Discussion. The compound is less stable than either the trihydrate or the α -tetrahydrate.

Interatomic distances and angles are given in Table 2; Fig. 1 is a view of the molecule showing the atomic nomenclature.

All features of the chelating bonds of the hydroxylamido ligands are essentially the same as those in the trihydrate and α -tetrahydrate compounds (Van Tets & Adrian, 1977; Adrian & Van Tets, 1977, 1978). Within experimental error, the O atoms of the hydroxylamido group lie in the equatorial plane through the U atom perpendicular to the uranyl group. The N atoms of the hydroxylamido group probably also lie in this plane, but could be slightly distorted out of the plane.

The neutral hydroxylamine ligands do not lie in this plane. The N-O bonds in these ligands make an angle of 52° with the uranyl group. To decide which of the two atoms of the N-O bond was the N atom, the

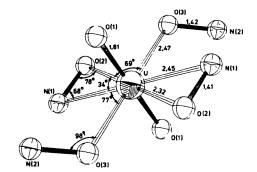


Fig. 1. A view of the molecule with the atomic nomenclature. The uncoordinated water O(4) is omitted.

scattering-factor curves of the atoms were interchanged. The structure with the O atom closest to the U atom gave an R value 0.002 lower. The neutral ligand is therefore coordinated to the U atom over a distance of 2.47 (1) Å through the O atom.

As with the trihydrate and α -tetrahydrate, the length of the uranyl group is greater than usual. The existence of hydrogen bonding similar to that found in these compounds is therefore indicated. This is confirmed by IR spectra which show a characteristic shift of the $v_{as}(UO_2)$ stretch frequency.

We thank Dr G. Gafner of the CSIR for making the X-ray diffractometer available, and the Atomic Energy Board for permission to publish this paper.

References

- Adrian, H. W. W. & Van Tets, A. (1977). Acta Cryst. B33, 2997–3000.
- Adrian, H. W. W. & Van Tets, A. (1978). Acta Cryst. B34, 88–90.
- CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LARSON, A. C. (1967). Acta Cryst. 23, 664-665.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- VAN TETS, A. & ADRIAN, H. W. W. (1977). J. Inorg. Nucl. Chem. 39, 1607–1610.
- VISSER, J. W. (1969). J. Appl. Cryst. 2, 89-95.

Acta Cryst. (1978). B34, 653-656

Tripotassium Monosodium Hexacyanonitrosylvanadate(I) Dihydrate

By Susan Jagner and Evert Ljungström

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden

(Received 1 July 1977; accepted 26 October 1977)

Abstract. K₃Na[V(CN)₆NO]. 2H₂O, monoclinic, $P2_1/m$, a = 9.243 (2), b = 11.736 (2), c = 7.786 (2) Å, $\beta = 118.86$ (2)°, Z = 2, $D_m = 1.86$, $D_c = 1.86$ g cm⁻³, μ (Cu K α) = 138.9 cm⁻¹. Least-squares refinement (957 reflections, single-crystal X-ray diffractometer data) gave R = 0.050 for 109 parameters. The complex ion has a pentagonal-bipyramidal configuration with the nitrosyl group axial. V–N = 1.806 (6), N–O = 1.235 (8) Å; axial V-C and C-N = 2.069 (6) and 1.167 (9) Å; mean equatorial V-C and C-N = 2.135 (2) and 1.150 (3) Å.

Introduction. An investigation concerning the nature of the chemical bonding in some transition-metal pentacyanonitrosyls (Vannerberg & Jagner, 1974) indicated that, while π contributions to the metal-cyanide bonds are slight, there is an appreciable π contribution to the metal-nitrosyl bond, this contribution increasing from Fe to V. In order to investigate whether a strong V \rightarrow $\pi^*(NO)$ transfer also occurred in the hexacyanonitrosvlvanadate(I) ion, a determination of the crystal structure of $K_4[V(CN)_6NO]$. H₂O was attempted (Jagner & Ljungström, unpublished). Although the main structural features were deduced, owing to twinning and/or disorder it proved impossible to refine the structure below $R \simeq 0.15$. In an attempt to prepare the Na salt of $[V(CN)_6NO]^{4-}$, 1.6 g NaClO₄ was added to a solution of 5 g $K_4[V(CN)_6NO]$. H₂O prepared according to Müller, Werle, Diemann & Aymonino (1972)] in 6 ml water. After filtration to remove precipitated potassium perchlorate, methanol was added and K₃Na[V(CN)₆NO].2H₃O precipitated as a yellow powder. The compound was washed with methanol and recrystallized from water, pale-yellow plates being formed. K₁Na[V(CN)₆NO].2H₂O may also be prepared by allowing a concentrated solution of $K_{4}[V(CN)_{6}NO]$. H₂O to pass through a Merck No. 1 ion-exchanger, saturated with sodium ions, and evaporating the resulting solution. The first method gives, however, a better vield of crystals.

The Na:K:V molar ratio 1.0:2.9:1.0 was determined by atomic-absorption spectroscopy using a Perkin Elmer 403 spectrometer. The cyanide content

Table 1. Fractional coordinates

Estimated standard deviations are given in parentheses.

| | Site | x | У | Ζ |
|------|---------------|------------|---------------------|-------------|
| v | 2(<i>e</i>) | 0.7412(2) | 0.2500 | 0.4492 (2) |
| K(1) | 2(e) | 0.2362 (2) | 0.2500 | 0.6328(2) |
| K(2) | 4(f) | 0.2908 (2) | -0.0538 (1) | 0.0358 (2) |
| Na | 2(<i>e</i>) | 0.1355 (3) | 0.2500 | 0.0706 (4) |
| N(1) | 2(<i>e</i>) | 0.6296 (6) | 0.2500 | 0.5860 (8) |
| O(1) | 2(<i>e</i>) | 0.5646 (7) | 0.2500 | 0.6924 (9) |
| C(2) | 2(<i>e</i>) | 0.8696 (7) | 0.2500 | 0.2931 (9) |
| N(2) | 2(<i>e</i>) | 0.9316 (8) | 0.2500 | 0.1933 (9) |
| C(3) | 4(f) | 0.6787 (6) | 0.0779 (5) | 0.3544 (7) |
| N(3) | 4(f) | 0.6419 (6) | <i>−</i> 0·0144 (4) | 0.2986 (7) |
| C(4) | 4(f) | 0.9235 (6) | 0.1439 (4) | 0.6712(7) |
| N(4) | 4(f) | 1.0157 (6) | 0.0905 (4) | 0.8019 (7) |
| C(5) | 2(<i>e</i>) | 0.5183 (9) | 0.2500 | 0.1754 (10) |
| N(5) | 2(<i>e</i>) | 0.3937 (8) | 0.2500 | 0.0345 (9) |
| O(2) | 4(f) | 0.2719 (6) | 0.1024 (4) | 0.3030 (6) |

was determined by the method described by Jagner & Vannerberg (1970), a $CN^{-}/K_3Na[V(CN)_6NO].2H_2O$ molar ratio of 6.0 being obtained. The IR spectrum (registered on a Beckman IR 10 spectrometer, using the KBr technique) showed good agreement with that determined for $K_4[V(CN)_6NO].H_2O$ (Müller *et al.*, 1972) with v(CN) 2110 and 2095 cm⁻¹ and v(NO) 1500 and 1475 cm⁻¹.

A crystal was ground to a sphere of radius 0.15 mm in a Bond (1951) sphere grinder and intensities were measured with a Syntex $P2_1$ diffractometer using the ω -2 θ scanning technique. Graphite-monochromatized Cu Ka radiation was used and data were collected for $\sin \theta / \lambda \leq 0.547$ Å⁻¹ with $h \geq 0$, the 2θ scan speed being varied between 1.5 and 8° min⁻¹. A 96-step profile was recorded for each reflection and the Lehmann & Larsen (1974) method was used to correct for background. Correction was made for Lorentz and polarization effects, while correction for absorption was applied first after an approximate structure had been deduced. Absorption correction factors for a sphere were taken from International Tables for X-ray Crystallography (1967). Symmetry-related reflections were averaged. Of the 1071 independent reflections measured, 957 for which $F_o^2 \ge 3\sigma(F_o^2)$, according to counting statistics, were regarded as being observed. The cell parameters and their standard deviations were determined by a least-squares procedure based on accurately determined setting angles for 11 reflections.

The structure was solved from Patterson and electron density calculations in conjunction with direct methods (MULTAN, Germain, Main & Woolfson, 1971). Preliminary least-squares refinement of the positional and isotropic thermal parameters, using the block-diagonal approximation, yielded R = 0.125. Refinement in $P2_1$ did not result in a lowering of the R value. Since, moreover, statistical tests (MULTAN, Germain et al., 1971) indicated the presence of a centre of symmetry, all subsequent calculations were carried out in P2/m. The final cycles of refinement were performed with a full-matrix least-squares program, anisotropic thermal parameters being included for all atoms. The F_o values were weighted according to $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ (Cruickshank, 1970) with a = 20.0, c = 0.020 and d = 0.0. The scattering factors for the neutral atoms were those of Doyle & Turner (1968). A final R of 0.050 was obtained for 109

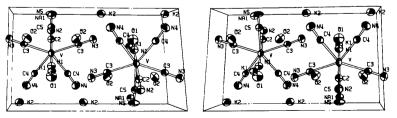


Fig. 1. A stereoview of the unit-cell contents as seen along a; b is across the page.

parameters; when the 114 unobserved reflections were included, R was 0.066. Atomic coordinates are listed in Table 1,* the numbering being in accordance with Fig. 1. A final difference map showed a maximum electron density of 0.7 e Å⁻³. It was not possible to locate the H atoms.

Calculations were carried out on an IBM 360/65– 370/145 computer system, using local versions of the following programs: data reduction, *LELA*, *SYN* (Lindqvist & Ljungström); Patterson and Fourier syntheses, *DRF* (Zalkin); block-diagonal least-squares refinement, *BLOCK* (Lindgren); full-matrix leastsquares refinement, *LALS* (Gantzel, Sparks & Trueblood); distances and angles, *DISTAN* (Zalkin); stereoscopic drawing, *ORTEP* (Johnson, 1965). *R* is defined as $\Sigma ||F_o|| - |F_c||/\Sigma ||F_o||$.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33100 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°) within the $[V(CN)_{6}NO]^{4-}$ ion

Estimated standard deviations are given in parentheses.

| V-N(1) | 1.806 (6) | N(1)-O(1) | 1.235 (8) |
|--|---|---|---|
| V-C(2) | 2.069 (6) | C(2)-N(2) | 1.167 (9) |
| V-C(3) | 2.133 (5) | C(3)-N(3) | 1.155 (7) |
| V-C(4) | 2.137 (5) | C(4)-N(4) | 1.148 (7) |
| V-C(5) | 2.133 (7) | C(5)-N(5) | 1.144 (10) |
| $\begin{array}{c} N(1)-V-C(2)\\ N(1)-V-C(3)\\ N(1)-V-C(4)\\ N(1)-V-C(5)\\ C(2)-V-C(3)\\ C(2)-V-C(4)\\ C(2)-V-C(5)\\ C(3)-V-C(4) \end{array}$ | 179.9 (4) 93.9 (2) 88.6 (2) 92.2 (3) 86.2 (1) 91.3 (2) 88.0 (3) 72.8 (2) | C(3)-V-C(5) C(4)-V-C(4) V-N(1)-O(1) V-C(2)-N(2) V-C(3)-N(3) V-C(4)-N(4) V-C(5)-N(5) | 71.6 (1) 71.3 (3) 175.2 (5) 175.3 (6) 178.3 (4) 173.5 (5) 176.0 (6) |

Discussion. A stereoscopic projection along **a** of the contents of one unit cell is shown in Fig. 1. Bond lengths and angles within the $[V(CN)_6NO]^{4-}$ ion are given in Table 2.

The configuration of ligands about V is pentagonal bipyramidal, as in $K_4[V(CN)_7]$.2H₂O (Levenson & Towns, 1974). The nitrosyl group is axial, the V-Nbond being significantly shorter than that in $(NH_4)_2$ - $[VO(NCS)_{4}]$. 5H₂O, 2.04 (3) Å (Hazell, 1963) and that in $Li_{3}[V(NCS)_{6}]$. 12H₂O, 2.06 (1) Å (Brattås & Jagner, in preparation), but slightly longer than that in $K_{3}[V(CN)_{5}NO]$.2H₂O, 1.66 (4) Å (Jagner & Vannerberg, 1970). The long N-O bond is in agreement with the low v(NO). There is a slight but significant deviation of the V-N-O linkage from linearity. As in $[V(CN), NO]^{3-}$, the short V–N and long N–O bonds in $[V(CN)_6 NO]^{4-}$ indicate a strong axial $V \rightarrow \pi^*(NO)$ transfer. Owing to the uncertainty in the determination of the V–N and N–O distances in $[V(CN), NO]^{3-}$ {because of disorder in the crystal structure of $K_{3}[V(CN), NO].2H_{2}O\}$ a comparison of the strengths of this transfer in the two ions is not, however, feasible.

The V atom lies in the best plane through the equatorial C atoms, the magnitudes of the deviations from this plane of all six atoms being 0.02-0.07 Å. There are no significant differences between the equatorial V-C or C-N distances, the mean values being 2.135 (2) and 1.150 (3) Å respectively. All the V-C-N linkages deviate somewhat from 180°, possibly for steric reasons.

Perhaps the most striking feature of the $[V(CN)_6NO]^{4-}$ ion is the short V-C distance *trans* to the nitrosyl group. This is in contrast to the transitionmetal pentacyanonitrosyl ions, which exhibit a slight *trans* effect, *i.e.* a somewhat longer metal-carbon bond opposite the nitrosyl group (Vannerberg & Jagner, 1974). Moreover, the axial C-N distance is slightly, though not significantly, longer than its equatorial counterparts. It would appear that, in addition to the strong axial V $\rightarrow \pi^*(NO)$ transfer, there is an

Table 3. Mean V–C and C–N bond lengths (Å) in some cyanovanadate ions

An asterisk denotes the mean equatorial bond length.

| Ion | Formal oxidation state | Ground state configuration | V–C | C–N | Reference |
|--------------------------------------|------------------------------|----------------------------------|------------------|-------------|--------------|
| V(CN) ₆ NO ⁴− | I | d^4 | 2.135 (2)* | 1.150 (3)* | (<i>a</i>) |
| [V(CN),NO] ³⁻ | Ι | d^4 | 2.166(6) | 1.142 (8) | (<i>b</i>) |
| $ V(CN)_{6} ^{4}$ | II | d^3 | $2 \cdot 161(4)$ | 1.153 (7) | (<i>c</i>) |
| $ V(CN)_{7} ^{4-}$ | III | d^2 | 2.149 (3)* | 1.144 (5)* | (<i>d</i>) |
| [VO(CN) ₅] ³⁻ | IV | ď١ | 2.137 (14)* | 1.154 (21)* | (<i>e</i>) |

References: (a) Present work. (b) Jagner & Vannerberg (1970). (c) Jagner (1975). (d) Levenson & Towns (1974). (e) Jagner & Vannerberg (1973).

appreciable axial $V \rightarrow \pi^*(CN)$ transfer, the π -bonding system thus being delocalized to embrace both axial ligands. This difference between $[V(CN)_6NO]^{4-}$ and the pentacyanonitrosyl ions may perhaps be due in part to the difference in symmetry. Further investigation involving X-ray photoelectron spectroscopy and *ab initio* FSGO calculations is in progress.

The mean equatorial V-C and C-N bond lengths may be compared with those in other cyanovanadates (Table 3). Although such a comparison is not strictly relevant, since V is seven-coordinated in two of the complexes but six-coordinated in the remaining three, it is seen that, if $[V(CN)_{c}NO]^{4-}$ is excluded, there is a trend towards a shorter V-C distance as the formal oxidation state of V increases. This has been interpreted (Jagner, 1975) in terms of a negligible π contribution to the V-C bond, the trend simply reflecting an increase in σ -bond strength with the increasing formal oxidation state of V. The mean equatorial V-C bond in $[V(CN)_6NO]^{4-}$ is seen to be more consistent with V^{III} or V^{IV} than V^{I} . The strong axial V $\rightarrow \pi^*$ (ligand) transfer must thus result in a formal oxidation state effectively higher than +I with respect to the equatorial ligands and a consequent increase in σ -bond strength. As in the other complex ions cited in Table 3, π contributions to the equatorial V-C bonds in $[V(CN)_{6}NO]^{4-}$ are undoubtedly slight.

The K-N and K-O contacts range from 2.740 (6) to 3.461 (5) Å for K(1) and from 2.841 (5) to 3.061 (5) Å for K(2). K(2) is surrounded by a distorted trigonal prism of four N and two O atoms, while the coordination polyhedron about K(1) may be described as a tricapped trigonal prism composed of six N and three O atoms. The Na ion is surrounded by a distorted octahedron of four N and two O atoms at distances of 2.380 (5)-2.621 (5) Å. The shortest contacts involving the water molecule O(2) are $O(2)\cdots Na$, $2\cdot 380$ (5), and $O(2)\cdots K(2)$, $2\cdot 841$ (5) Å, while the shortest contact to a N or O atom is $O(2)\cdots N(3)$, $2\cdot 989$ (6) Å.

The authors thank Professor N.-G. Vannerberg for valuable discussions. Support of this work by the Swedish Natural Science Research Council (NFR, Contract No. 2286-026) is gratefully acknowledged.

References

- BOND, W. L. (1951). Rev. Sci. Instrum. 22, 344-345.
- CRUICKSHANK, D. W. J. (1970). Crystallographic Computing, p. 195. Copenhagen: Munksgaard.
- DOYLE, P. A. & TURNER, P. S. (1968). Acta Cryst. A24, 390–397.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368-376.
- HAZELL, A. C. (1963). J. Chem. Soc. pp. 5745-5752.
- International Tables for X-ray Crystallography (1967). Vol. II, 2nd ed., pp. 302–303. Birmingham: Kynoch Press.
- JAGNER, S. (1975). Acta Chem. Scand. Ser. A, 29, 255-264.
- JAGNER, S. & VANNERBERG, N.-G. (1970). Acta Chem. Scand. 24, 1988–2002.
- JAGNER, S. & VANNERBERG, N.-G. (1973). Acta Chem. Scand. 27, 3482–3498.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LEHMANN, M. S. & LARSEN, F. K. (1974). Acta Cryst. A30, 580–584.
- LEVENSON, R. A. & TOWNS, R. L. R. (1974). *Inorg. Chem.* **13**, 105–109.
- Müller, A., Werle, P., DIEMANN, E. & AYMONINO, P. J. (1972). Chem. Ber. 105, 2419–2420.
- VANNERBERG, N.-G. & JAGNER, S. (1974). Chem. Scr. 6, 19–21.

Acta Cryst. (1978). B34, 656-659

trans, cis, cis-abc, fed-Bis[(S)-2,4-diaminobutyrato-O,N,N']cobalt(III) Bromide Hydrate

By WADE A. FREEMAN

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680, USA

(Received 24 May 1977; accepted 8 August 1977)

Abstract. $Co(C_4H_9N_2O_2)_2Br.1.71H_2O, M_r = 403.97,$ orthorhombic, $C222_1, a = 14.164$ (10), b = 9.809 (5), c = 10.719 (4) Å, V = 1482.86 Å³, $D_o = 1.79, D_c$ (Z = 4) = 1.81 g cm⁻³. Purple crystals of the title compound were prepared from optically pure (S)-2,4diaminobutyric acid, separated from other isomers by ion-exchange, and recrystallized from water. Each amino-acid residue serves as a tridentate ligand; the complex ion consists of two fused-ring systems related by a crystallographic twofold axis passing through the cobalt atom. The approximately octahedral complex has donor oxygen atoms *trans*, 2-nitrogen donor atoms