Woodward, *J. Chem. Soc.* (*A*), 1968, 2882.

[16] E. G. Brame, jun., F. A. Johnson, E. M. Larsen, and V. W. Meloche, *J. Inorg. Nuclear Chem.*, 1958, **6**, 99.

absorption limited the i.r. data, so most of our conclusions for this region are drawn from the Raman spectra.

TABLE 2

Vibrational spectra of octacyano-niobates, -molybdates, and -tungstates (200—2 200 cm^{-1})

		ν(CN)	ν(MC), δ(MCN), or δ(CMC)
(*a*) Octacyanoniobates			
$K_4[Nb(CN)_8]\cdot 2OH_2$	Raman	2 138(3), 2 131(8), 2 123(10), 2 096(3), 2 074(1)	496(2), 450(5), 427(6), 397(4), 362(6), 345(2), 320(1), 301(2), 278(6), 241(1)
	Raman [a]	2 127(10)p, 2 114(6)dp	438(4), 414(6)p, 370(2), 260(3)
	I.r.	2 136s, 2 129s, 2 123s, 2 114vs, 2 070w, 2 027w	498b, 471s, 439s, 377 (sh), 342vs
	I.r. [a]	2 122 (sh), 2 115vs, b	
$[Pr^n_2H_2N]_4[Nb(CN)_8]$	Raman	2 129(10), 2 124(8), 2 112(5), 2 093(4)	528(1), 443(2), 417(4), 399(3), 319(10), 292(7), 268(3), 243(3)
	Raman [b]	2 133(10)p, 2 120(4)dp, 2 114(1)	426(2), 404(2), 368(1), 320(6), 298(4)
	I.r.	2 145w, 2 124m, 2 119s, 2 115m, 2 103s, 2 101 (sh), 2 090s	450m, 432w, 414vw, 370m, 341s, 300vw
	I.r. [b]	2 124m (sh), 2 118vs	450m, 347s
$K_5[Nb(CN)_8]$ [c]	Raman	2 101(6), 2 095(5), 2 072(4), 2 052(10), 2 032w	556(1), 504(2), 448(6), 390(5), 384(3), 236w
	I.r.	2 091vs, 2 069w, 2 066w, 2 046vs, b, 2 042 (sh), 2 007w	471s, 442w, 431m, 386s, 343vs, 317w, 311w, 305w
(*b*) Octacyanomolybdates(v)			
$Na_3[Mo(CN)_8]\cdot 4OH_2$ [d]	Raman	2 166(10), 2 161(7), 2 156(4)	452(3), 428(3), 404(3)b, 376(5), 290(2), 228(9)
	Raman [a]	2 158(10)p, 2 150(6)dp, 2 140(4)dp	448(3), 428(2), 401(10)p, 378(6), 272(1)
	I.r.	2 166w, 2 160m, 2 156vs, 2 151s, 2 141m	552w, 504s, 457s, 426w, 392m, 365vs, 282w
$K_3[Mo(CN)_8]\cdot OH_2$	Raman	2 153(10), 2 149(7), 2 145(4)	514(1), 440(2), 396(8), 308(2), 200(1)b
	I.r.	2 159 (sh), 2 157m, 2 149vs, 2 146s, 2 142m, 2 136m	565s, 502s, 460m, 362vs, 302w
$[Bu^n_4N]_3[Mo(CN)_8]$	Raman	2 147(10), 2 131(9), 2 084(1)	562(1), 520b, 488(1), 452(2), 436(2), 385(10), 340(1), 300(4)
	Raman [b]	2 154(10p), 2 148(6)dp, 2 138(1)	535(1), 440(4), 404(10)p, 372(2), 302(2)
	I.r.	2 141vs, 2 124s	506m, 465m, 362vs, 347m, 335w
	I.r. [e]	2 138s, 2 130 (sh)	370s
(*c*) Octacyanotungstates(v)			
$Na_3[W(CN)_8]\cdot 4OH_2$ [d]	Raman	2 166(10), 2 162(7), 2 157(2)	460(0.5), 436(5)b, 408(6), 388(1), 346(6)
	Raman [a]	2 162(10)p, 2 148(4)dp	460(3), 441(1), 417(8)p, 387w, 346(2), 320(1)
	I.r.	2 170m, 2 164m, 2 160vs, 2 154vs, 2 146m, 2 144m	562b, 472m, 452s, 417w, 402w, 382vs, 354w
$K_3[W(CN)_8]\cdot OH_2$	Raman	2 153(10), 2 144(7), 2 136(2)	460(4), 433(6), 412(10), 376(8)
	I.r.	2 162w, 2 159m, 2 151vs, 2 148vs, 2 142vs, 2 138m	562s, 442s, 402m, 379vs, 314w, 295m
$[Bu^n_4N]_3[W(CN)_8]$	Raman	2 146(10), 2 137(6), 2 112(1)	545(1), 490(2), 457(4), 401(8), 300(3)
	Raman [a]	2 162(10)p, 2 155(4)dp	580(1), 463(8), 431(6), 417(10)p, 364(2), 306(4)
	I.r.	2 140s, 2 130vs	440m, 379vs
	I.r. [e]	2 136s	480m, b, 397m

Data on solids, except solutions in [a] water, [b] methanol, and [e] acetonitrile. Relative intensities of the Raman bands are given in parentheses. [c] For an aqueous solution of $Na_5[Nb(CN)_8]$, $\bar{\nu}$(CN = 2 050p (Raman) and 2 088m and 2 050vs (i.r.). [d] For aqueous solutions of $Na_3[M(CN)_8]\cdot 4OH_2$, $\bar{\nu}$(CN) = 2 144vs (Mo) and 2 142vs (W) (i.r.).

For all the solutions studied only one polarised Raman band was found in the cyanide-stretching region (and also in the metal–carbon stretching region at *ca.* 400 cm^{-1}), consistent with D_{4d} rather than D_{2d} symmetry for the solute anions. It is possible that a second, weak, partially depolarised A_1 mode at a slightly lower frequency {as suggested for $[M(CN)_8]^{4-}$}[14] has escaped detection (D_{2d} symmetry requires two A_1 modes) but we believe this to be unlikely. Over the range 200—2 200 cm^{-1} the Raman spectra for $[M(CN)_8]^{3-}$ in aqueous solution were basically similar in profile to those of both the solid sodium and potassium salts; the $Na_3[M(CN)_8]\cdot 4OH_2$ salts are known to contain D_{4d} anions.[11]

The i.r. and Raman spectra of solid $Na_3[M(CN)_8]\cdot 4OH_2$ and $K_3[M(CN)_8]\cdot OH_2$ were similar in profile and less complicated than those of the D_{2d} solids $K_4[M(CN)_8]\cdot 2OH_2$ (M = Mo, W, or Nb). Since the selection rules[14] predict that octacyano-complexes with D_{2d} symmetry have a considerably larger number of vibrational modes than D_{4d}, we suggest that the $[M(CN)_8]^{3-}$ anions have the latter symmetry in these solid sodium and potassium salts as well as in the aqueous solutions. Such conclusions can be tentative only since solid-state splittings can make arguments based on the complexity of spectra somewhat hazardous.

Solid $[Bu^n_4N]_3[Mo(CN)_8]$ is known to contain a D_2 anion differing little from D_{2d} symmetry.[13] Although its i.r. spectrum, like that of its tungsten analogue, was unexpectedly simple, Raman and i.r. spectra of its solutions in organic solvents were very different from those of the solids, again suggesting a change in symmetry to D_{4d}. This is also indicated by the e.p.r. spectra of glasses of the tungsten[12] and molybdenum salts (Table 1). A drastic change and simplification of profiles is observed when the Raman and infrared spectra of solid $K_4[Nb(CN)_8]\cdot 2OH_2$ and $[Pr^n_2H_2N]_4[Nb(CN)_8]$ are compared with those of the corresponding solutions in water and methanol respectively.

The intense colour of solutions of $[Nb(CN)_8]^{5-}$ precluded the recording of good Raman solution spectra, but the i.r. spectrum of the aqueous solution from 2 000 to 2 200 cm^{-1} was similar to that of the solid, which may indicate retention of symmetry of the anion from solid to solution. X-Ray studies are in progress on $K_5[Nb(CN)_8]$.

Electronic Spectra of $[Nb(CN)_8]^{n-}$.—These are reproduced in Figure 2 for aqueous solutions of $[Nb(CN)_8]^{4-}$ and $[Nb(CN)_8]^{5-}$. The spectrum of the latter is very similar to those of the $[M(CN)_8]^{4-}$ salts,[17] which have been interpreted on the basis of D_{2d} symmetry.[18]

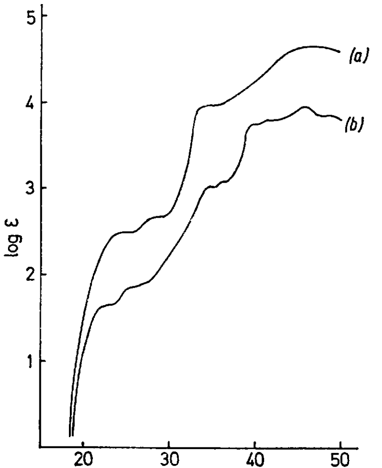

FIGURE 2 Electronic spectra of aqueous solutions of (*a*) $[Nb(CN)_8]^{5-}$, (*b*) $[Nb(CN)_8]^{4-}$

Conclusions.—The e.p.r. and vibrational data both suggest that there is a change in the configuration of the anion from D_{2d} in solid $K_4[Nb(CN)_8]\cdot 2OH_2$ or $[Pr^n{}_2H_2N]_4$-$[Nb(CN)_8]$ to D_{4d} in solution. The vibrational spectra suggest that the e.p.r. evidence for a similar change for $[M(CN)_8]^{3-}$ may not apply to the pure $K_3[M(CN)_8]\cdot OH_2$ salts. Both e.p.r. and vibrational spectra support the presence of D_{4d} anions in solutions of $[M(CN)_8]^{3-}$.

EXPERIMENTAL

Potassium Octacyanoniobate(IV) *Dihydrate*, $K_4[Nb(CN)_8]\cdot 2OH_2$.—Niobium pentachloride (20 g) was dissolved in methanol (25 cm^3) and the solution diluted with more methanol (50 cm^3) and reduced electrolytically under nitrogen, using a mercury-pool cathode with a current of 1 A for 3 h. The solution volume was maintained by further additions of methanol. The deep blue reduced solution was added dropwise to a stirred solution of potassium cyanide (100 g) in water (150 cm^3) under nitrogen with ice–salt cooling. Stirring was continued for 1 h, and at room temperature for a further 12 h. The brick red $K_5[Nb(CN)]_8$ was removed by centrifugation and stirred with water (100 cm^3), hydrogen peroxide (10%) being added dropwise until the solution became yellow. Addition of methanol to the filtered solution precipitated yellow *crystals*, which were recrystallised from water–methanol and washed with methanol and diethyl ether (yield 15%) (Found: C, 19.8; H, 0.8; K, 32.0; N, 22.9; O, 6.7. $C_8H_4K_4N_8NbO_2$ requires C, 19.5; H, 0.8; K, 31.6; N, 22.7; O, 6.5%), gram susceptibility (χ_g) 2.05×10^{-6} c.g.s. units (23 °C) ($\mu_{eff.}$ 1.69 B.M.); electronic spectrum in aqueous solution [$\lambda_{max.}$/nm (ε/l mol^{-1} cm^{-1})] 445 (43), 390 (74), 284 (1.1×10^3), 275 (1.1×10^3), 250 (5.7×10^3), 240 (5.7×10^3), 218 (8.8×10^3), and 206 (7.2×10^3).

Tetrakis (*di-n-propylammonium*) *Octacyanoniobate*(IV), $[Pr^n{}_2H_2N]_4[Nb(CN)_8]$.—A solution of the potassium salt (2 g) in water (10 cm^3) was passed quickly down a column of Zeo-karb 325 cation-exchange resin (H^+ form). The resulting red solution was run into a stirred solution of di-n-propylamine (5 cm^3) in ethanol (50 cm^3). After filtration, addition of diethyl ether precipitated the yellow *salt*, which was filtered off, washed with acetone and ether, and recrystallised from methanol–ether (yield 90%) (Found: C, 53.2; H, 9.1; N, 22.9. $C_{33}H_{64}N_9Nb$ requires C, 52.8; H, 9.1; N, 23.1%), χ_g 1.04×10^{-6} c.g.s. units (23 °C) ($\mu_{eff.}$ 1.70 B.M.).

Tetrathallium(I) *Octacyanoniobate*(IV), $Tl_4[Nb(CN)_8]$.—To a strong solution of the potassium salt, a saturated solution of thallium(I) acetate was added dropwise, with stirring, until precipitation was complete. The resulting deep pink *crystals* were filtered off, washed with 50% aqueous methanol, methanol, and diethyl ether (Found: C, 8.7; N, 9.7. $C_8N_8NbTl_4$ requires C, 8.6; N, 10.0%).

Tetracaesium Octacyanoniobate(IV) *Dihydrate*, $Cs_4[Nb(CN)_8]\cdot 2OH_2$.—To a concentrated aqueous solution of caesium chloride was added a stoicheiometric amount of the Tl^I salt. After shaking for *ca.* 1 min, the solution was filtered and methanol was added to precipitate golden *crystals* of the caesium salt. These were filtered off and washed with methanol and diethyl ether (Found: C, 11.2; H, 0.6; N, 12.5. $C_8H_4Cs_4N_8NbO_2$ requires C, 11.1; H, 0.5; N, 12.9%).

Tetrasodium Octacyanoniobate(IV) *Tetrahydrate*, $Na_4[Nb(CN)_8]\cdot 4OH_2$.—To a saturated aqueous solution of sodium chloride was added a stoicheiometric amount of the Tl^I salt. Addition of ethanol to the filtered solution yielded a yellow oil, which was separated and left in a vacuum desiccator, in the dark, over phosphorus pentaoxide to give orange-yellow *crystals* of the sodium salt (Found: C, 21.1; H, 1.5; N, 24.0. $C_8H_8N_8Na_4NbO_4$ requires C, 20.6; H, 1.7; N, 24.1%).

Pentapotassium Octacyanoniobate(III), $K_5[Nb(CN)_8]$.—To a stirred solution of $K_4[Nb(CN)_8]\cdot 2OH_2$ (1 g) in water (10 cm^3) potassium amalgam was slowly added under nitrogen, until precipitation of the red solid was complete. The *salt* was filtered off, washed with 50% aqueous methanol, methanol, and diethyl ether, and recrystallised from deoxygenated water (yield 80%) (Found: C, 19.7; K, 39.8; N, 22.7. $C_8K_5N_8Nb$ requires C, 19.4; K, 39.3; N, 22.6%); λ/nm (ε/l mol^{-1} cm^{-1}) 414 (2.9×10^2), 350 (4.6×10^2), 295 (8.7×10^3), and 216 (4.3×10^4).

The following salts were made by the literature methods, as indicated: tripotassium octacyanomolybdate(V) hydrate, $K_3[Mo(CN)_8]\cdot OH_2$ [19] (Found: C, 22.1; H, 0.9; N, 25.0. Calc. for $C_8H_2K_3MoN_8O$: C, 21.9; H, 0.5; N, 25.5%). trisodium octacyanomolybdate(V) tetrahydrate, Na_3-$[Mo(CN)_8]\cdot 4OH_2$, as for the potassium salt [19] using sodium chloride instead of potassium chloride (Found: C, 21.7;

---

[17] R. M. Golding and A. Carrington, *Mol. Phys.*, 1962, **5**, 377.

[18] A. Golebiewski and R. Nalewajski, *Z. Naturforsch.*, 1972, **A27**, 1672.

[19] W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 1927, 2981.

H, 1.6; N, 24.8. Calc. for $C_8H_8MoN_8Na_3O_4$: C, 21.6; H, 1.8; N, 25.2%); tris(tetra-n-butylammonium) octacyanomolybdate(V), $[Bu^n_4N]_3[Mo(CN)_8]$ [13] (Found: C, 65.8; H, 10.2; N, 15.0. Calc. for $C_{56}H_{108}MoN_{11}$: C, 65.2; H, 10.5; N, 15.0%). tripotassium octacyanotungstate(V) hydrate, $K_3[W(CN)_8]\cdot OH_2$ [20] (Found: C, 18.6; H, 0.4; N, 21.4. Calc for $C_8H_2K_3N_8OW$: C, 18.3; H, 0.4; N, 21.2%); trisodium octacyanotungstate(V) tetrahydrate, $Na_3[W(CN)_8]\cdot 4OH_2$, as for the potassium salt [20] using NaCl instead of KCl (Found: C, 18.1; H, 2.0; N, 20.7. Calc. for $C_8H_8N_8Na_3O_4W$: C, 18.0; H, 1.5; N, 21.0%); and tris(tetra-n-butylammonium) octacyanotungstate(V), $[Bu^n_4N]_3[W(CN)_8]$ [12] (Found: C, 59.7; H, 9.8; N, 13.8. Calc. for $C_{56}H_{108}N_{11}W$: C, 60.1; H, 9.7; N, 13.8%).

E.p.r. spectra were recorded on a Varian E12 spectrometer, with 100 kHz modulation, electronic spectra on a Perkin–Elmer 402 instrument (800—200 nm), i.r. spectra on a Perkin–Elmer 325 instrument (2 200—2 000 and 600—200 cm^{-1}) as Nujol mulls in caesium iodide plates, aqueous solutions in balanced calcium fluoride cells, or methanol–acetonitrile films between Polythene plates, and Raman spectra on a Cary 81 instrument with a CRL 52MG laser (argon–krypton), using 6 471 Å excitation. Microanalyses were by the Microanalytical Department at Imperial College (oxygen analyses by Franz Pascher, Bonn). Potassium was estimated gravimetrically as the tetraphenylborate.

We thank Dr. J. F. Gibson and Mr. G. M. Lack for assistance with interpretation of the e.p.r. spectra and the S.R.C. for the award of a studentship (to P. M. K.).

[5/594 *Received, 2nd April*, 1975]

[20] E. L. Goodenow and C. S. Garner, *J. Amer. Chem. Soc.*, 1955, **77**, 5272.