Crystal Structure of Potassium Heptacyanorhenate(III) Dihydrate

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The crystal structure of $K_4[Re(CN)_7]\cdot 2H_2O$ has been determined from three-dimensional *X*-ray diffraction data; 1 648 reflections have been observed and refined by least-squares methods to $R = 0.012$. The crystals are monoclinic, space group $I2$ with $Z = 2$, in a unit cell of dimensions $a = 9.244(2)$, $b = 8.998(2)$, $c = 9.241(2)$ Å, and $\beta = 92.53(2)°$. The anion is pentagonal bipyramidal, with essentially similar Re–C axial [2.077(3) Å] and mean equatorial [2.090(5) Å] distances, and with mean C–N distances of 1.161(5) Å. The structure is compared with those of other heptacyano-species.

As part of our continuing studies on cyano-complexes of the early transition metals we have determined the *X*-ray crystal structure of $K_4[Re(CN)_7]\cdot 2H_2O$, the preparation of which we recently reported.[1,2] The determination was carried out in order to check the correctness of our previous conclusions,[1-3] from Raman and i.r. spectra, that the anion in solid $K_4[Re(CN)_7]\cdot 2H_2O$ has pentagonal-bipyramidal (D_{5h}) symmetry, and to extend the range of structural studies on cyano-complexes of high co-ordination numbers.

EXPERIMENTAL

X-Ray Crystallography.—Crystals suitable for an *X*-ray investigation were prepared by the literature method.[1,2] A pale yellow multifaced crystal measuring 0.15 × 0.28 × 0.225 mm was selected, and Weissenberg and precession photographs taken with Cu-K_α and Mo-K_α radiations showed it to be monoclinic. The space group was determined to be either the centric $I2/m$ or the acentric groups $I2$ and Im (extinctions hkl, with $h + k + l$ odd), which are non-standard settings of $C2/m$, $C2$, and Cm. The body-centred cell was chosen for reasons of convenient β angle and easier comparisons with the cell of $K_4[V(CN)_7]\cdot 2H_2O$.[4] Least-squares lattice parameters and intensity data were collected on a Philips computer-controlled PW1100 diffractometer by the ω—2θ scan technique, the crystal being mounted approximately along the spindle axis [010].

Crystal data. $C_7H_4K_4N_7O_2Re$, $M = 560.76$, Monoclinic, $a = 9.244(2)$, $b = 8.998(2)$, $c = 9.241(2)$ Å, $\beta = 92.53(2)°$, $U = 768.0$ Å^3, $D_m = 2.45$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 2.42$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, graphite monochromatized, $\mu(\text{Mo-}K_\alpha) = 93.7$ cm^{-1}.

The intensities of 1 648 reflections were measured within the limits $2 < \theta < 35°$ (collection range $-14 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 11$). The intensities of three standard reflections (440, $\bar{4}40$, and $\bar{4}\bar{4}0$) measured every 60 min showed no systematic trend. The data were corrected for Lorentz and polarization effects. Standard deviations were calculated as previously described [5] using a p value of 0.04. Of the 1 648 reflections thus measured, all are considered as observed $[F_o^2 \geqslant 3\sigma(F_o^2)]$. Significant intensity variation for a few reflections was observed when rotating around the diffraction vector, so an absorption correction was made. Minimum and maximum transmission factors were 0.437 and 0.537.

Structural solution and refinement. The solution of the structure was based on conventional Patterson and Fourier methods. Three-dimensional Patterson maps revealed the rhenium and potassium atoms. The centrosymmetric space group $I2/m$ was rejected since it is not possible for a seven-co-ordinate polyhedron to possess $2/m$ symmetry. The absence of Harker lines ($\frac{1}{2}$, v, $\frac{1}{2}$) and the existence of Harker planes (u, $\frac{1}{2}$, w) suggested the space group $I2$, and this was subsequently confirmed by refinement of the structure. The rhenium atom was assumed to be at the origin lying on the binary axis, so the y co-ordinate was fixed at 0.0 to specify the origin in space group $I2$. Refinement was based on F_o, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The weights, w, were taken as $4\ F_o^2/\sigma^2(F_o^2)$. A difference-Fourier synthesis after preliminary refinements of the heavy atoms (values of 0.094 and 0.135 for the agreement indices R and R' were obtained for 838 observations) showed the positions of the non-hydrogen atoms. Subsequent cycles by full-matrix least squares with anisotropic thermal parameters for Re, K, C, N, and O atoms led to R and R' values of 0.017 and 0.021 for 1 648 observations. The thermal ellipsoid parameters for the water oxygen atoms suggested that the latter were disordered and this was further suggested by careful examination of a difference-Fourier map. Two-position disorder models for oxygen were then incorporated into a least-squares refinement (the R and R' values converged to 0.016 and 0.020 respectively); the site separation of the disordered water oxygen atoms was 0.8(1) Å, the occupancy factors being fixed at 0.5 owing to the relative peak heights in the difference maps.

At this point the refinement was expanded to include an enantiomeric model (B) related to the original arbitrary choice (A) by inversion. The anomalous dispersion terms for Re, K, N, and C were introduced and included in F_c during subsequent calculations. The two enantiomeric models were refined under identical conditions to values of 0.012 (R) and 0.016 (R') for enantiomer (A) and 0.022 and 0.029 for enantiomer (B). Model (B) was therefore rejected. The thermal parameters U_{11} (0.111 Å^2) for C(1) and U_{11} (0.233 Å^2) for N(1) were relatively large indicating a possibility of disorder. A difference electron-density map computed after a structure-factor calculation excluding C(1) and N(1) from the structure showed no resolved peaks in the map but an elongated one for this cyanide group. A least-squares refinement was attempted with a two-position disorder model and half-occupancy for both C(1) and N(1). Although there was no change in the R factor, refinement of this model gave satisfactory positions for C(1) and N(1), with appreciably lower temperature factors for these atoms. The site separation of the two C(1) and N(1) sites was respectively 0.40(3) and 0.59(4) Å. Parameter changes

TABLE 1

Final positional parameters for all non-hydrogen atoms in $K_4[Re(CN)_7]\cdot 2H_2O$ with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Re	0	0 [a]	0
K(1)	0.256 1(1)	0.404 8(2)	0.090 2(1)
K(2)	0.125 29(7)	−0.423 25(8)	−0.285 25(8)
C(1) [b]	0.021 7(14)	−0.232 1(6)	−0.000 1(29)
N(1) [b]	0.031 8(21)	−0.360 9(8)	0.001 6(23)
C(2)	−0.054 1(3)	−0.072 0(3)	0.205 3(3)
N(2)	−0.082 9(4)	−0.112 0(4)	0.320 3(4)
C(3)	−0.041 3(3)	0.188 1(3)	0.123 9(4)
N(3)	−0.067 3(6)	0.294 4(4)	0.187 3(5)
C(6)	0.215 0(2)	0.013 2(11)	0.073 8(3)
N(6)	0.334 7(3)	0.033 2(6)	0.113 7(4)
O(1) [b]	0.308 7(13)	−0.337 9(12)	−0.019 4(12)
O(2) [b]	0.394 2(17)	−0.307 8(14)	0.014 3(16)

[a] Co-ordinate chosen to define the origin. [b] Atom in crystallographic disorder (site population 0.5).

for other atoms were insignificant. The existence of disorder in the C(1) and N(1) positions is consequently proposed; this is consistent with the disorder of the water molecules to which they are hydrogen-bonded.

A final difference electron-density map showed no peaks greater than 0.8 e Å^{-3} in the vicinity of the rhenium atom (0.66 Å). Elsewhere in the map the features were less than 0.5 e Å^{-3} and the disordered hydrogen atoms could not be found. The final refinement resulted in values of 0.012 and 0.016 for *R* and *R′* with 1 648 observations and 113 variables. There was no evidence for secondary extinction.

The atomic scattering factors for rhenium, potassium, carbon, nitrogen, and oxygen atoms were taken from ref. 6, as were corrections for the real and imaginary part of the anomalous dispersion for the same atoms. All calculations were performed using the CII IRIS 80 computer system of the University P. and M. Curie. Anisotropic thermal parameters, observed and calculated structure factors, and root-mean-square components of thermal displacement along the principal ellipsoidal axes are available as Supplementary Publication No. SUP 22607 (12 pp.).[*] Table 1 lists positional parameters for all atoms.

DISCUSSION

Distances and angles about the metal atom are reported in Table 2. An overall view of the $[Re(CN)_7]^{4-}$ anion with the atomic numbering scheme is shown in Figure 1, and a stereoview of the crystal packing is presented in Figure 2.

The configuration of the cyanide ligands about Re is pentagonal bipyramidal as in $K_4[V(CN)_7]\cdot 2H_2O$.[4] In the rhenium complex the polyhedron has an imposed C_2 symmetry with the diad axis running through Re and the medium position of the disordered cyanide group [C(1)–N(1)]. Distortion from perfect D_{5h} symmetry is evident in the bond angles involving the axial ligands, which range between 86.4(3) and 98.5(6)°. The non-disordered carbon atoms of the pentagonal girdle are nearly coplanar, none of them being displaced more than 0.065 Å out of the least-squares plane (see Table 3) while the disordered carbon atom C(1) is displaced by 0.180 Å out of the equatorial least-squares plane in accord with a site separation of 0.40(3) Å between the two C(1) sites.

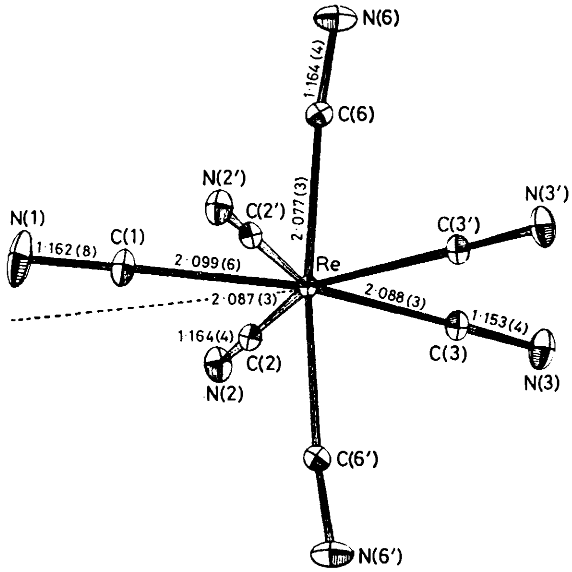

FIGURE 1 Perspective view of the $[Re(CN)_7]^{4-}$ anion. Atoms related by the diad axis are primed. Only one carbon atom C(1) and one nitrogen atom N(1) of the disordered cyanide group is given. The dotted line indicates the alternative position of the C(1)–N(1) group

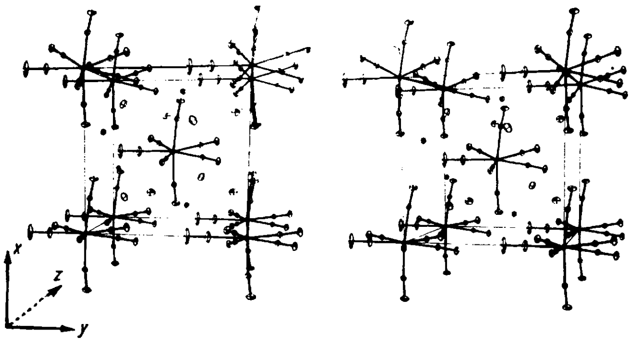

FIGURE 2 Stereoscopic drawing of the unit cell of $K_4[Re(CN)_7]\cdot 2H_2O$. The ellipsoids for all atoms represent 50% probability contours of thermal motion. Only the median position of the disordered cyanide group has been drawn

In most ML_7 complexes the metal–ligand axial bonds are shorter than the equatorial bonds.[7] In this structure the Re–C_{eq} bond distances average 2.090 ± 0.005 Å,[†] and the Re–C_{ax} bond distance 2.077 (3) Å is not significantly different. The mean Re^{III}–C (2.086 ± 0.008 Å) bond length may be compared with those in another complex of rhenium with different formal oxidation state and co-ordination. This average distance is comparable with the Re^{IV}–C distance of 2.09(2) Å reported[8] for $[PPh_4]_4[Re_4(CN)_{12}(\mu_3\text{-}S)_4]\cdot 3H_2O$. The C–N bonds average 1.161 ± 0.005 Å, a value consistent with other recent results of seven-co-ordinated cyano-complexes.[4,9] The angle C(6)–Re–C(6′) [173.4(6)°, C(6) and C(6′) being the axial carbon atoms] deviates less

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[*] For details see Notices to Authors, No. 7, *J.C.S. Dalton*, 1979, Index issue.

[†] Estimated standard deviations for any parameter are shown in parentheses, while average deviations are given as ±.

TABLE 2

Bond lengths (Å) and angles (°) within the $[Re(CN)_7]^{4-}$ anion [a]

(*a*) Distances

Re–C(1)	2.099(6)	C(1)–N(1)	1.162(8)
Re–C(2)	2.087(3)	C(2)–N(2)	1.164(4)
Re–C(3)	2.088(3)	C(3)–N(3)	1.153(4)
		C(6)–N(6)	1.164(4)
mean R–C$_{eq}$	2.090(5)	mean C–N	1.161(5)
Re–C(6)	2.077(3)		
mean Re–C	2.086(8)		

(*b*) Angles [b]

C(1)–Re–C(2)	73.6(7)	C(1)–Re–C(6)	88.1(6)
C(1)–Re–C(2′)	70.3(7)	C(1)–Re–C(6′)	98.5(6)
C(2)–Re–C(3)	72.3(1)	C(2)–Re–C(6)	89.1(1)
C(3)–Re–C(3′)	71.7(2)	C(2)–Re–C(6′)	93.0(1)
		C(3)–Re–C(6)	88.2(3)
		C(3)–Re–C(6′)	86.4(3)
C(6)–Re–C(6′)	173.4(6)	Re–C(1)–N(1)	178.8(1.5)
		Re–C(2)–N(2)	179.3(5)
		Re–C(3)–N(3)	177.1(4)
		Re–C(6)–N(6)	174.4(8)

[a] Estimated standard deviations are given in parentheses.
[b] Atoms related by the diad axis are primed.

TABLE 3

Least-squares planes for $[Re(CN)_7]^{4-}$

(*a*) Planes in crystal co-ordinates

(1): $8.796x + 0.034y + 2.452z = 0.003$
(2): $8.796x - 0.034y + 2.452z = -0.003$
(3): $8.801x + 0.038y + 2.436z = 0.004$
(4): $8.801x + 0.002y + 2.436z = -0.003$

(*b*) Deviations (Å) of various atoms from the plane. Estimated standard deviations are given in parentheses for the atoms which determined the least-squares planes

Atom	Plane 1	Plane 2	Plane 3	Plane 4
C(1)	0.180(13)		0.178(13)	
C(1′)		−0.180(13)		−0.189(13)
C(2)	0.021(3)	0.033(3)	0.017(3)	0.027(3)
C(2′)	−0.033(3)	−0.021(3)	−0.031(3)	−0.021(3)
C(3)	−0.057(3)	−0.063(3)	−0.059(3)	−0.059(3)
C(3′)	0.063(3)	0.057(3)	0.065(3)	0.065(3)
N(1)	0.268		0.266(17)	
N(1′)		−0.292		−0.280(17)
N(2)	0.049	0.063	0.042(4)	0.053(4)
N(2′)	−0.063	−0.049	−0.059(4)	−0.048(4)
N(3)	−0.126	−0.139	−0.129(5)	−0.133(5)
N(3′)	0.139	0.126	0.143(5)	0.139(5)
Re	−0.003	0.003	0.004	0.003

from linearity than the corresponding angle in the vanadium cyano-complex. Although the axial Re–C–N angles deviate significantly from 180°, the equatorial angles Re–C(1)–N(1) and Re–C(2)–N(2) are almost linear.

The $K\cdots N$ and $K\cdots O$ intermolecular contacts less than 3.4 Å are listed in Table 4. The closest $K\cdots N_{ax}$ distance is 2.832(3) Å for K(2)–N(6), the closest $K\cdots N_{eq}$ contact being 2.758(4) Å for $K(2)\cdots N(3)$. As shown in Table 4, the potassium ion K(1) is not involved in short intermolecular $K\cdots N$ contacts, but there is a strong $K\cdots O$ interaction [K(1)–O(1) 2.582(12) Å].

The distortion from the expected 180° of the Re–C–N angles, particularly those involving N(3) and N(6), appears to result from non-bonded interaction between those nitrogen atoms and the potassium ion K(2), and these short intermolecular contacts may explain the bending of the C(6)–Re–C(6′) angle. The shortest contacts involving the disordered oxygen atoms O(1) and O(2) to a nitrogen atom or to another oxygen atom related by symmetry are listed in Table 4. We were not able to find the hydrogen atoms of the water molecule, presumably because of the disorder.

The adoption by rhenium(III) of seven-co-ordination in $[Re(CN)_7]^{4-}$ is understandable since it thereby achieves an 18-electron configuration. All heptacyano-complexes which have been subjected to *X*-ray study have now been shown to have regular or distorted D_{5h} pentagonal-bipyramidal (p.b.) co-ordination: the d^2 $[V(CN)_7]^{4-}$ ion in $K_4[V(CN)_7]\cdot 2H_2O$,[4] the d^4 $[Mo(CN)_7]^{5-}$ ion in $K_5[Mo(CN)_7]\cdot H_2O$ [9] and in $Na_5[Mo(CN)_7]\cdot 10H_2O$,[9] and the d^4 ion $[Re(CN)_7]^{4-}$. Although it is claimed, from e.s.r. and spectroscopic data, that d^3 $[Mo(CN)_7]^{4-}$ in $K_4[Mo(CN)_7]\cdot 2H_2O$ has capped trigonal-prismatic geometry,[10] it is almost certainly p.b. in aqueous solution,[3] as are $[V(CN)_7]^{4-}$,[3,11] $[Mo(CN)_7]^{5-}$,[3] and $[Re(CN)_7]^{4-}$.[2,3] Furthermore, the d^2 ion $[Mo_2(CN)_{12}S]^{6-}$ in $K_7[Mo_2(CN)_{12}S]\cdot 0.5[MoO_4]^{2-}$,[12] and the formally d^3 ions $[Mo_2(CN)_8S_2]^{6-}$ in $Ba_3[Mo_2(CN)_8S_2]\cdot 14H_2O$ [12] and $[Re_2(CN)_8S_2]^{4-}$ in $[PPh_4]_4[Re_2(CN)_8S_2]\cdot 6H_2O$,[13] have distorted p.b. structures (if in the latter two cases the metal–metal bonds are taken into consideration). Since the cyanide ligand has none of the steric restraints associated with polydenticity or bulkiness, it seems likely that electronic factors are responsible for the adoption of p.b. symmetry over the energetically very similar [7] capped trigonal-prismatic or capped octahedral configuration. The extended Hückel molecular-orbital calculations of Hoffmann *et al.*[14] indicate a slight preference for the p.b. configuration for d^4 ML_7 complexes in which L is a π-acceptor ligand such as cyanide; crystal-field-stabilization-energy arguments also suggest that a p.b. configuration with a degenerate (e'') ground state will be slightly favoured.[4] It will

TABLE 4

Intermolecular contacts (in Å) $\leqslant 3.4$ Å: environments of K(1), K(2), and of the oxygen atom in $K_4[Re(CN)_7]\cdot 2H_2O$

(*a*) K(1) interaction

$K(1)\cdots O(1^{I})$	2.582(12)	$K(1)\cdots N(6^{III})$	3.120(4)
$K(1)\cdots N(2^{II})$	2.964(3)	$K(1)\cdots N(3^{IV})$	3.197(5)
$K(1)\cdots O(2^{I})$	2.982(15)	$K(1)\cdots N(1^{I})$ *	3.044(15)
$K(1)\cdots N(2^{III})$	3.101(4)	$K(1)\cdots N(3)$	3.312(5)

(*b*) K(2) interaction

$K(2)\cdots N(3^{V})$	2.758(4)	$K(2)\cdots O(1)$	3.022(12)
$K(2)\cdots N(6^{VI})$	2.832(3)	$K(2)\cdots N(6^{VII})$	3.099(4)
$K(2)\cdots N(2^{IV})$	2.845(3)	$K(2)\cdots N(1^{IV})$ *	3.104(15)
$K(2)\cdots N(1)$ *	2.879(18)	$K(2)\cdots N(2^{VIII})$	3.299(4)

(*c*) Oxygen environment

$O(1)\cdots N(1)$ *	2.584(22)	$O(1)\cdots N(1^{IV})$ *	3.166(22)
$O(1)\cdots O(2^{IX})$	2.758(22)	$O(1)\cdots N(3^{VIII})$	3.217(12)
$O(1)\cdots N(2^{VIII})$	3.069(10)	$O(2)\cdots N(3^{VIII})$	3.194(16)

Superscripts refer to the following symmetry positions (if no superscript appears *x*, *y*, *z* is implied):

I	$x, 1 + y, z$	VI	$-\frac{1}{2} + x, -\frac{1}{2} + y, -\frac{1}{2} + z$
II	$\frac{1}{2} + x, \frac{1}{2} + y, -\frac{1}{2} + z$	VII	$\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
III	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	VIII	$\frac{1}{2} + x, -\frac{1}{2} + y, -\frac{1}{2} + z$
IV	$-x, +y, -z$	IX	$1 - x, y, -z$
V	$-x, -1 + y, -z$		

* These atoms have crystallographic disorder and only the chemically reasonable interatomic distances are given.

clearly be of interest to examine further structures of heptacyano-complexes both in the solid state by *X*-ray crystallography and in solution by e.s.r. or vibrational spectroscopic techniques in order to establish whether p.b. co-ordination is general for these species.

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