Studies on Transition-metal Cyano-complexes. Part 3.[1] Heptacyano-complexes of Tungsten, Molybdenum, and Vanadium, and a Hydrido-heptacyano-complex of Tungsten

By **Ana-Maria Soares** and **William P. Griffith**,* Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The new complexes $K_5[W(CN)_7]\cdot H_2O$ and $K_4[WH(CN)_7]\cdot 2H_2O$ are reported, and have been characterised by ^1H, ^{13}C n.m.r., and vibrational spectra. Vibrational and e.s.r. data are also presented for the new salt $NaK_3[Mo(CN)_7]\cdot 2H_2O$ and earlier data are extended for $K_4[Mo(CN)_7]\cdot 2H_2O$ and $K_4[V(CN)_7]\cdot 2H_2O$.

We recently reported the crystal structure of $K_4[Re(CN)_7]\cdot 2H_2O$ [2] and the preparation of $K_5[Mo(CN)_7]$.[3] *X*-Ray crystal-structure determinations of $K_5[Mo(CN)_7]\cdot H_2O$ and of $Na_5[Mo(CN)_7]\cdot 10H_2O$ have also appeared in the literature.[4] We continue our studies on seven- and eight-co-ordination in cyanide complexes of the early transition metals by reporting the isolation of $K_5[W(CN)_7]\cdot H_2O$ and $K_4[WH(CN)_7]\cdot 2H_2O$ which have been mentioned in a preliminary communication; [5] these are respectively the first heptacyano-complex of tungsten and the first eight-co-ordinate cyanide hydride. We also extend earlier vibrational and e.s.r. studies [6] on $K_4[Mo(CN)_7]\cdot 2H_2O$, and give such spectra for the new salt $NaK_3[Mo(CN)_7]\cdot 2H_2O$, which we have shown by single-crystal *X*-ray studies [7] to contain a pentagonal-bipyramidal anion.

RESULTS AND DISCUSSION

Heptacyano-complexes of Tungsten.—(*i*) *Potassium heptacyanotungstate*(II), $K_5[W(CN)_7]\cdot H_2O$. Although the salt $K_4[Mo(CN)_7]\cdot 2H_2O$ has long been known [8] and salts of $[Mo(CN)_7]^{5-}$ are now well characterised,[3,4] the corresponding tungsten analogues have not hitherto been made. The only low-oxidation-state cyano-complexes of tungsten in the literature are ' $K_4[W(CN)_6]$ ', made from molecular hydrogen and $K_4[W(CN)_8]\cdot 2H_2O$ at 390 °C,[9] and ' $K_3[W(CN)_6]$ ', obtained by the above method [9] or by reaction of ' $K_4[W(CN)_6]$ ' with nitrosyl chloride.[10]

We first attempted to prepare $K_5[W(CN)_7]\cdot 2H_2O$ by treating the tungsten(II) complex of the anion of 2-hydroxy-6-methylpyridine, $[W_2(OC_5H_3NMe)_4]$,[11] with an excess of potassium cyanide, since $K_5[Mo(CN)_7]$ is readily made [3] from $[Mo^{II}_2(O_2CMe)_4]$ and cyanide, but a complex and intractable mixture was obtained. However, reaction of $K_3[W_2Cl_9]$ with an excess of cyanide under anaerobic conditions and with u.v. irradiation gave the yellow crystalline product $K_5[W(CN)_7]\cdot H_2O$ in good yield. In the absence of u.v. light an unidentified green cyano-complex was formed; in air, $K_3[W_2Cl_9]$ is known [12] to react with cyanide to give $K_4[W(CN)_8]\cdot 2H_2O$.

The salt $K_5[W(CN)_7]\cdot H_2O$ is bright yellow and rapidly oxidised by moist air. The aqueous solution is stable only in the presence of excess of OH^- or CN^- and is very air-sensitive. The salt is diamagnetic. Although we have not yet succeeded in obtaining crystals suitable for a full structure determination, *X*-ray powder photographs show it to be isomorphous with $K_5[Mo(CN)_7]\cdot H_2O$, which is known [4] to contain a pentagonal-bipyramidal (D_{5h}) anion. Infrared and Raman spectra of the solid (Table) are very similar in profile to those of $K_5[Mo(CN)_7]\cdot H_2O$, again suggesting that the anion has D_{5h} symmetry. In aqueous solution containing an excess of hydroxide ion there are three Raman bands (two polarised, one depolarised) and two i.r. bands at different frequencies [see Figure 2(*c*)]. This is in full agreement with the selection rules for D_{5h} symmetry (Raman, $2A_1' + E_2'$; i.r., $A_2'' + E_1'$). It appears that, as with other heptacyano-complexes,[13] D_{5h} symmetry is maintained from the solid to aqueous solution. This is also suggested by the fact that there is little difference in the profiles of the Raman spectra of solid and solution. The i.r. spectrum of solid $K_5[W(CN)_7]\cdot H_2O$ is very similar in the ν(CN) region to that reported for ' $K_4[W(CN)_6]$ ' [9] and we suggest that the latter may well be $K_5[W(CN)_7]\cdot H_2O$.

(*ii*) *Potassium heptacyanohydrogentungstate*(II), $K_4[WH(CN)_7]\cdot 2H_2O$. In an attempt to prepare the unknown complex $K_4[W(CN)_7]$ we repeated the reported [9] reaction between $K_4[W(CN)_8]\cdot 2H_2O$ and molecular hydrogen at 390 °C. A dark material was obtained, the i.r. spectrum of which indicated that it contained *trans*-$K_4[WO_2(CN)_4]$,[14] $K_5[W(CN)_7]$, and a new cyano-complex. Recrystallisation from water–methanol gave a dark green solid analysing for $K_4[W(CN)_7]\cdot 2H_2O$. However, *X*-ray powder photographs showed it not to be isomorphous with $K_4[M(CN)_7]\cdot 2H_2O$ (M = V or Re), both of which are known to contain pentagonal-bipyramidal anions,[2,15] nor with $K_4[Mo(CN)_7]\cdot 2H_2O$. Furthermore, the salt is diamagnetic in the solid state and in aqueous solution, whereas $K_4[W(CN)_7]$ would be expected to be paramagnetic (d^3). On the basis of these and the following ^{13}C and ^1H n.m.r. data, we formulate it as a hydride, $K_4[WH(CN)_7]\cdot 2H_2O$. Attempts to obtain a crystal suitable for a full *X*-ray study have so far been unsuccessful.

(*iii*) *Carbon*-13 *and* ^1H *n.m.r. spectra of* $[WH(CN)_7]^{4-}$ *and* $[W(CN)_7]^{5-}$. The ^{13}C spectrum without proton decoupling of a solution of 0.2 mol dm^{-3} $[WH(CN)_7]^{4-}$ in 0.01 mol dm^{-3} CN^- is shown in Figure 1(*a*). The peak at 167.8 p.p.m. (all δ values relative to $SiMe_4$ on its low-field

Raman and i.r. spectra (cm^{-1}) of tungsten and molybdenum cyano-complexes [a]

Complex	Raman (R) or i.r.	ν(CN)	ν(MC) and δ(MCN)
$K_5[W(CN)_7]\cdot H_2O$	R	2 100(4), 2 072(8), 2 058(6), 2 036(6), 2 010(1) 1 989(9), 1 975(7)	420(6), 400(5), 390(3), 360(6), 345(7)
	R [b]	2 078(6) p, 2 050(4) p, 1 965(5) dp	
	I.r.	2 086w, 2 070s, 2 042w, 2 028s, 2 010s, 1 986s, 1 950vs	520s, 460w, 375w, 335w, 315vs, 294s
	I.r.[b]	2 100s, 2 078vs	
$K_4[WH(CN)_7]\cdot 2H_2O$	R	2 126(5), 2 116(7), 2 096(6), 2 088(6), 1 835w [ν(M–H)]	
	R [b]	2 128(6) p, 2 111(7) p, 2 082(6), 2 050(2), 1 835(2) [ν(M–H)]	470w, 450w, 390w
	I.r.	2 126w, 2 112w, 2 100vs, 2 080vs, 2 050vs, 2 045m, 1 830w [ν(M–H)] [c]	845w [δ(W–H)],[c] 490s, 445w, 420w, 390w, 363s
	I.r.[b]	2 090s, 2 070vs, 2 020vw, 1 830vw [ν(M–H)]	
$NaK_3[Mo(CN)_7]\cdot 2H_2O$	R	2 124(5), 2 110(10), 2 100(5), 2 089(9), 2 065(10)	
	R [b]	2 115(8) p, 2 100(5) p, 2 063(8)	
	I.r.	2 110m, 2 090vs, 2 070m, 2 043vs	550s, 460m, 360vs
	I.r.[b]	2 079m, 2 040m	
$K_4[Mo(CN)_7]\cdot 2H_2O$	R	2 115s, 2 097vs, 2 080vs, 2 060w	465w, 365w, 270w
	I.r.	2 110(sh), 2 100m, 2 064vs, 2 030 (sh)	498w, 460w, 430w, 390m, 360m, 340m, 294 (sh)
$K_5[Mo(CN)_7]\cdot H_2O$	R	2 105(2), 2 077(5), 2 062(5), 2 045(3), 2 018(3), 2 003(3), 1 990(8)	388(5), 365(4), 345(4), 330(4)
	R [b]	2 110(6) p, 2 070(8) p, 1 980(6)	330(4)
	I.r.	2 088w, 2 070vs, 2 050s, 2 040vs, 2 030s, 2 010s, 1 990m, 1 960vs	570w, 526s, 487w, 468w, 407w, 387w, 365w, 348w
	I.r.[b]	2 000m, 1 950vs	

[a] Data on solids unless otherwise indicated. Relative Raman intensities are given in parentheses; p = polarised, dp = depolarised. [b] Aqueous solution. [c] $\nu(W-{}^2H)$ 1 310, $\delta(W-{}^2H)$ 615 cm^{-1} in i.r.

side) is due to free CN^-, but those centred on 153.9 (doublet) and 148.5 p.p.m. are due to tungsten cyano-species since they show symmetrically placed tungsten satellites (^{183}W, 14.4% natural abundance, spin $\frac{1}{2}$). With proton decoupling the doublet at 153.9 p.p.m. collapses to a singlet and so must arise from a monohydrido-complex of tungsten [$J(^{13}C-^{1}H)$ 11.1, $J(^{183}W-^{13}C)$ 62.9 Hz] and we assign it to $[WH(CN)_7]^{4-}$. The peak at 148.5 p.p.m. [$J(^{183}W-^{13}C)$ 57.3 Hz] is assigned to $[W(CN)_7]^{5-}$. On addition of base (1.0 mol dm^{-3}) to the solution [Figure 1(*b*)] the intensity of the peak at 153.9 p.p.m. decreases while that at 148.5 p.p.m. increases, suggesting than an equilibrium (1) may be operative.

$$[WH(CN)_7]^{4-} + OH^- \rightleftharpoons [W(CN)_7]^{5-} + H_2O \quad (1)$$

By using long pulse-delay times (16 s) to allow for possible different relaxation times of the two species, a value of 0.4 $dm^3 mol^{-1}$ for $K = [W(CN)_7{}^{5-}]/[WH(CN)_7{}^{4-}][OH^-]$ was obtained. The sharpness of the ^{13}C resonances suggests that, on the n.m.r. time scale, there is no exchange of free and co-ordinated CN^- in either complex, and that these have fluxional structures as is likely to be the case for $[M(CN)_8]^{4-}$ (M = Mo or W)[16] and $[Nb(CN)_8]^{5-}$.[17]

Further evidence for the above equilibrium and formulation of the hydrido-complex is provided by the ^1H n.m.r. spectra of $[WH(CN)_7]^{4-}$ in aqueous CN^- solution which show a hydride resonance on the high-field side of the water peak at δ 2.4 p.p.m. with symmetrically placed tungsten satellites [$J(^{183}W-^{1}H)$ 34.0 Hz]; such relatively low-field metal hydride shifts have been noted for nine- and seven-co-ordinated hydridophosphine complexes of molybdenum and tungsten.[18] These low shifts may arise from the high co-ordination number of the metal,[19] since octahedral cyanide hydrides show large upfield shifts.[20] No signal is obtained in D_2O, presumably due to deuterium exchange with the proton. On addition of base to the green solution, the colour changes to yellow and the hydride peak becomes weaker, finally disappearing in 5 mol dm^{-3} OH^-; on careful addition of glacial acetic acid the peak re-appears. Addition of ethanol to the yellow alkaline solution gives $K_5[W(CN)_7]\cdot H_2O$, again suggesting that the equilibrium (1) is operative. The complex $K_4[WH(CN)_7]\cdot 2H_2O$ is the first eight-co-ordinate cyanide hydride and the first cyanide hydride of tungsten to be established. Although a hydrido-species $[WH(CN)_7(OH_2)]^{2-}$ has been postulated[21] as an intermediate in the photoaquation of $[W(CN)_8]^{4-}$, it was not isolated and its electronic spectrum is quite different from those of $[WH(CN)_7]^{4-}$ or $[W(CN)_7]^{5-}$.

(*iv*) *Vibrational spectra.* Raman and i.r. spectra (Table) of solid $K_4[WH(CN)_7]\cdot 2H_2O$ show, in addition to bands clearly assignable to ν(CN), bands near 1 830 and 845 cm^{-1}. These also appear in the Raman spectrum of the solution, and the band at 1 830 cm^{-1} in the i.r. spectrum of the aqueous solution. On deuteriation of the complex they shift to 1 310 and 615 cm^{-1}. We assign these bands to W–H stretching and deformation vibrations, similar bands and shifts being observed in $K_3[MH(CN)_5]$ (M = Co,[22] Rh,[23] or Ir[24]). The profiles of the Raman spectra of $K_4[WH(CN)_7]\cdot 2H_2O$ in the solid state and in aqueous solution are similar, suggesting that the stereochemistry of the anion may be little changed from solid to solution. The presence of four rather than three Raman bands in the solution suggests that the $W(CN)_7$ moiety is not pentagonal bipyramidal. There is a striking similarity between the profiles of the Raman

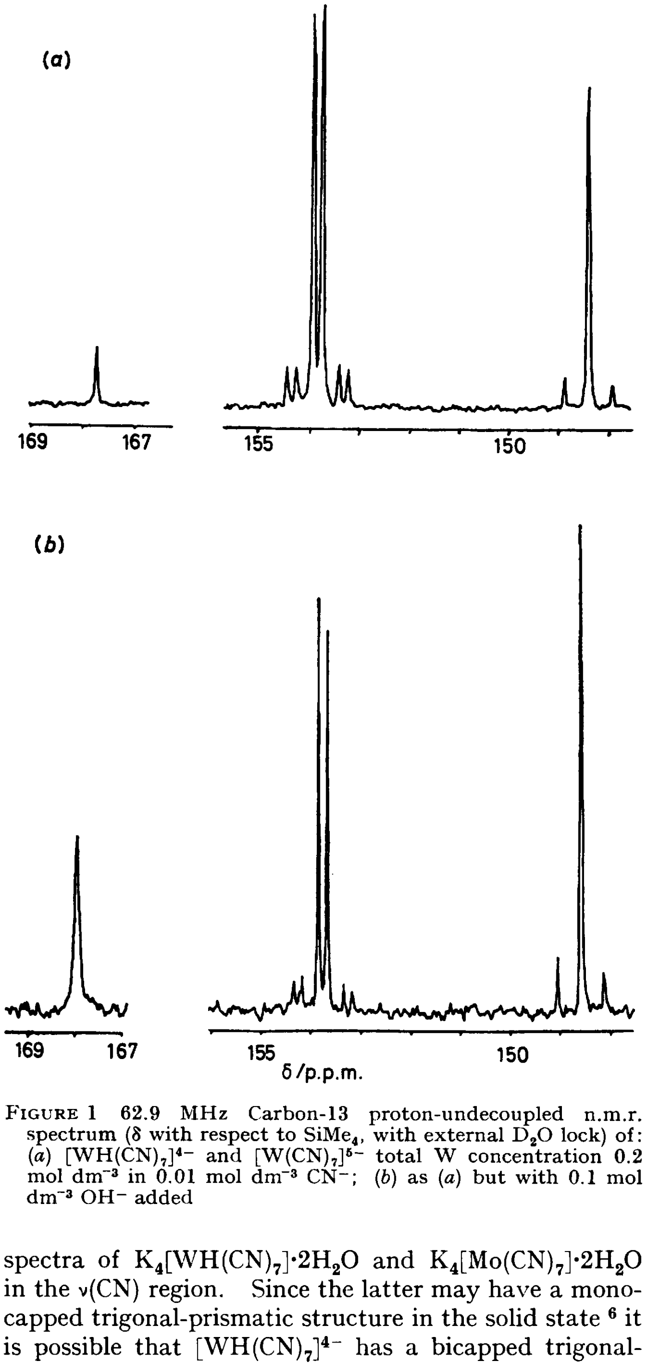

FIGURE 1 62.9 MHz Carbon-13 proton-undecoupled n.m.r. spectrum (δ with respect to $SiMe_4$, with external D_2O lock) of: (a) $[WH(CN)_7]^{4-}$ and $[W(CN)_7]^{5-}$ total W concentration 0.2 mol dm^{-3} in 0.01 mol dm^{-3} CN^-; (b) as (a) but with 0.1 mol dm^{-3} OH^- added

spectra of $K_4[WH(CN)_7]\cdot 2H_2O$ and $K_4[Mo(CN)_7]\cdot 2H_2O$ in the ν(CN) region. Since the latter may have a mono-capped trigonal-prismatic structure in the solid state [6] it is possible that $[WH(CN)_7]^{4-}$ has a bicapped trigonal-prismatic structure, as recently found for $Cs_3[Mo(CN)_8]\cdot 2H_2O$,[25] the hydride ligand occupying one cap and a cyanide ligand the other.

The i.r. spectrum of $K_4[WH(CN)_7]\cdot 2H_2O$ is similar to that reported for ' $K_3[W(CN)_6]$ ',[9] suggesting that the latter species may in fact be $K_4[WH(CN)_7]$.

By measuring the Raman spectra of a number of aqueous solutions of known initial concentrations of $[WH(CN)_7]^{4-}$ (containing 0.01 mol dm^{-3} CN^- and 0.60 mol dm^{-3} SO_4^{2-}) with known added amounts of OH^- (from 0 to 3.39 mol dm^{-3}) at a constant total ionic strength of 5.5 mol dm^{-3} at 25 °C, a value of $K = 0.2(1)$ dm^3 mol^{-1} was obtained; areas under the peak at 2 110 cm^{-1} of $[WH(CN)_7]^{4-}$ and that at 1 970 cm^{-1} of $[W(CN)_7]^{5-}$ were used to determine the concentrations of these two species. The peak at 982 cm^{-1} (ν_1) of SO_4^{2-} was used as an internal intensity reference for the measurements. Three such spectra are shown in Figure 2; in (a) there is almost pure $[WH(CN)_7]^{4-}$, in (b) approximately equal amounts of $[WH(CN)_7]^{4-}$ and $[W(CN)_7]^{5-}$, while in (c), the solution of which contains a large excess of OH^-, almost pure $[W(CN)_7]^{5-}$ is present. From this value of K, which is reasonably close to the less accurate value obtained from the ^{13}C n.m.r. data, the pK_a of $[WH(CN)_7]^{4-}$ is ca. 14.4, so it is a stronger acid than $[CoH(CN)_5]^{3-}$ (pK_a 20.0 [26]).

(v) *Chemical reactions of* $[WH(CN)_7]^{4-}$. Although no hydrogenation reactions seem to have been reported for $[RhH(CN)_5]^{3-}$ or $[IrH(CN)_5]^{3-}$, $[CoH(CN)_5]^{3-}$ is an active catalyst for hydrogenation reactions,[27] particularly for dienes.[28] However, $[WH(CN)_7]^{4-}$ in aqueous solution in the presence of an excess of CN^- at room temperatures does not react with but-2-yne, buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, cyclopentadiene, or cyclo-octa-1,3-diene over a period of 3 d, either in the presence or absence of molecular hydrogen. It does react with cyclohexa-1,3-diene and cyclohepta-1,3-diene giving cyclohexene and cycloheptene in 50 and 25% yields respectively (detection by g.l.c.), and there is some evidence for a small degree of isomerisation of hex-1-ene to hex-2-ene by the complex. Acrylonitrile, methyl methacrylate, and isoprene are polymerised in low yield, but styrene is polymerised in very high yield by the complex. None of these reactions is affected by the presence of molecular hydrogen.

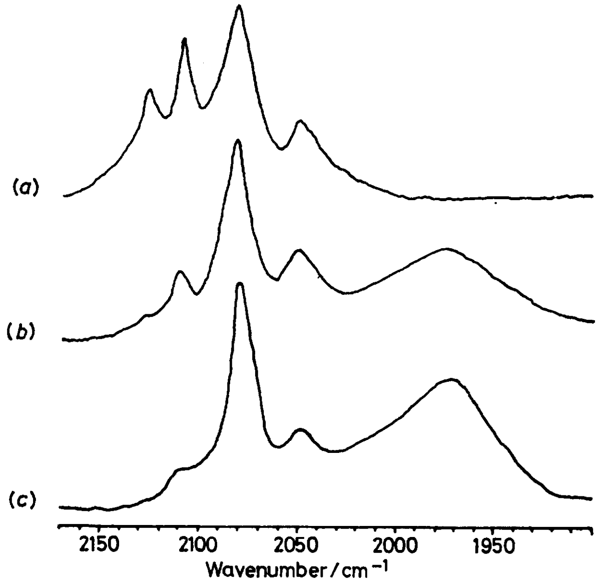

FIGURE 2 Raman spectra in the C≡N stretching region of $[WH(CN)_7]^{4-}$ and $[W(CN)_7]^{5-}$. (a) Total W concentration 0.04 mol dm^{-3} in 0.1 mol dm^{-3} CN^-; (b) as (a) but with 2.2 mol dm^{-3} OH^- added; (c) as (a) but with 3.4 mol dm^{-3} OH^- added

With sulphur dioxide, an aqueous solution of [WH-

$(CN)_7]^{4-}$ in excess of cyanide yields the new complex $K_4[W(OSO_2H)(CN)_7]$; this was characterised by elemental analyses. The bands assigned to co-ordinated HSO_3^- (at 1 180, 1 100, 1 053, 1 020, and 970 cm^{-1}, see Experimental section) are similar in position to those found[29] in $[Ru(OSO_2H)_2(NH_3)_4]$. With oxygen, a transient deep green colour is formed which quickly turns orange; the Raman spectrum of the latter solution shows, in addition to bands due to $[W(CN)_8]^{4-}$ and *trans*-$[WO_2(CN)_4]^{4-}$, a band at 855 cm^{-1} which could arise from a co-ordinated peroxo-ligand. Both $[CoH(CN)_5]^{3-}$ [30] and $[RhH(CN)_5]^{3-}$ [31] give peroxo- or hydroperoxo-complexes with dioxygen. Nitric oxide reacts with $[WH(CN)_7]^{4-}$ to give $[W(CN)_8]^{4-}$ probably *via* a nitrosyl cyano-intermediate. Hydrazine or OH^- gives $[W(CN)_7]^{5-}$; there is no reaction with H_2S or 2,2'-bipyridyl, and we were unable to prepare salts of $[WH(CN)_7]^{4-}$ with organic cations.

Preliminary observations suggest that $[MoH(CN)_7]^{4-}$ also exists, and this is now under investigation.

Heptacyano-complexes of Molybdenum.—The salts $K_4[Mo(CN)_7]\cdot 2H_2O$,[8] $K_5[Mo(CN)_7]$,[3] $K_5[Mo(CN)_7]\cdot H_2O$,[4] and $Na_5[Mo(CN)_7]\cdot 10H_2O$ [4] have been reported, and the anions of the latter two have been shown to have pentagonal-bipyramidal (D_{5h}) structures in the solid state. We have briefly reported that the anion in $NaK_3[Mo(CN)_7]\cdot 2H_2O$ has a D_{5h} structure.[7] Salts of $[Mo(CN)_7]^{4-}$ are of interest because e.s.r. and limited vibrational spectroscopic data suggested that $K_4[Mo(CN)_7]\cdot 2H_2O$ might contain a capped trigonal-prismatic (C_{2v}) structure in the solid state with a pentagonal-bipyramidal (D_{5h}) structure in solution.[6] We therefore prepared this salt, examined its e.s.r. spectra down to 13 K, measured its vibrational spectra in the solid state and aqueous solution, and performed the same measurements on the new salt $NaK_3[Mo(CN)_7]\cdot 2H_2O$. Vibrational data are also given for $K_5[Mo(CN)_7]\cdot H_2O$.

(*a*) *Sodium tripotassium heptacyanomolybdate*(III), $NaK_3[Mo(CN)_7]\cdot 2H_2O$. This new salt was made by reaction of $K_3[MoCl_6]$ with sodium cyanide. It forms deep green monoclinic crystals. A single-crystal *X*-ray study showed the anion to be pentagonal bipyramidal [Mo–C 2.160(2), C≡N 1.151(4) Å].[7] Raman and i.r. spectra of the solid are listed in the Table; the Raman spectra of the solid and its aqueous solution are similar, suggesting little change in the structure of the anion from solid to solution. The presence of three C≡N stretches in the Raman spectrum and of two in the i.r. spectra of the solutions is fully consistent with the retention of D_{5h} symmetry in solution.

The e.s.r. spectrum of the solid at liquid-helium temperatures [Figure 3(*a*)] is broad with $g_{\parallel}$ 3.89 and $g_{\perp}$ 1.17 at 2.4 and at 16.8 K; it becomes weaker as the temperature is raised, disappearing at 50 K. This behaviour is expected for a low-spin d^3 complex with a doubly degenerate *E* ground state, for which fast spin–lattice relaxation would be expected.[6] The salt is paramagnetic in the solid state ($\mu_{eff.}$ 1.78 B.M.* at 298 K) and in aqueous solution ($\mu_{eff.}$ 1.84 ± 0.05 B.M. at 298 K).

(*b*) *Potassium heptacyanomolybdate*(III), $K_4[Mo(CN)_7]\cdot 2H_2O$. Attempts to grow single crystals of this in a form suitable for *X*-ray structural analysis were unsuccessful, but *X*-ray powder-diffraction data show that the salt is not isomorphous with $K_4[M(CN)_7]\cdot 2H_2O$ (M = V or Re). Since these are known [2,15] to contain pentagonal-bipyramidal anions this finding supports the suggestion of Gray and co-workers[6] that the anion is not pentagonal bipyramidal in the dihydrated salt.

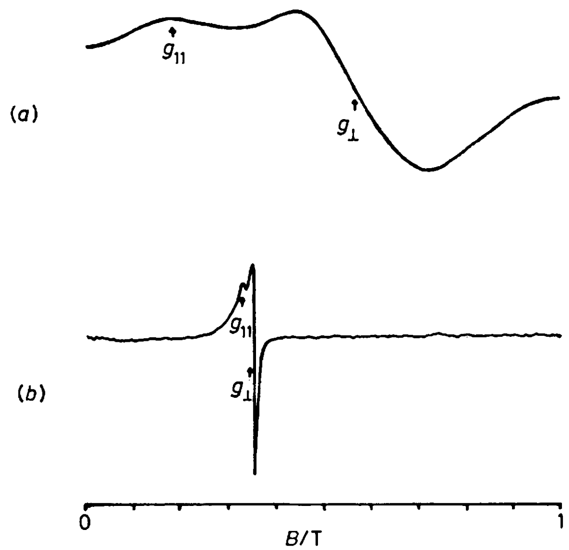

FIGURE 3 E.s.r. spectra: (*a*) pure $NaK_3[Mo(CN)_7]\cdot 2H_2O$ at 16.8 K, gain 2 500, power 40 dB; and (*b*) pure $K_4[Mo(CN)_7]\cdot 2H_2O$ at 14.3 K, gain 400, power 30 dB

We have extended the earlier e.s.r. data[6] on the salt by taking the measurements down to liquid-helium temperatures (14 K) for the undiluted solid (no isomagnetic host lattice is available for solid solution studies). The spectrum at 14 K [Figure 3(*b*)] is very different from that of $NaK_3[Mo(CN)_7]\cdot 2H_2O$ [Figure 3(*a*)]; it is much sharper and stronger. At 14 K, $g_{\parallel} = 2.11$ and $g_{\perp} = 1.98$, in close agreement with literature data for measurements at 77 K.[6] The signal broadens and loses structure above 100 K and is barely detectable at 200 K.

The magnetic moment ($\mu_{eff.}$) of the salt in aqueous solution at 297 K as measured by the Evans' method [32] is 1.84 ± 0.05 B.M.; in the solid at 297 K it is 1.80 B.M., in agreement with earlier data.[6,33]

Raman and i.r. spectra of the solid and its aqueous solution are listed in the Table; the data agree with earlier work[6] but are more extensive. The band splitting in the ν(CN) region for $K_4[Mo(CN)_7]\cdot 2H_2O$ is more complex than that in $NaK_3[Mo(CN)_7]\cdot 2H_2O$, again supporting the suggestion that $[Mo(CN)_7]^{4-}$ in the former salt has a lower symmetry than D_{5h}.

Reaction of $K_4[Mo(CN)_7]\cdot 2H_2O$ in aqueous cyanide with nitric oxide gave $K_4[Mo(CN)_8]\cdot 2H_2O$ as the major product.

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

(*c*) *Potassium heptacyanomolybdate*(II), $K_5[Mo(CN)_7]\cdot H_2O$. This is known from *X*-ray studies [4] to contain a pentagonal-bipyramidal anion (mean Mo–C 2.14 and C≡N 1.16 Å).[4] The Raman and i.r. spectra are listed in the Table together with data for the solution in base; for the latter, the appearance of three C≡N stretches in the Raman and two non-coincident i.r. C≡N stretches is in accordance with D_{5h} symmetry, and the similarity in profiles of the Raman spectra of the solid and solution suggests that pentagonal-bipyramidal symmetry is maintained from solid to solution. Our earlier suggestion [3] that solid $K_5[Mo(CN)_7]$ and its aqueous solution had lower symmetry than D_{5h} is erroneous, and probably arose from the poor quality of the Raman spectra then measured.

(*d*) *Potassium heptacyanovanadate*(III), $K_4[V(CN)_7]\cdot 2H_2O$. We attempted to measure the e.s.r. spectrum of this ion for the pure undiluted solid, for its solid solution in the isomorphous [2,15] diamagnetic host lattice $K_4[Re(CN)_7]\cdot 2H_2O$, and for its aqueous solution. However, like earlier workers,[34,35] we were unable to obtain a spectrum which was not overlaid by those of the decomposition products $[VO(CN)_5]^{3-}$ and $[V(CN)_6]^{4-}$.

EXPERIMENTAL

All operations were carried out under argon unless otherwise stated, and solvents were freed from dissolved oxygen by freezing and then allowing them to melt *in vacuo*.

Potassium Heptacyanotungstate(II) *Monohydrate*, $K_5[W(CN)_7]\cdot H_2O$.—*Method* (*a*). A saturated aqueous solution of K[CN] (10 cm³) was added to $K_3[W_2Cl_9]$ (0.1 g, 1.2 mmol). The suspension was irradiated with u.v. light while stirring. After 30 min, the temperature of the system had risen to 60 °C and the solid dissolved, the solution being dark green. After 8 h the solution was brownish yellow and a fine yellow precipitate was observed. The solution was allowed to cool at room temperature when oxygen-free methanol (20 cm³) was added, and some more very fine yellow precipitate was formed. After filtration, the gold-yellow product was washed three times with oxygen-free methanol and then dried under vacuum. Yield 0.1 g (80%).

Method (*b*). A 0.1 mol dm⁻³ aqueous solution of K[CN] (5 cm³) was added to $K_4[WH(CN)_7]\cdot 2H_2O$ (0.5 g, 0.9 mmol). When the solid had dissolved, Na[OH] (3.0 g) was added and the solution turned gold-yellow when all the hydroxide had dissolved. After 15 min methanol was added until no more precipitation of yellow microcrystals was observed. The precipitate was filtered off and washed three times with methanol and dried under vacuum. Yield 0.4 g, 80% (Found: C, 14.6; H, 0.4; K, 34.0; N, 16.8. $C_7H_2K_5N_7OW$ requires C, 14.5; H, 0.3; K, 33.8; N, 16.9%).

Electronic spectrum. Absorptions at 287 ($\varepsilon = 541.8$), 355 ($\varepsilon = 103.5$), and 410 nm ($\varepsilon = 35.7$ dm³ mol⁻¹ cm⁻¹) are observed for a solution of $K_5[W(CN)_7]\cdot H_2O$ in 0.1 mol dm⁻³ CN⁻.

Potassium Heptacyanohydrogentungstate(II) *Dihydrate*, $K_4[WH(CN)_7]\cdot 2H_2O$.—*Method* (*a*). The compound $K_4[W(CN)_8]\cdot 2H_2O$ (2.0 g, 3.4 mmol), and K[CN] (0.5 g, 7.6 mmol) were ground together and placed in a flask equipped with a thermometer and an exit tap. Air was displaced by argon on a vacuum line and the solid mixture was heated at 150 °C for 1 h, under argon. The temperature was then increased to 390 °C and hydrogen passed over the mixture in place of argon. The heating continued for 6 h during which time the solid changed from gold-yellow to black-green. The flask was cooled, and when the solid reached room temperature water was added and the remaining black residue was filtered off. To the mother-liquor, drops of methanol were added until a brown precipitate was observed. This was also filtered off. Repeated precipitation and filtrations were necessary to remove all the brown material before the green $K_4[WH(CN)_7]\cdot 2H_2O$ crystallised. The dark green product was washed three times with methanol and dried under vacuum. Yield 1.4 g, 74% (Found: C, 15.5; H, 0.6; K, 28.7; N, 17.4. $C_7H_5K_4N_7O_2W$ requires C, 15.0; H, 0.7; K, 28.0; N, 17.6%).

Method (*b*). The compound $K_5[W(CN)_7]\cdot H_2O$ (0.5 g, 0.9 mmol) was placed under argon in a Schlenk tube, and an aqueous solution of K[CN] (5 cm³, 0.01 mol dm⁻³) was added. The solid dissolved completely. The yellow solution was kept at 0 °C in the dark until the solution became green. Methanol was added and green flakes then formed. After filtration the solid was washed three times with methanol and dried under vacuum. Yield 0.3 g, 60% {N.B. if yellow $K_5[W(CN)_7]\cdot H_2O$ is precipitated together with the green $K_4[WH(CN)_7]\cdot 2H_2O$ the procedure must be repeated from the beginning} (Found: C, 15.3; H, 0.6; K, 28.7; N, 17.4. $C_7H_5K_4N_7O_2W$ requires C, 15.0; H, 0.7; K, 28.0; N, 17.6%).

Electronic spectrum. For an aqueous solution in 0.1 mol dm⁻³ CN⁻ absorptions at 404 ($\varepsilon = 896$), 355 ($\varepsilon = 2\ 455$), 323 ($\varepsilon = 2\ 570$), and 251.5 nm ($\varepsilon = 40\ 046$ dm³ mol⁻¹ cm⁻¹) are observed.

Sodium Tripotassium Heptacyanohydrogentungstate(II) *Dihydrate*, $NaK_3[WH(CN)_7]\cdot 2H_2O$.—Recrystallisation of $K_4[WH(CN)_7]\cdot 2H_2O$ from water–methanol in the presence of Na^+ produces the salt $NaK_3[WH(CN)_7]\cdot 2H_2O$ (Found: C, 15.1; H, 0.8; N, 17.4. $C_7H_5K_3N_7NaO_2W$ requires C, 15.5; H, 0.9; N, 18.0%).

Potassium Heptacyano(*hydrogensulphito*)*tungstate*(IV), $K_4[W(OSO_2H)(CN)_7]$.—The compound $K_4[W(CN)_7H]\cdot 2H_2O$ (0.5 g, 0.89 mmol) was transferred to a Schlenk tube and the air replaced by argon. Aqueous 0.01 mol dm⁻³ K[CN] solution (5 cm³) was added and, when the solid was completely dissolved, sulphur dioxide was bubbled into the solution for 30 min. The solvent was then removed under vacuum and an orange precipitate formed. Yield 0.46 g, 85% (Found: C, 14.1; N, 16.7; S, 5.5. $C_7HK_4N_7O_3SW$ requires C, 14.0; N, 16.2; S, 5.3%).

Infrared spectrum. Bands at 2 100vs, 1 180m, 1 100vs, 1 053m, 1 020w, and 970 cm⁻¹ were observed.

Sodium Tripotassium Heptacyanomolybdate(III) *Dihydrate*, $NaK_3[Mo(CN)_7]\cdot 2H_2O$.—This was obtained by a modification of the literature method for $K_4[Mo(CN)_7]\cdot 2H_2O$.[8] The salt $K_3[MoCl_6]$ (2.0 g, 4.7 mmol) and Na[CN] (4.0 g, 80 mmol) were mixed under argon. Water (20 cm³) was then added and the final solution was stirred for 18 h, during which time it became clear. Ethanol (30 cm³) was then added and the solution was allowed to cool to 0 °C. The dark crystals formed were filtered off, washed three times with ethanol, and then dried under vacuum. Yield 1.0 g, 47% (Found: C, 18.6; H, 0.8; N, 21.6. $C_7H_4K_3MoN_7NaO_2$ requires C, 18.2; H, 0.9; N, 21.6%).

Potassium Heptacyanomolybdate(III) *Dihydrate*, $K_4[Mo(CN)_7]\cdot 2H_2O$.—This procedure is a modification of that described by Gray and co-workers.[6] The compounds

$K_3[MoCl_6]$ (0.7 g, 1.6 mmol) and K[CN] (1.2 g, 18 mmol) were introduced into a 50-cm^3 two-necked flask. The air was replaced by argon on a vacuum line. Water (7 cm^3) was transferred to the flask and the mixture stirred for 24 h. The red-brown solution gradually assumed an opaque, black, colloidal appearance and, after 24 h, became transparent and yellow-brown in colour. Ethanol (3 cm^3) was added and a dark green precipitate was formed. After filtration, the solid was washed three times with 80% ethanol, then three times with pure ethanol, and dried under vacuum. Yield 0.7 g, 91% (Found: C, 18.2; H, 0.6; N, 20.8. $C_7H_4K_4MoN_7O_2$ requires C, 17.9; H, 0.9; N, 20.9%).

Potassium Heptacyanomolybdate(II) *Hydrate*, $K_5[Mo(CN)_7]\cdot H_2O$.—This procedure is a modification of that described in ref. 3. To a stirred saturated aqueous solution of potassium cyanide (5 cm^3) was added finely divided tetrakis(acetato)dimolybdenum(II) (0.5 g, 1.2 mmol) in small portions. The solution immediately became dark brown before lightening again and depositing yellow crystals. After filtration, water (5 cm^3) was added and the mixture heated to 60 °C in order to dissolve the solid. Methanol (10 cm^3) was added and the product precipitated as yellow crystals. This procedure was repeated twice and finally the solid was washed three times with methanol and dried under vacuum. Yield 0.9 g, 82% (Found: C, 17.4; H, 0.4; N, 20.0. $C_7H_2K_5MoN_7O$ requires C, 17.7; H, 0.4; N, 20.7%).

Potassium Heptacyanovanadate(III) *Dihydrate*, $K_4[V(CN)_7]\cdot 2H_2O$.—Many methods for preparing $K_4[V(CN)_7]\cdot 2H_2O$ have been reported [36-38] but we found that a modification based on the reported procedure [8] for $K_4[Mo(CN)_7]\cdot 2H_2O$ gave the best results.

Vanadium trichloride (1.0 g, 6.3 mmol) and K[CN] (4.1 g, 63 mmol) were placed in a 50-cm^3 three-necked flask (equipped with a magnetic stirrer bar). The air was replaced by argon on a vacuum line, water (27 cm^3) was added, and the mixture was stirred at room temperature for 22 h. The resulting violet precipitate was filtered off and the filtrate kept at 0 °C overnight. The deep red crystals formed were filtered off, washed with oxygen-free ethanol and then with diethyl ether. The product was recrystallised from a mixture of 5% aqueous K[CN] and methanol. A second crop of crystals was obtained by adding ethanol to the mother-liquor and following the above procedure. Total yield 73% (Found: C, 20.6; H, 0.4; N, 22.7. $C_7H_4K_4N_7O_2V$ requires C, 19.7; H, 0.4; N, 23.1%).

Raman spectra were measured on a Spex Ramalog 5 double monochromator with krypton-ion laser using yellow (5 682 Å) or red (6 471 Å) radiation; solids were studied as spinning discs on a KBr base and solutions in spinning cells under argon. Infrared spectra were measured on Perkin-Elmer 683, 597, and 325 instruments as mulls in liquid paraffin between caesium iodide plates, or as aqueous solutions between calcium fluoride plates. N.m.r. spectra were measured (^1H) on a Perkin-Elmer R32 90-MHz instrument or (^{13}C) on a Bruker WM 250 Fourier-transform spectrometer with samples of natural ^{13}C abundance. E.s.r. spectra were measured on a Varian E12 instrument at *ca.* 9.26 Hz using direct immersion in liquid nitrogen or by using cooled nitrogen and helium gases boiled directly from the liquid. Microanalyses were performed by Mr. K. Jones of the Imperial College Microanalytical Department; potassium was determined by flame photometry. *X*-Ray powder photographs were measured by Dr. R. Osborn.

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