1. Davies, H., Erdtman, H. and Nilsson, M. *Tetrahedron Letters* **1966** 2491.
2. Teuber, H. J. and Steinmetz, G. *Chem. Ber.* **98** (1965) 666.
3. Teuber, H. J. and Dietrich, M. *Chem. Ber.* **100** (1967) 2908.

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Note on the Crystal Structure of Potassium Pentacyanonitrosylvanadate(I), $K_3V(CN)_5NO \cdot 2H_2O$

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Potassium pentacyanonitrosylvanadate was first prepared in 1958 by Griffith, Lewis and Wilkinson [1] who formulated the compound as $K_5V(CN)_5NO \cdot H_2O$. The crystal structure of the isoelectronic pentacyanonitrosylmanganate, $K_3Mn(CN)_5NO \cdot 2H_2O$ [2] and the structures of the related chromium and molybdenum complexes, $K_3Cr(CN)_5NO$ [3] and $K_4Mo(CN)_5NO$ [4] have been determined at this department as part of a series of structural investigations of the transition metal pentacyanonitrosyls. The crystal structure of potassium pentacyanonitrosylvanadate, which should perhaps be reformulated as $K_3V(CN)_5NO \cdot 2H_2O$, has now also been investigated and a preliminary report will be given in this note.

Potassium pentacyanonitrosylvanadate was prepared according to the method of Griffith, Lewis and Wilkinson [1] whereby an alkaline solution of ammonium vanadate was first treated with a solution of potassium cyanide and then with hydroxylammonium chloride. The orange oily liquid phase which separated when the solution was subsequently poured on to alcohol was washed several times with alcohol, dissolved in water, reseparated with alcohol and then allowed to stand under alcohol. After several days bright orange plate-like crystals separated from the oil. A suitable crystal was picked out under the microscope, dried between filter papers and mounted in a glass capillary. Rotation photographs and Weissenbergs photographs of the layers $h0l$—$h4l$, inclusive, were recorded using multiple film equi-inclination Weissenberg techniques and Cu$K\alpha$ radiation. The relative intensities of the 463 reflections thus registered were estimated by visual comparison with a standard scale.

The crystal was found to be orthorhombic with the approximate cell dimensions:

$$a = 15.6 \text{ Å}, \; b = 7.2 \text{ Å}, \; c = 11.7 \text{ Å}$$

The observed conditions of reflection,

$$0kl{:}\, l = 2n$$
$$h0l{:}\, l = 2n$$
$$hk0{:}\, h+k = 2n$$

are in accordance only with space group No. 56, *Pccn*. The calculated density based on four formula units of $K_5V(CN)_5NO \cdot H_2O$ in the unit cell is 2.15 $g \cdot cm^{-3}$ (1.84 $g \cdot cm^{-3}$ for four formula units of $K_3V(CN)_5NO \cdot 2H_2O$). The experimental density was determined by the method of flotation using mixtures of bromoform and carbon tetrachloride to be 1.83 $g \cdot cm^{-3}$.

Three potassium atoms and the vanadium atom could be located from a "three-dimensional" Patterson synthesis of the reflection data. There were, however, no peaks which could be attributed to the two additional potassium atoms required by the formula $K_5V(CN)_5NO \cdot H_2O$. Successive Fourier syntheses based on the vanadium and the two preliminary potassium positions revealed the positions of all light atoms, including the oxygen atom O(1) of a water molecule situated in 8*e*, the *R*-value being 0.151. The arrangement of the six ligand groups around vanadium was approximately octahedral and all groups were at this stage treated as cyanide. After five cycles of isotropic least squares refinement the *R*-value dropped to 0.117. The preliminary atomic parameters and isotropic temperature coefficients obtained after the last cycle are given in Table 1.

It was obvious that since vanadium occupies the position 4*c* and no ligands are aligned along the diad axis, the structure must be disordered, and, as expected, there are two shorter V—C distances (1.79 Å) corresponding to V—C(2) and four longer V—C distances, two of 2.20 Å (V—C(1)) and two of 2.16 Å (V—C(3)). The nitrosyl

Table 1. Approximate atomic parameters and isotropic temperature coefficients for $K_3V(CN)_5NO{\cdot}2H_2O$.

Atom		*x*	*y*	*z*	*B* (Å²)
K(1)	4*d*	0.2500	0.7500	0.3810	5.20
K(2)	8*e*	−0.0009	0.1042	0.3455	3.64
V	4*c*	0.2500	0.2500	0.1558	2.93
O(1)	8*e*	0.0000	0.2312	0.0701	3.99
C(1)	8*e*	0.3322	0.1249	0.2852	3.95
C(2)	8*e*	0.3096	0.1286	0.0501	1.77
C(3)	8*e*	0.1666	0.0150	0.1773	3.81
N(1)	8*e*	0.3827	0.0484	0.3452	4.22
N(2)	8*e*	0.1542	0.0357	0.4805	2.92
N(3)	8*e*	0.1218	0.8865	0.1932	4.96

group and a cyanide group must thus occupy the C(2)—N(2) positions statistically.

The arrangement of potassium ions, water molecules, and complex ions is very similar to that found in $K_3Mn(CN)_5NO{\cdot}2H_2O$ [2] and there is good agreement between comparable interatomic distances in the two compounds.

This preliminary structure analysis would indicate that either there are two different potassium pentacyanonitrosylvanadates or that potassium pentacyanonitrosylvanadate should be reformulated as $K_3V(CN)_5NO{\cdot}2H_2O$, giving vanadium a formal oxidation state of I rather than −I. The latter suggestion seems to us to be the more probable since, although a large number of crystals from different batches have been examined during the collection of the X-ray data, no crystal has yet been observed with unit cell dimensions or space group differing from that given above. Moreover, it has proved to be extremely difficult to completely purify the crystals from an adhering layer of potassium cyanide, the presence of which is not visible to the naked eye. An infrared spectrum recorded for potassium pentacyanonitrosylvanadate(I), incompletely purified from adhering potassium cyanide, showed, besides a minor peak at 2080 cm^{-1} corresponding to the stretching frequency of the free cyanide ion,[5] peaks at 2110 cm^{-1} and 1530 cm^{-1} which could be attributed to the cyanide and nitrosyl stretching frequencies, respectively, of the complex ion. The former frequency is, however, somewhat higher and the latter somewhat lower than the corresponding frequencies reported by Griffith, Lewis and Wilkinson [1] (2095 cm^{-1} and 1575 cm^{-1}, respectively) for $K_5V(CN)_5NO{\cdot}H_2O$. An analysis of the potassium and vanadium content of $K_3V(CN_5)NO{\cdot}2H_2O$ will be performed by means of atomic absorption spectroscopy on substantially KCN-free crystals picked out under the microscope.

Refinement of the structure based on the above X-ray data together with intensity data from the layers $hk0-hk6$ and $0kl-5kl$ is near completion and a full report will be published shortly.

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1. Griffith, W., Lewis, J. and Wilkinson, G. *J. Chem. Soc.* **1959** 1632.
2. Tullberg, A. and Vannerberg, N.-G. *Acta Chem. Scand.* **21** (1967) 1462.
3. Vannerberg, N.-G. *Acta Chem. Scand.* **20** (1966) 1571.
4. Svedung, D. and Vannerberg, N.-G. *Acta Chem. Scand.* **22** (1968) 1551.
5. Stallcup, W. D. and Williams, D. *J. Chem. Phys.* **10** (1942) 199.

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