Preparation and Properties of the Heptacyanomolybdate(II) Anion and the Crystal and Molecular Structures of its Sodium and Potassium Salts †

By **Michael G. B. Drew,*** **Philip C. H. Mitchell,*** and **Christopher F. Pygall,** Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The compounds $M^{I}_5[Mo(CN)_7]\cdot xH_2O$ [(II), M^{I} = Na, $x = 10$; (I) M^{I} = K, $x = 1$] have been isolated from the reaction of molybdate(VI) with cyanide and hydrogen sulphide in aqueous solution and by reduction of the $[Mo(CN)_4(O)_2]^{4-}$ ion with hydrazine. Crystals of (I) are triclinic, $Z = 2$, space group $I1$, $a = 9.069(8)$, $b = 9.218(8)$, $c = 9.029(8)$ Å, $\alpha = 89.51(8)$, $\beta = 90.17(9)$, $\gamma = 92.47(8)°$. Crystals of (II) are triclinic, $Z = 2$, space group $P\bar{1}$, $a = 16.527(12)$, $b = 8.355(8)$, $c = 8.324(9)$ Å, $\alpha = 105.48(9)$, $\beta = 80.90(9)$, $\gamma = 107.43(9)°$. 1 175 (K) and 2 790 (Na) independent reflections were measured on a diffractometer for the two compounds; structures were solved by the heavy-atom method and refined by full-matrix least squares to R 0.081 and 0.066 respectively.

In both salts the geometry of the heptacyanide ion is best described as a pentagonal bipyramid, but while in the Na salt the symmetry is D_{5h}, in the K salt the ion is much more distorted due to packing effects, one CN group being displaced (C 1.03, N 1.54 Å) from the MoC_4 plane giving a C_s structure. I.r. and u.v.–visible spectra and magnetic properties are reported and discussed.

As part of a study of sulphido-bridged molybdenum complexes we have re-investigated the reaction of an aqueous solution of sodium molybdate and potassium cyanide with hydrogen sulphide. Two of the products were previously formulated as being $K_3[MoS(CN)_4]\cdot 2H_2O$ (ref. 1) and $K_6[Mo_2S(CN)_{12}]\cdot 4H_2O$,[2] and our work on these compounds is reported in ref. 3. We observed also among the products of the reaction a small quantity of yellow crystals which proved to be the potassium salt of a new molybdenum(II) complex ion, the heptacyanomolybdate(II) ion, $[Mo(CN)_7]^{5-}$. Subsequently we prepared the potassium and sodium salts of this ion by reduction of aqueous solutions containing the tetracyanodioxomolybdate(IV) ion, $[Mo(CN)_4(O)_2]^{4-}$.‡ We have determined by single-crystal X-ray crystallography the structures of the sodium and potassium salts of the $[Mo(CN)_7]^{5-}$ ion and investigated their chemical and physical properties (electronic and i.r. spectra and magnetic susceptibilities). The structure of the $[Mo(CN)_7]^{5-}$ ion is of considerable interest as so few examples of seven-co-ordinate complexes containing equivalent unidentate ligands are known.[4] Apart from the heptafluorides, whose geometries are very often dependent upon the number of cations $\{M'_3[MF_7]$ having a pentagonal bipyramidal (PB), and $M'_2[MF_7]$ capped trigonal prismatic geometry (CTP)$\}$, only three examples are known which have been characterised by X-ray diffraction. These are $[Mo(CNR)_7]^{2+}$ (a regular CTP),[5] $[V(CN)_7]^{4-}$ (a regular PB),[6] and $[Er(dmp)_7]^{2+}$ (dmp = 2,6-dimethyl-4-pyrone).[7] The latter is a distorted PB with L_{ax}–M–L_{eq} angles ranging between 82 and 107°. The reasons for the geometry adopted in seven-co-ordination are not well understood and so more structure determinations are important.

Postulating a structure without X-ray work is hazardous but has been attempted for $[Ti(CN)_7]^{4-}$ (CTP from electronic spectra alone)[8] and for $K_4[Mo(CN)_7]\cdot 2H_2O$ (PB in solution but a CTP in the solid state from e.s.r., i.r., Raman, and electronic spectra).[9] $K_4[Re(CN)_7]\cdot 2H_2O$ is isomorphous with $K_4[V(CN)_7]\cdot 2H_2O$.[10]

EXPERIMENTAL

Preparations.—All experiments were carried out under oxygen-free nitrogen and solutions were deoxygenated before use. (*a*) *Potassium heptacyanomolybdate*(II) *hydrate*, $K_5[Mo(CN)_7]\cdot H_2O$, (I).

(i) *Reaction of molybdate*(VI), *cyanide, and hydrogen sulphide.* Potassium cyanide (31.6 g) was added to an aqueous solution (100 cm³) of potassium hydroxide (5.8 g) and molybdenum(VI) oxide (7.0 g). Hydrogen sulphide was bubbled through the solution for *ca.* 0.5 h and the solution set aside overnight. A small quantity of brown crystals which had collected on the nitrogen inlet tube was dissolved in water and reprecipitated with ethanol as a golden yellow powder. More crystals were obtained by filtering the final solution and cooling the filtrate in ice. The yellow crystals were washed with ethanol and dried *in vacuo* (1.0 g, 4%) (Found: C, 17.3; H, 0.6; K, 39.9; Mo, 19.6; N, 19.5. Calc. for $C_7H_2K_5MoN_7O$: C, 17.1; H, 0.4; K, 39.7; Mo, 19.6; N, 19.95%).

(ii) *Reduction of the* $[Mo(CN)_4(O)_2]^{4-}$ *ion with hydrazine.* $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ (2.3 g) and KCN (1.3 g) were dissolved in water (15 cm³). Hydrazine hydrate (2 cm³) was added to the solution which was then heated on a water-bath at *ca.* 60 °C for 2 h. The initially blue solution became green and when set aside overnight deposited yellow crystals

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† Reported at the Autumn Meeting of the Chemical Society, 1975, Abstract B7.

‡ Recently Kiernan and Griffith have reported the preparation of $K_5[Mo(CN)_7]$.[10]

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[2] A. Muller and P. Christophliemk, *Angew. Chem. Internat. Edn.*, 1969, **8**, 753.

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[6] R. A. Levenson and R. L. R. Towns, *Inorg. Chem.*, 1974, **13**, 105.

[7] C. Castellani Bisi, M. Gorio, E. Cannillo, A. Coda, and V. Tazzoli, *Acta Cryst.*, 1975, **A31**, S134.

[8] D. Nicholls, T. A. Ryan, and K. R. Seddon, *J.C.S. Chem. Comm.*, 1974, 635.

[9] G. R. Rossman, F.-D. Tsay, and H. B. Gray, *Inorg. Chem.*, 1973, **12**, 824.

[10] P. M. Kiernan and W. P. Griffith, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 377.

which were washed several times with ethanol, and dried *in vacuo* (0.7 g, 30%). More crystals were deposited when the solution was set aside for a further 10 days (Found: C, 17.1; H, 0.50; N, 20.0. Calc. for $C_7H_2K_5MoN_7O$: C, 17.1; H, 0.41; N, 19.95%). The i.r. spectrum was identical to that of a sample prepared as in (i).

(*b*) *Sodium heptacyanomolybdate*(II) *penta- and decahydrate*, (II), $Na_5[Mo(CN)_7]\cdot nH_2O$ (n = 5 *or* 10). These were prepared similarly. The decahydrate crystallised from aqueous solution. Hydrate water is readily lost (*e.g.*, *in vacuo* within a few min at room temperature). The pentahydrate crystallised from the hydrazine reduction reaction mixture (Found: C, 17.4; H, 0.86; Mo, 20.4; N, 20.3. Calc. for $C_7H_{10}MoN_7Na_5O_5$: C, 17.4; H, 2.09; Mo, 19.9; N, 20.3%). The low hydrogen analysis is due to loss of hydrate water during purging with argon immediately before combustion in our microanalytical procedure.

TABLE 1

Final positional co-ordinates (× 10^4) and isotropic thermal parameters for $K_5[Mo(CN)_7]\cdot H_2O$ (I), with standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*	Δ*d* *
Mo	0 000 †	0 000 †	0 000 †		0.00
K(1)	−2 895(8)	−3 325(8)	−1 175(8)		0.77
K(2)	1 199(7)	4 202(7)	−2 748(7)		0.11
K(3)	−1 431(8)	4 149(7)	2 657(8)		0.20
K(4)	2 341(8)	−3 748(7)	1 020(8)		0.38
K(5)	4 709(10)	2 681(12)	−0 014(9)		
C(1)	0 876(37)	2 212(36)	0 200(37)	40(7)	0.83
N(1)	1 516(31)	3 324(33)	0 401(34)	47(7)	1.45
C(2)	0 455(32)	0 721(32)	−2 234(33)	31(6)	0.16
N(2)	0 581(27)	1 097(27)	−3 470(29)	34(6)	0.34
C(3)	0 309(28)	−1 873(28)	−1 360(28)	21(5)	0.15
N(3)	0 469(31)	−2 923(32)	−2 048(32)	47(7)	0.22
C(4)	−0 636(30)	−1 833(31)	1 281(31)	28(6)	0.24
N(4)	−0 894(25)	−2 963(25)	1 951(26)	29(5)	0.25
C(5)	−0 693(30)	0 695(30)	2 142(31)	27(6)	0.14
N(5)	−1 125(33)	1 104(32)	3 258(33)	49(7)	0.27
C(6)	−2 267(28)	0 051(29)	−0 600(29)	16(6)	0.25
N(6)	−3 547(30)	−0 071(32)	−0 990(32)	42(6)	0.40
C(7)	2 178(33)	−0 355(34)	0 862(34)	26(7)	0.19
N(7)	3 171(40)	−0 532(40)	1 381(38)	57(8)	0.34
O(1)	−2 241(38)	3 574(37)	−0 590(37)	69(10)	

* Difference in position (Å) between equivalent atoms in potassium salt and vanadium complex. See text for method of calculation. † Parameters fixed.

Physical Measurements.—I.r. spectra (Nujol mulls) were recorded on a Perkin-Elmer 577 spectrophotometer. U.v. and visible spectra were recorded for powdered solids by diffuse reflectance with a Unicam SP 700 C spectrophotometer against MgO reference, and for solutions with a Unicam SP 1800 spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Faraday method.

Crystal Data.—$K_5[Mo(CN)_7]\cdot H_2O$, (I), M = 491.60, Triclinic, a = 9.069(8), b = 9.218(8), c = 9.029(8) Å, α = 89.51(8), β = 90.17(9), γ = 92.47(8)°, U = 754.1 Å^3, D_m = 2.12(3), Z = 2, D_c = 2.16, Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 22.0 cm^{-1}. Space group $I\bar{1}$ or $I1$, shown by successful refinement to be the latter.

$Na_5[Mo(CN)_7]\cdot 10H_2O$, (II) M = 573.23, Triclinic, a = 16.527(12), b = 8.355(8), c = 8.324(9) Å, α = 105.48(9), β = 80.90(9), γ = 107.43(9)°, U = 1 053.0 Å^3, D_m = 1.84, Z = 2, D_c = 1.81, μ(Mo-K_α) = 7.83 cm^{-1}. Space group $P\bar{1}$ or $P1$, shown by successful refinement to be the former. A General Electric XRD 5 apparatus was used to measure cell dimensions by least-squares refinement of high-angle reflections and diffraction intensities by the stationary-crystal–stationary-counter method. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. For (I), a crystal *ca.* 0.3 × 0.2 × 0.2 mm was mounted with the *a** axis parallel to the instrument axis. All crystals were twinned with *h0l* common; both twins being of approximate equivalent intensity. Data were taken on one twin, and *h0l* data were given a relative scale factor (later refined) of 0.5. There were few problems of overlap and 1 335 reflections were measured with 2θ < 50° of which 1 175 with $I > 3\sigma(I)$ were considered observed and used in subsequent calculations. For (II), a crystal *ca.* 0.1 × 0.2 × 1.0 mm

TABLE 2

Positional parameters (× 10^5 for Mo, × 10^4 for Na, C, N, O, × 10^3 for H) for $Na_5[Mo(CN)_7]\cdot 10H_2O$ (II), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	21 750(4)	36 622(9)	21 646(9)
C(1)	3 161(5)	3 598(12)	0 163(12)
N(1)	3 684(5)	3 604(11)	−0 957(10)
C(2)	3 148(5)	6 042(11)	2 696(11)
N(2)	3 668(5)	7 355(10)	2 937(12)
C(3)	1 806(5)	5 300(10)	4 439(10)
N(3)	1 626(4)	6 255(9)	5 648(10)
C(4)	0 907(5)	2 260(10)	3 079(9)
N(4)	0 248(4)	1 537(9)	3 543(9)
C(5)	1 823(5)	1 255(10)	0 358(10)
N(5)	1 650(5)	−0 026(10)	−0 642(10)
C(6)	1 730(5)	4 923(11)	0 714(11)
N(6)	1 584(4)	5 687(12)	−0 120(11)
C(7)	2 839(5)	2 593(10)	3 410(10)
N(7)	3 259(5)	2 049(11)	4 045(11)
Na(1)	0 007(2)	1 700(4)	6 702(4)
Na(2)	0 000 *	5 000 *	0 000 *
Na(3)	−1 404(2)	0 811(5)	3 680(5)
Na(4)	7 503(2)	2 288(5)	1 753(5)
Na(5)	4 834(2)	3 049(4)	3 531(4)
Na(6)	5 000 *	0 000 *	0 000 *
O(1)	−0 006(4)	2 087(8)	−0 397(8)
O(2)	−0 006(4)	4 591(8)	−2 927(8)
O(3)	1 501(4)	−1 144(9)	3 342(9)
O(4)	1 510(4)	2 212(10)	−3 285(9)
O(5)	3 472(4)	5 901(10)	6 853(10)
O(6)	3 199(6)	−0 236(12)	6 350(13)
O(7)	5 011(4)	6 081(8)	3 632(8)
O(8)	5 000(4)	−2 860(8)	−0 551(8)
O(9)	4 896(4)	−0 331(8)	−2 926(8)
O(10)	3 432(4)	9 278(10)	0 531(10)
H(11)	−048(8)	133(16)	018(15)
H(12)	050(8)	208(15)	006(15)
H(21)	−046(8)	487(16)	−310(15)
H(22)	047(8)	554(16)	−325(15)
H(31)	161(9)	−183(17)	277(17)
H(41)	160(8)	304(16)	−226(16)
H(42)	182(8)	280(16)	−402(16)
H(51)	349(8)	522(17)	740(16)
H(52)	311(8)	527(16)	582(16)
H(61)	314(8)	026(17)	571(17)
H(62)	335(8)	076(17)	719(16)
H(71)	540 *	620 *	270 *
H(72)	452(8)	619(16)	349(15)
H(81)	477 *	−359 *	−058 *
H(82)	544(8)	−310(15)	−009(15)
H(91)	449 *	−030 *	−318 *
H(92)	533 *	066 *	−300 *
H(101)	337(8)	1 000(17)	145(17)
H(102)	332(8)	867(17)	131(17)

* Parameter fixed.

was mounted with the (011) planes perpendicular to the instrument axis. 3 710 independent reflections were measured with $2\theta < 50^\circ$ of which 2 790 with $I > 3\sigma(I)$ were considered observed. No absorption or extinction corrections were made for either compound.

Both structures were solved by the heavy-atom method and refined by least squares. Atomic scattering factors for molybdenum, potassium, sodium, oxygen, carbon, nitrogen, and hydrogen were taken from ref. 11, as were corrections for the real and imaginary part of the anomalous dispersion for molybdenum, potassium and sodium. The potassium salt was refined with molybdenum and potassium anisotropic, and carbon, nitrogen, and oxygen isotropic, to R 0.081. The hydrogen atoms on the water molecule were not located. The opposite enantiomorph gave R 0.082 and was rejected. The sodium salt (II) was refined with all atoms except hydrogen anisotropic to R 0.066. 19 of the 20 hydrogen atoms on the water molecules were located on a difference-Fourier map and included in the structure-factor calculations. We attempted to refine the positional parameters of these atoms and this was successfully achieved for all but four. For these four parameters were fixed, as were the isotropic thermal parameters of all hydrogen atoms at values equivalent to those of the oxygen atoms to which they were bonded. For both structures full-matrix least squares were used and the weighting scheme, which was chosen to give average values of $w\Delta^2$ independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < F^*$ and $\sqrt{w} = F^*/F_o$ for $F_o > F^*$. F^* was 60 in (I) and 30 in (II). Calculations were made on a C.D.C. computer at the University of London Computer Centre with the programs listed in ref. 12 and on an I.C.L. 1904S computer at Reading University. In both structures, refinement was stopped when all shifts were $< 0.20\sigma$. The anisotropic thermal parameters are defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_j)$; $i,j = 1,2,3$; b_i being the i^{th} reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$.

TABLE 3

Bond lengths (Å) and angles (°) in $[Mo(CN)_7]^{5-}$ in (I) and (II)

	(I)	(II)
Mo–C(1)	2.16(3)	2.140(9)
Mo–C(2)	2.15(3)	2.139(8)
Mo–C(3)	2.16(3)	2.140(7)
Mo–C(4)	2.10(3)	2.201(7)
Mo–C(5)	2.15(3)	2.146(7)
Mo–C(6)	2.13(3)	2.129(11)
Mo–C(7)	2.16(3)	2.125(10)
C(1)–N(1)	1.17(4)	1.168(12)
C(2)–N(2)	1.17(4)	1.163(10)
C(3)–N(3)	1.17(4)	1.165(10)
C(4)–N(4)	1.21(4)	1.139(9)
C(5)–N(5)	1.17(4)	1.156(10)
C(6)–N(6)	1.23(4)	1.152(15)
C(7)–N(7)	1.03(5)	1.184(15)
Mo–C(1)–N(1)	171(3)	177(1)
Mo–C(2)–N(2)	175(3)	177(1)
Mo–C(3)–N(3)	177(2)	177(1)
Mo–C(4)–N(4)	174(2)	179(1)
Mo–C(5)–N(5)	176(3)	178(1)
Mo–C(6)–N(6)	173(2)	172(1)
Mo–C(7)–N(7)	174(3)	175(1)
C(1)–Mo–C(2)	74.6(12)	72.0(3)
C(1)–Mo–C(3)	138.6(11)	142.1(3)
C(1)–Mo–C(4)	141.8(12)	144.7(3)
C(1)–Mo–C(5)	74.8(12)	71.1(3)
C(1)–Mo–C(6)	108.5(11)	82.9(4)
C(1)–Mo–C(7)	79.1(12)	88.0(4)
C(2)–Mo–C(1)	71.2(10)	70.2(3)
C(2)–Mo–C(4)	143.1(11)	143.2(3)
C(2)–Mo–C(5)	143.8(11)	143.1(3)
C(2)–Mo–C(6)	86.0(10)	84.1(3)
C(2)–Mo–C(7)	102.4(11)	88.5(3)
C(3)–Mo–C(4)	73.2(10)	73.0(3)
C(3)–Mo–C(5)	144.2(10)	146.6(3)
C(3)–Mo–C(6)	91.8(10)	91.2(3)
C(3)–Mo–C(7)	86.1(10)	93.0(3)
C(4)–Mo–C(5)	71.0(10)	73.6(3)
C(4)–Mo–C(6)	85.6(10)	96.0(3)
C(4)–Mo–C(7)	84.6(10)	94.2(3)
C(5)–Mo–C(6)	85.7(10)	91.0(3)
C(5)–Mo–C(7)	90.3(10)	90.7(3)
C(6)–Mo–C(7)	170.1(10)	169.7(3)

For the potassium salt a few peaks with $F_o \gg F_c$ were carefully remeasured and it was often possible to distinguish between contributions from the two twins. Six reflections for which it was not possible were given zero weight. Apart from this there were no serious discrepancies among all reflections, including those zero-weighted, nor were there in the sodium salt. The final difference-Fourier maps showed no significant peaks. Final positional co-ordinates and thermal factors for (I) and (II) are given in Tables 1 and 2 and molecular dimensions for both structures are given in Table 3. Final observed and calculated structure factors and anisotropic thermal parameters in both structures, and the proposed hydrogen-bonding scheme in (II) are listed in Supplementary Publication No. SUP 21947 (14 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Structures.—The geometry of the $[Mo(CN)_7]^{5-}$ ion is different in the Na and K salts. In the sodium salt the geometry is a PB with only minor deviations. The C_{ax}–Mo–C_{eq} angles are spread between 82.9(4) and 96.0(3)°, very similar to those found in $[V(CN)_7]^{4-}$. This spread is a consequence of the C_{ax}–Mo–C_{ax} angle being 169.7° rather than any non-planarity of the girdle. The Mo–C(4) equatorial bond is longer than the others [2.201(7) *vs.* a mean of 2.141 Å], probably because of molecular contacts [N(4) having three close contacts to sodium ions, more than any other nitrogen atom]. A similar dependence of metal–ligand bond lengths on ligand–cation contacts is often found in seven-co-ordinate compounds [4] (see *e.g.* $[NbF_7]^{2-}$). Least-squares plane calculations show that the maximum deviation of any atom from the MC_5 girdle is 0.03 Å, and this is the Mo atom. Because of the Mo position the nitrogen atoms are all to one side of the MC_5 plane with deviations of up to 0.10 Å. It is often found [4] in the PB that M–L_{ax} distances are shorter than M–L_{eq}. We find such a difference in our sodium salt but it is only 0.01 Å, which may not be significant. Despite the irregularity of the packing of the anions in the sodium salt (see later, Figure 4), the regular geometry of the anion is quite striking particularly in view of the geometry in the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[11] ' International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1975.

[12] ' *X*-Ray '67 ' system of programs, ed. J. M. Stewart, University of Maryland Technical Report, TR 67, 58, 1967, revised July 1970.

potassium salt, where C_{ax}–Mo–C_{eq} angles are between 79.1 and 108.5°. From the least-squares planes calculations (Table 4), the nature of the distortion can be considered to be C_2 [from plane (1)] or C_s [from plane (2)]. However, if the C_{ax}–M–C_{eq} angles are taken into account it is clear that the best description is that in which C(1) and N(1) have been displaced from the equatorial plane by 1.03 and 1.54 Å respectively, leaving the molecule with a C_s distortion. This description is also in accord with the reason for the non-planarity, which is intermolecular contacts (see later). The symmetry of the anion is far from C_s, however [*e.g.*, C(7)–Mo–C(2), 102.4(11), C(7)–Mo–C(5), 90.3(10)°].

TABLE 4

Least-squares planes for the pentagonal girdle in the K and Na salts in the form $Ax + By + Cz = D$ where x,y,z are the crystallographic fractional co-ordinates of the atoms. Distances (Å) of relevant atoms from the planes are given in square brackets

(I): Plane (1): Mo, C(1)—(5)

$$8.81x - 1.00y + 2.02z = 0.14$$

[Mo −0.14, C(1) 0.45, C(2) −0.26, C(3) 0.05, C(4) 0.27, C(5) −0.38]

(II): Plane (1): Mo, C(1)—(5)

$$11.18x - 5.98y + 5.94z = 1.50$$

[Mo 0.03, C(1) −0.02, C(2) 0.01, C(3) −0.01, C(4) −0.01, C(5) 0.00, N(1) −0.10, N(2) −0.05, N(3) −0.07, N(4) −0.04, N(5) −0.02]

(I): Plane (2): Mo, C(2)—(5)

$$8.76x + 0.84y + 2.00z = -0.04$$

[Mo 0.04, C(2) +0.05, C(3) −0.12, C(4) +0.11, C(5) −0.08, C(1) 1.03]

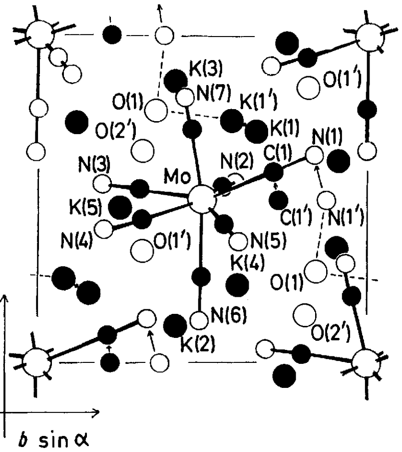

FIGURE 1 Structure of $K_5[Mo(CN)_7]\cdot H_2O$ (I) in the *c* projection. Closed circles: medium, K; small, C; open circles: large, Mo; medium, O; small, N. Positions of O(1), O(2), C(1), N(1), and K(1) in $K_4[V(CN)_7]\cdot 2H_2O$ are also shown and differentiated by primes. Arrows represent changes in position between the two structures. Dotted lines represent the close contacts that lead to the distorted structure

We will now show that packing effects cause the irregularity in the girdle of the potassium salt (Figure 1). $K_4[V(CN)_7]\cdot 2H_2O$ (III) (D_{5h} symmetry) has equivalent cell dimensions (within 3%) to those of our potassium salt.[6] Co-ordinates of the two structures are compatible with a pseudo-two-fold axis at $x = 0$, $z = 0$ running through V, and C(1) and N(1) atoms are paired (co-ordinates x,y,z and $\bar{x},y,\bar{z}$). Such an axis is still observable in (I) though to a less extent. (Atom numbering in (I) conforms with that for (III) to facilitate comparisons, although our enantiomorph is opposite to that given by the co-ordinates of ref. 6.) The differences between the two structures arise because associated with the V complex ion are $2H_2O$ and with the Mo complex ion $1H_2O + 1K^+$. The relative positions are shown in Figure 1, which is the unit cell in the *c* projection. It is obvious, from the contacts listed in Table 5, that K(5) in (I) cannot occupy either of the H_2O positions [O(1) and O(2)] in (III) since these are too close to other cations (in neither structure are there any K ··· K contacts <3.75 Å); it therefore occupies a different position with close contacts to four nitrogen atoms. Consequently a different position is needed for the water molecule; it is close to $3K^+$ [including K(5)]. The new positions of K(5) and O(1) necessitate changes in the positions of K(1) [which would otherwise be 2.19 Å from O(1)] and N(1) [2.11 Å from

TABLE 5

Intermolecular contacts for (I) <3.5 Å

(*a*) Environments of K(5) and O(1) in K salt (I) compared to those of O(1) and O(2) in V complex (III)

(i) In (I)

K(5) ··· N(3^{I})	2.82	O(1) ··· N(7^{IV})	2.87
K(5) ··· N(4^{II})	2.85	O(1) ··· K(5^{V})	2.90
K(5) ··· O(1^{III})	2.90	O(1) ··· K(1^{VI})	2.99
K(5) ··· N(1)	3.01	O(1) ··· K(3)	3.07
K(5) ··· N(6^{III})	3.18	O(1) ··· C(6)	3.25
K(5) ··· N(7)	3.45	O(1) ··· C(1)	3.22

(ii) In (III)

O(1) ··· O(2^{III})	2.77	O(2) ··· O(1^{V})	2.77
O(1) ··· K(4^{VI})	2.77	O(2) ··· K(1^{VI})	2.79
O(1) ··· N(5^{II})	3.17	O(2) ··· K(3)	3.35
O(1) ··· K(2)	3.34	O(2) ··· N(2^{VII})	3.15
O(1) ··· C(1)	3.32	O(2) ··· C(1)	3.33
O(1) ··· N(1)	3.24	O(2) ··· N(1)	3.25
O(1) ··· C(7)	3.40	O(2) ··· N(3^{VII})	3.22
O(1) ··· N(7)	3.50		
O(1) ··· N(4^{II})	3.24		

(*b*) Other K ··· N,O contacts <3.5 Å in (I)

K(1) ··· N(4)	3.36	K(2) ··· N(2)	2.97
K(1) ··· N(6)	3.09	K(2) ··· N(3^{VI})	2.84
K(1) ··· N(1^{VIII})	3.48	K(2) ··· N(1)	2.97
K(1) ··· N(5^{VIII})	3.00	K(2) ··· N(4^{II})	3.39
K(1) ··· N(7^{VIII})	3.19	K(2) ··· N(5^{II})	3.07
K(1) ··· N(2^{IX})	2.84	K(2) ··· N(6^{II})	3.01
K(1) ··· N(3)	3.16	K(2) ··· N(7^{IV})	2.87
K(3) ··· N(4^{VI})	2.76	K(4) ··· N(3)	3.34
K(3) ··· N(1)	3.48	K(4) ··· N(4)	3.17
K(3) ··· N(5)	2.88	K(4) ··· N(7)	3.05
K(3) ··· O(1)	3.06	K(4) ··· N(1^{XI})	2.83
K(3) ··· N(^{VII})	3.46	K(4) ··· N(6^{X})	3.05
K(3) ··· N(3^{VII})	3.34	K(4) ··· N(2^{X})	2.98
K(3) ··· N(7^{VII})	3.40	K(4) ··· N(5^{XII})	2.87
K(3) ··· N(6^{I})	2.95		

Roman numerals as superscripts refer to the following equivalent positions with respect to the molecule at x, y, z:

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

O(1)].[*] This movement is illustrated in Figure 1. The effect is greatest for K(1), C(1), and N(1) (Table 1). We conclude that the PB is the preferred geometry for the $[Mo(CN)_7]^{5-}$ ion and that the difference of energy between the regular structure and the distorted structure in our potassium salt is less than the difference of packing energy between this space group and any other. The heptafluorides and other seven-co-ordinate molecules with other first-row donor atoms often have irregular geometries much affected by packing.[4]

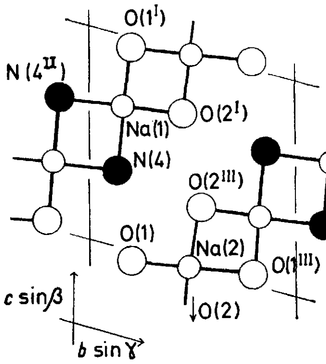

FIGURE 2 Arrangement of atoms at x *ca.* 0.00 showing sheets containing Na(1) and Na(2). Co-ordination octahedra are completed by axial atoms

The bond lengths in (I) have large standard deviations, no doubt because of the twinning, and so we cannot compare the lengths of the $Mo-C_{ax}$ and $Mo-C_{eq}$ bonds. In the vanadium complex all the V–C bonds are equivalent.

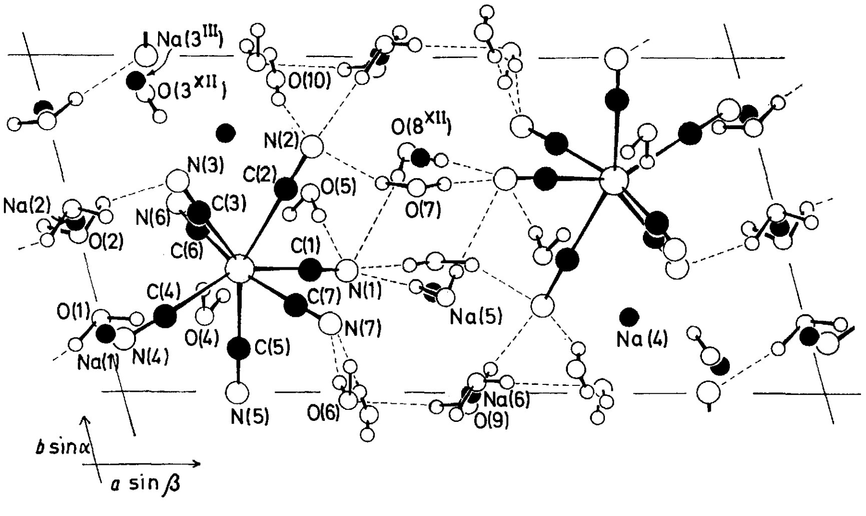

FIGURE 4 The unit cell of $Na_5[Mo(CN)_7]\cdot 10H_2O$ in the c projection. Open circles: large, Mo; medium, N; small, O; very small, H; closed circles: medium, C; small, Na. Postulated hydrogen bonds shown as dotted lines

The packing of the $[Mo(CN)_7]^{5-}$ ion with Na^+ and $10H_2O$ is complicated (Figures 2—4 and Table 6). The six independent sodium atoms have approximately octahedral environments. There are infinite sheets (Figures 2 and 3) of sodium and oxygen atoms parallel to (100); Na(1), Na(2), O(1), O(2) at $x = 0$, and Na(5), Na(6), O(7)—(9) at $x = 0.5$ in which the environment of the sodium atom is square planar. The co-ordination octahedron is completed by two more contacts in axial positions. These four sodium ions are bound to more oxygen than nitrogen atoms (Table 6). Na(3) and Na(4), with different x co-ordinates, have more contacts with the heptacyanides (3O + 3N nearest neighbours). We were able to find and refine most of the hydrogen atoms of the water molecules presumably because they are involved in hydrogen bonding (see Supplementary Publication). The majority of hydrogen bonding is to nitrogen rather than to other water molecules, with $O \cdots N$ contacts of *ca.* 2.9 Å. The $O-H \cdots N$ angles are as expected close to 180°; most $H \cdots N-C$ angles are *ca.* 110° but there are two of *ca.* 180°. Figure 4 is a packing diagram in the c projection.

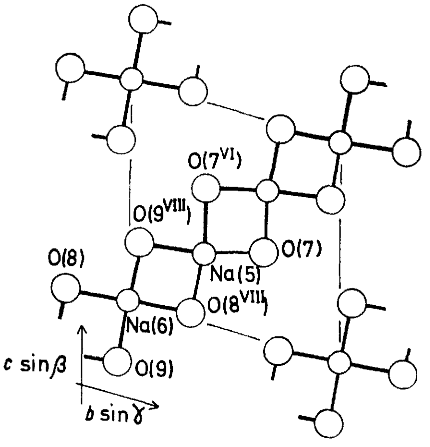

FIGURE 3 Arrangement of atoms at x *ca.* 0.50 showing sheets containing Na(5) and Na(6). Co-ordination octahedra are completed by axial atoms

Spectra.—I.r. spectra. Spectra in the ν(CN) region are listed in Table 7. For a pentagonal-bipyramidal $[Mo(CN)_7]^{5-}$ ion (D_{5h} symmetry) we expect two i.r.-active fundamental ν(CN) modes (a_2'' and e_1'). In

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[*] These values were calculated from a distance calculation which used the cell dimensions and co-ordinates (all signs reversed) of (III) and the co-ordinates of (I).

$K_5[Mo(CN)_7]\cdot H_2O$ (I) the symmetry of the anion is approximately C_s and we expect all seven fundamental stretching vibrations to be i.r.-active. None of the bands appears to be accidentally degenerate and all seven are observed. For $Na_5[Mo(CN)_7]\cdot 10H_2O$ (II) the symmetry of the anion is much closer to D_{5h} (the major deviation being a bending of the axial ligands away from their true axial positions), but we observe more than two ν(CN) bands presumably because of hydrogen bonding, and interaction of the CN groups with cations, which gives low site-symmetry.

TABLE 6

Intermolecular contacts in Na salt (II).* Environments of the sodium ions <3.0 Å

$Na(1) \cdots O(1^{I})$	2.35	$Na(4) \cdots O(5^{VI})$	2.48
$Na(1) \cdots O(2^{I})$	2.36	$Na(4) \cdots N(6^{VII})$	2.46
$Na(1) \cdots O(4^{I})$	2.39	$Na(4) \cdots O(10^{VII})$	2.47
$Na(1) \cdots O(3^{II})$	2.40	$Na(4) \cdots N(3^{VI})$	2.60
$Na(1) \cdots N(4)$	2.57	$Na(4) \cdots N(5^{VIII})$	2.58
$Na(1) \cdots N(4^{II})$	2.57	$Na(4) \cdots O(6^{IX})$	2.54
$Na(2) \cdots N(6),N(6^{III})$	2.50	$Na(5) \cdots N(7)$	2.49
$Na(2) \cdots O(1),O(1^{III})$	2.36	$Na(5) \cdots O(7)$	2.44
$Na(2) \cdots O(2),O(2^{III})$	2.37	$Na(5) \cdots O(7^{VI})$	2.31
$Na(3) \cdots O(3^{II})$	2.40	$Na(5) \cdots O(8^{VIII})$	2.42
$Na(3) \cdots N(3^{IV})$	2.49	$Na(5) \cdots O(9^{VIII})$	2.35
$Na(3) \cdots O(4^{V})$	2.41	$Na(5) \cdots O(5^{VI})$	2.67
$Na(3) \cdots O(6^{II})$	2.86	$Na(6) \cdots O(8),O(8^{VIII})$	2.31
$Na(3) \cdots N(5^{V})$	2.50	$Na(6) \cdots O(9),O(9^{VIII})$	2.40
$Na(3) \cdots N(4)$	2.60	$Na(6) \cdots O(10^{X}),O(10^{VII})$	2.47

* Roman numerals as superscripts refer to an atom in the following equivalent positions relative to the reference molecule (Table 1) at x,y,z

I	$x, y, 1+z$	VII	$1-x, 1-y, -z$
II	$-x, -y, 1-z$	VIII	$1-x, -y, -z$
III	$-x, 1-y, -z$	IX	$1-x, -y, 1-z$
IV	$-x, 1-y, 1-z$	X	$x, -1+y, z$
V	$-x, -y, -z$	XI	$x, y, -1+z$
VI	$1-x, 1-y, 1-z$	XII	$x, 1+y, z$

TABLE 7

I.r. spectra of $[Mo(CN)_7]^{5-}$ salts [a]

$Na_5[Mo(CN)_7]\cdot 10H_2O$	$Na_5[Mo(CN)_7]\cdot 5H_2O$	$K_5[Mo(CN)_7]\cdot H_2O$
1 968s	1 985sh	1 958s
1 999sh		1 989s
		2 014s
2 030s	2 031s	2 030s
		2 042s
2 044sh	2 061sh	2 058m
	2 072s	
2 078w, shp	2 078sh	2 074s
	2 080sh	
2 098s, shp		
2 108sh		
2 113sh		
2 142w, shp		
	530s	563w
	510sh	524s
	410m	485w
	250m	460w, sh
		406m

[a] Nujol mulls. Peak positions ($\tilde{\nu}/cm^{-1}$) and relative intensities (s = strong, m = medium, w = weak, sh = shoulder, shp = sharp). In addition to the bands listed all samples show broad absorptions at 3 500 and 1 630 cm^{-1} assigned to lattice water.

Electronic spectra. Peak positions and intensities are given in Table 8. The spectrum of (I) differs from that of solid (II) and the solution spectrum in having a band at 17 000 cm^{-1}. This is presumed to be a consequence of the distortion observed in the solid. For the solution spectrum the three bands of lowest energy are assigned to *d–d* transitions on the basis of the extinction coefficients and the reported energy-level diagram for the isostructural $[V(CN)_7]^{5-}$ ion.[13]

Magnetic Properties.—Magnetic susceptibilities, after correcting for diamagnetic contributions, corresponded to apparent magnetic moments 0.2—0.4 B.M. at 293 K. Thus the compounds are diamagnetic as expected for a $^1A_1'$ ground state with an $(e_1'')^4$ electronic configuration.

TABLE 8

U.v.–visible spectra [a]

$[Mo(CN)_7]^{5-}$, aq. $\tilde{\nu}/10^3\ cm^{-1}$	(23.0)	(25.6)	(28.2)	34.6 [b]	44.4
$\varepsilon/dm^3\ cm^{-1}\ mol^{-1}$	96	240	350	2 600	12 500
$Na_5[Mo(CN)_7]\cdot 10H_2O$, solid	23.0	27.4br		33.5	44.0
$K_5[Mo(CN)_7]\cdot H_2O$, solid	17.0	23.0	(25.2)	27.8	

[a] Peak positions and extinction coefficients for compounds in aqueous solution and peak positions in reflectance spectra of the solids relative to MgO standard. [b] May be due to $[Mo(CN)_7]^{4-}$ impurity.

General Discussion.—The heptacyanomolybdate(II) anion adds a fifth member to the series of heptacyano-complexes. Details of work on all five are given in Table 9. Our work has shown that deduction of the structures of the heptacyanides by any method other than single-crystal *X*-ray crystallography is difficult. For example, there are more bands in the i.r. spectrum of our sodium salt than expected for a PB structure, but our structure determination has shown this geometry to be correct. Similarly, *X*-ray powder photographs show that $K_5[Mo(CN)_7]\cdot H_2O$ and $K_4[V(CN)_7]\cdot 2H_2O$ are isomorphous, although we have shown that they do not have identical structures. The analogous rhenium

TABLE 9

Structures of heptacyano-complexes [a]

Complex anion	Metal electronic configuration	Structure
$[Ti(CN)_7]^{4-}$	d^1	$K_4[Ti(CN)_7]\cdot KCN$, CTP(?) solid (electronic spec.) [b]
$[V(CN)_7]^{4-}$	d^2	$K_4[V(CN)_7]\cdot 2H_2O$,PB solid (*X*-ray), PB soln. (electronic spec.) [c]
$[Mo(CN)_7]^{4-}$	d^3	$K_4[Mo(CN)_7]\cdot 2H_2O$, PB(?) soln. (i.r., Raman, electronic spec.); CTP(?) solid (i.r., electronic, e.s.r. spec.); $Cs_4[Mo(CN)_7]\cdot xH_2O$, PB(?) solid (i.r., Raman) [d]
$[Mo(CN)_7]^{5-}$	d^4	$Na_5[Mo(CN)_7]\cdot 10H_2O$, PB solid (*X*-ray). $K_5[Mo(CN)_7]\cdot H_2O$, PB distorted (*X*-ray). $K_5[Mo(CN)_7]$, CTP(?) solid and soln. (i.r., Raman) [e]
$[Re(CN)_7]^{4-}$	d^4	$K_4[Re(CN)_7]\cdot 2H_2O$, PB(?) (i.r., Raman, isomorph. V cpd.) [f]

[a] CTP, mono-capped trigonal prismatic (C_{2v}); PB, pentagonal bipyramidal (D_{5h}). Only those structures derived from single crystal *X*-ray crystallography can be regarded as established (see text). [b] Ref. 8. [c] Ref. 6. [d] Ref. 9. [e] This work. [f] Ref. 10.

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[13] R. A. Levenson and R. J. G. Dominguez, *Inorg. Chem.*, 1973, **12**, 2342.

heptacyanide may, however, be a PB since it is a dihydrate like the vanadium complex. Electronic spectra are also unreliable as a guide to structure, particularly for the CTP, as the relative positions of the energy levels are unknown; theoretical calculations are dependent on the choice of input parameters.[4] We are therefore sceptical about the claims that the d^1 Ti^{III} and d^3 Mo^{III} heptacyanides have the CTP structure.[8,9] We consider that prediction of geometry on the basis of spectra can only be justified for a seven-co-ordinate molecule which exhibits the two electronic bands, two i.r., and three Raman bands of the D_{5h} symmetry PB.

There is a further problem with the d^3 Mo^{III} heptacyanides: if it is a PB in solution, why does it not crystallize in the low-energy $I1$ space group found in the vanadium, the rhenium complexes, and our potassium salt?

However it is certain that both the d^2 V^{III} and the d^4 Mo^{II} compounds have the PB structures in accordance with theoretical expectation for the doubly degenerate ground-state (e_1'').[6] Any theory of seven-co-ordinate structures must also account for the fact that the $[Mo(CNR)_7]^{2+}$ ion, also d^4 Mo^{II}, is almost a perfect CTP.

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