The First Eight-co-ordinate Cyanide Hydride, $K_4[W(CN)_7H].2H_2O$ and a New Heptacyano-complex, $K_5[W(CN)_7].H_2O$

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Summary The preparation of the title compounds and their characterisation by ^{13}C n.m.r. and vibrational spectroscopy are described.

The only cyanide hydrides which have hitherto been isolated are salts of $[M(CN)_5H]^{3-}$ (M = Co, Rh, Ir).[1] We report here the first eight-co-ordinate cyanide hydride, and the first heptacyano-complex of tungsten.

We find that the anaerobic reaction of $K_3[W_2Cl_9]$ with excess of aqueous potassium cyanide under u.v. light gives the yellow, diamagnetic salt $K_5[W(CN)_7].H_2O$ (**1**). This is isomorphous with $K_5[Mo(CN)_7].H_2O$, which is known to contain a pentagonal bipyramidal anion.[2] The Raman and i.r. spectra of the solid and aqueous solutions are similar; the three Raman bands (2076 and 2050 cm^{-1} polarised, 1970 cm^{-1} depolarised) and two i.r. bands (2100 and 2070 cm^{-1}) indicate that D_{5h} symmetry is maintained in solution, as with other heptacyano-complexes.[3]

Reaction of $K_4[W(CN)_8].2H_2O$ with molecular hydrogen at 400 °C gives a dark material which, after recrystallisation from water–methanol under anaerobic conditions, gives the dark green salt $K_4[W(CN)_7H].2H_2O$ (**2**); earlier reports claimed that $K_4[W(CN)_6]$ was the product of this reaction.[4] The salt is not isomorphous with $K_4[M(CN)_7].2H_2O$ (M = V, Mo, Re). Elemental analyses† and its diamagnetism suggest that it might be a hydrido species, and this has now been confirmed by n.m.r. spectroscopy.

The ^{13}C n.m.r. spectrum, without proton decoupling, of (**2**) in 0·1 M aqueous cyanide solution is shown in the Figure; the peak at (a) is due to free CN$^-$, but those at (b) and (c) show tungsten satellites [^{183}W, 14·4% natural abundance, spin 1/2; J (^{183}W–^{13}C) 62·9 and 57·3 Hz for (b) and (c) respectively] and so are due to tungsten complexes. With proton decoupling the main doublet (b) collapses to a singlet and clearly arises from a monohydride [J (^{13}C–^{1}H) 11·1 Hz]; we assign it to $[W(CN)_7H]^{4-}$ and the line at (c) to $[W(CN)_7]^{5-}$. The ^{1}H n.m.r. spectrum of (**2**) in water shows a resonance at δ 2·8 with tungsten satellites [J (^{183}W–^{1}H) 34·0 Hz]; similar low-field hydride shifts are observed in other eight-co-ordinate tungsten hydride complexes.[5] On addition of base (KOH) to the solution the hydride resonance decreases in intensity and finally

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† 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%.

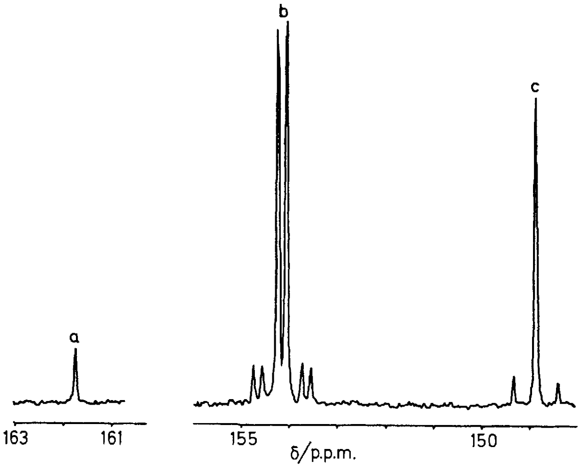

FIGURE. ^{13}C (62·9 MHz) proton-undecoupled n.m.r. spectrum (δ with respect to Me_4Si; with external D_2O lock) of $[W(CN)_7H]^{4-}$ (b) and $[W(CN)_7]^{5-}$ (c) in aqueous solution in the presence of free cyanide ion (a).

disappears; addition of ethanol to the solution at this stage gives (**1**). Similarly, in the ^{13}C spectrum, the intensity of resonance (c) increases at the expense of (b) if KOH is added to the solution; addition of acetic acid reverses both these effects, consistent with the equilibrium (1).

$$[W(CN)_7H]^{4-} + OH^- \rightleftharpoons [W(CN)_7]^{5-} + H_2O \qquad (1)$$

The sharpness of resonances (a), (b), and (c) suggests that, on an n.m.r. time scale, there is no exchange of free and co-ordinated CN^- and that the structures of (**1**) and (**2**) are probably fluxional in solution, as for $[M(CN)_8]^{4-}$ (M = Mo, W)[6] and for $[Nb(CN)_8]^{5-}$.[7]

I.r. and Raman spectra of (**2**) show, in addition to bands in the cyanide stretching region, bands at 1830 and 834 cm^{-1} which shift to 1310 and 615 cm^{-1} on deuteriation of the salt. We assign these to W–H stretching and deformation modes respectively {similar frequencies are found for eight-co-ordinate tungsten hydrido phosphines[5] and for $K_3[Rh(CN)_5H]$}.[8]

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