

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 hydroxyl-amido 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

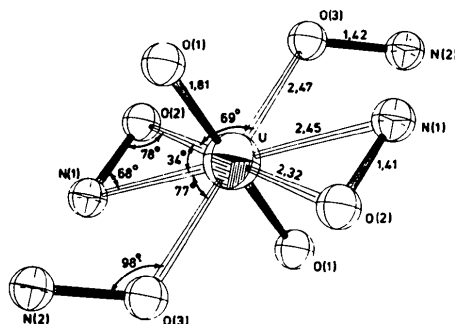


Fig. 1. A view of the molecule with the atomic nomenclature. The uncoordinated water O(4) is omitted.

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 $\nu_{\text{as}}(\text{UO}_2)$ 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.

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Acta Cryst. (1978). **B34**, 653–656

Tripotassium Monosodium Hexacyanonitrosylvanadate(I) Dihydrate

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(Received 1 July 1977; accepted 26 October 1977)

Abstract. $\text{K}_3\text{Na}[\text{V}(\text{CN})_6\text{NO}] \cdot 2\text{H}_2\text{O}$, 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 $^{-3}$, $\mu(\text{Cu } K\alpha) = 138.9$ 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. $\text{V}-\text{N} = 1.806$ (6), $\text{N}-\text{O} =$

1.235 (8) Å; axial $\text{V}-\text{C}$ and $\text{C}-\text{N} = 2.069$ (6) and 1.167 (9) Å; mean equatorial $\text{V}-\text{C}$ and $\text{C}-\text{N} = 2.135$ (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

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 $0.7 \text{ e } \text{Å}^{-3}$. 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 least-squares 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)₆NO]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)
N(1)–V–C(2)	179.9 (4)	C(3)–V–C(5)	71.6 (1)
N(1)–V–C(3)	93.9 (2)	C(4)–V–C(4)	71.3 (3)
N(1)–V–C(4)	88.6 (2)	V–N(1)–O(1)	175.2 (5)
N(1)–V–C(5)	92.2 (3)	V–C(2)–N(2)	175.3 (6)
C(2)–V–C(3)	86.2 (1)	V–C(3)–N(3)	178.3 (4)
C(2)–V–C(4)	91.3 (2)	V–C(4)–N(4)	173.5 (5)
C(2)–V–C(5)	88.0 (3)	V–C(5)–N(5)	176.0 (6)
C(3)–V–C(4)	72.8 (2)		

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 K₄[V(CN)₇].2H₂O (Levenson & Towns, 1974). The nitrosyl group is axial, the V–N bond being significantly shorter than that in (NH₄)₂[VO(NCS)₄].5H₂O, 2.04 (3) Å (Hazell, 1963) and that in Li₃[V(NCS)₆].12H₂O, 2.06 (1) Å (Brattås & Jagner, in preparation), but slightly longer than that in K₃[V(CN)₅NO].2H₂O, 1.66 (4) Å (Jagner & Vannerberg, 1970). The long N–O bond is in agreement with the low $\nu(\text{NO})$. There is a slight but significant deviation of the V–N–O linkage from linearity. As in [V(CN)₅NO]³⁻, the short V–N and long N–O bonds in [V(CN)₆NO]⁴⁻ indicate a strong axial V → $\pi^*(\text{NO})$ transfer. Owing to the uncertainty in the determination of the V–N and N–O distances in [V(CN)₅NO]³⁻ {because of disorder in the crystal structure of K₃[V(CN)₅NO].2H₂O} 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 transition-metal 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 → $\pi^*(\text{NO})$ 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)*	(a)
[V(CN) ₅ NO] ³⁻	I	d^4	2.166 (6)	1.142 (8)	(b)
[V(CN) ₆] ⁴⁻	II	d^3	2.161 (4)	1.153 (7)	(c)
[V(CN) ₇] ⁴⁻	III	d^2	2.149 (3)*	1.144 (5)*	(d)
[VO(CN) ₅] ³⁻	IV	d^1	2.137 (14)*	1.154 (21)*	(e)

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

appreciable axial V → π*(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)₆NO]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 → π*(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)₆NO]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)···Na, 2.380 (5), and O(2)···K(2), 2.841 (5) Å, while the shortest contact to a N or O atom is O(2)···N(3), 2.989 (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.

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Acta Cryst. (1978). **B34**, 656–659

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

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(Received 24 May 1977; accepted 8 August 1977)

Abstract. Co(C₄H₉N₂O₂)₂Br·1.71H₂O, *M_r* = 403.97, orthorhombic, *C*222₁, *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*)-2,4-diaminobutyric 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