Inorganica Chimica Acta, 45 (1980) L81–L82
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The X-ray Crystal Structure of $NaK_3[Mo(CN)_7]\cdot 2H_2O$ and the Structure of its Anion in Aqueous Solution

M. B. HURSTHOUSE, K. M. A. MALIK

Department of Chemistry, Queen Mary College, London, E1 4NS, U.K.

A. M. SOARES, J. F. GIBSON and W. P. GRIFFITH

Inorganic Chemistry Research Laboratories, Imperial College, London, SW7 2AY, U.K.

Received April 9, 1980

It has been suggested on the basis of EPR and vibrational spectra that the $[Mo(CN)_7]^{4-}$ ion has a pentagonal bipyramidal structure in the anhydrous potassium salt and in aqueous solution, but that in $K_4[Mo(CN)_7]\cdot 2H_2O$ it has a capped trigonal prismatic structure [1]. Since all other heptacyano complexes which have been subjected to X-ray study have been found to have pentagonal bipyramidal anions ($K_4[M(CN)_7]\cdot 2H_2O$, M = V [2], Re [3]; $K_5[Mo(CN)_7]\cdot H_2O$ [4], $Na_5[Mo(CN)_7]\cdot 10H_2O$ [4]) we have studied salts of $[Mo(CN)_7]^{4-}$. The potassium salt has so far not yielded crystals suitable for X-ray study, but we have for the first time prepared the mixed salt $NaK_3[Mo(CN)_7]\cdot 2H_2O$ and report here its X-ray crystal structure, EPR and vibrational spectra.

The salt was made by slow aerial oxidation of $Na_5[Mo(CN)_7]\cdot 10H_2O$ in an aqueous solution containing sodium cyanide, potassium borohydride and methanol. The dark green crystals are monoclinic, space group $P2_1/m$ with $a = 8.046(2)$, $b = 11.686(1)$, $c = 8.737(3)$ Å, $\beta = 110.60(3)°$, $U = 768.97$ Å, $D_m = 1.95$ g cm^{-3}, $Z = 2$, $D_c = 1.96$ g cm^{-3} and μ(Mo-Kα) 15.8 cm^{-1}.

Intensity data ($1.5 < \theta < 28°$) wre recorded on a Nonius CAD4 diffractometer [5] using Mo-K$_\alpha$ radiation. Of 2521 reflections measured, 2227 were considered observed [$F_o > 3\sigma(F_o)$] and used in the structure solution (heavy atom method) and refinement (full-matrix least-squares). The R factor is currently 0.033 (all non-hydrogen atoms anisotropic).

The structure of the $[Mo(CN)_7]^{4-}$ anion is shown in Fig. 1. The coordination about the molybdenum atom is that of a relatively undistorted pentagonal bipyramid. The mean molybdenum–carbon distance of 2.160(3) Å is comparable with that (2.140 Å) observed [4] in $Na_5[Mo(CN)_7]\cdot 10H_2O$. The axial and equatorial Mo–C distances are equal within experimental error, as is the case with the corresponding parameters in $K_4[M(CN)_7]\cdot 2H_2O$ (M = V [2], Re [3]). In agreement with this, the EPR spectrum of an undiluted sample of the powdered material is broad and anisotropic ($g_\perp = 1.77$, $g_\parallel = 3.89$ between 2.4 and 24 K); the signal becomes progressively weaker with increasing temperature and is not observed at 50 K. Such behaviour is to be expected for a low-spin d^3 complex of D_{5h} symmetry [1]. The Raman spectrum of the solid shows four bands in the C≡N stretching region at 2110, 2098, 2088 and 2065 cm^{-1} (three $2A_1' + E_2'$ are expected for D_{5h} symmetry) and two strong bands in the infrared (2090 and 2042 cm^{-1}; $A_2'' + E_2'$).

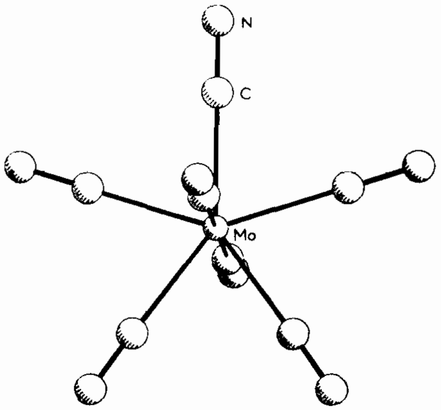

Fig. 1. The structure of $[Mo(CN)_7]^{4-}$ ion showing the pentagonal bipyramidal geometry. Some important geometry parameters are: Mo–C, 2.157–2.164(2) A; C–N, 1.138–1.160(4) A; Mo–C–N, 175.6–179.1(3)°; C–Mo–C angles in the pentagon 71.4–73.2(1)°.

Measurement at 13 K of the EPR spectrum of $K_4[Mo(CN)_7]\cdot 2H_2O$ as an undiluted solid shows sharp signals similar to those observed by Gray *et al.* [1] ($g_\parallel$ 2.11, $g_\perp$ 1.98) in good agreement with the values expected for the $^2A_1$ $(a_2)^2(a_1)^1$ ground state (g_x 1.983, g_y 1.981, g_z 2.107) predicted for C_{2v} geometry of the anion [1]. The same spectrum is seen at 77 K but collapses to a single isotropic line ($g = 2.00$) at 120 K and disappears above 200 K.

The X-ray powder photographs of $K_4[Mo(CN)_7]\cdot 2H_2O$ and $NaK_3[Mo(CN)_7]\cdot 2H_2O$ show that these salts are not isomorphous. The vibrational spectra of $K_4[Mo(CN)_7]\cdot 2H_2O$ differ somewhat from those of $NaK_3[Mo(CN)_7]\cdot 2H_2O$ in the CN region (2060w, 2080s, 2097s, 2115w cm^{-1} in the Raman spectrum and 2030m, 2064s, 2100m, 2110sh, cm^{-1} in the infrared). The anion $[Mo(CN)_7]^{4-}$ is stable in aqueous solution only in the presence of excess cyanide or hydroxide ion [1]. Raman spectra of such solutions show three bands (2115 and 2100 cm^{-1}, polarised, and a weak depolarised band at 2063 cm^{-1}), and infrared spectra of such solutions show two bands (2080 and 2040 cm^{-1}), consistent with

D_{5h} symmetry for the species in solution. No signal characteristic of a D_{5h} species could be seen in the EPR spectra of aqueous solutions down to 13 K; it is possible that the line is too broad to be detected under these circumstances.

We conclude that $[Mo(CN)_7]^{4-}$ has D_{5h} pentagonal bipyramidal symmetry in $NaK_3[Mo(CN)_7] \cdot 2H_2O$ and in aqueous solution, but agree with earlier workers [1] that the symmetry of the anion in $K_4[Mo(CN)_7] \cdot 2H_2O$ may be lower.

Acknowledgement

We thank the Science Research Council, for the X-ray equipment, and thank the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico, Brazil, for a scholarship to one of us (A.M.S.).

References

1 R. G. Rossman, F. D. Tsay and H. B. Gray, *Inorg. Chem., 12,* 824 (1973).
2 R. A. Levenson and R. L. R. Towns, *Inorg. Chem., 13, 105 (1974).*
3 J. M. Manoli, C. Potvin, J-M. Bregeault and W. P. Griffith, *J. Chem. Soc. Dalton,* 192 (1980).
4 M. G. Drew, P. C. H. Mitchell, and C. E. Pygall, *J. Chem. Soc. Dalton,* 1071 (1977).
5 M. B. Hursthouse, R. A. Jones, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc., 101,* 4128 (1979).