Sodium Hexakis(isothiocyanato)vanadate(III) Dodecahydrate

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Abstract. $Na_3[V(NCS)_6].12H_2O$, triclinic, $P\bar{1}$, $a = 9.903$ (2), $b = 9.355$ (1), $c = 8.921$ (1) Å, $\alpha = 97.67$ (1), $\beta = 97.20$ (1), $\gamma = 110.79$ (1)°, $Z = 1$, $D_m = 1.48$, $D_c = 1.51$ g cm^{-3}, μ(Mo $K\alpha$) = 8.5 cm^{-1}. Least-squares refinement (1851 reflections, single-crystal X-ray diffractometer data) gave $R = 0.053$ for 176 parameters. The complex ion has an octahedral configuration with mean V–N 2.044 (2), N–C 1.152 (3) and C–S 1.631 (2) Å. The V–N–C and N–C–S linkages are approximately linear.

Introduction. In an investigation concerning the nature of the chemical bonding in some transition-metal cyanonitrosyls, short V–N bonds have been found in $[V(CN)_5NO]^{3-}$ (Jagner & Vannerberg, 1970) and $[V(CN)_6NO]^{4-}$ (Jagner & Ljungström, 1978) which have been interpreted as indicative of strong V → π^*(NO) transfers. There is, however, little information available on the lengths of normal V–N bonds in comparable complexes. Moreover, since V has been shown to be seven-coordinated in the cyano-vanadate(III) ion, the ion thus being $[V(CN)_7]^{4-}$ instead of $[V(CN)_6]^{3-}$ (Levenson & Towns, 1974), it was of interest to investigate the configuration of ligands about V^{III} in the corresponding isothiocyanato complex.

$Na_3[V(NCS)_6].12H_2O$ was prepared by dissolving 1 g VCl_3 and 3.7 g NaSCN in 28 ml water, heating the solution to 75°C in a water bath and evaporating to dryness *in vacuo* at the same temperature. The residue was leached with 96% ethanol and the resulting ethanolic solution evaporated to dryness *in vacuo*. On recrystallization from water, dark-red plates of $Na_3[V(NCS)_6].12H_2O$ were formed. The crystals are efflorescent, decomposition being accelerated by cleavage. Crystal fragments thus disintegrate fairly rapidly, whereas well-formed crystals appear to be stable for two or three weeks.

Intensities from a crystal, 0.02 × 0.025 × 0.03 cm, were measured with a Syntex $P2_1$ diffractometer using the ω–2θ scanning technique. Graphite-mono-chromatized Mo $K\alpha$ radiation was used and data were collected for sin $\theta/\lambda \leq 0.617$ Å^{-1} with $h \geq 0$, the 2θ scan speed being varied between 2 and 8° min^{-1}. The intensity of the 040 reflection, measured after every

fiftieth reflection, decreased by approximately 4% during the collection of the data. 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 but not for absorption. Of the 2960 independent reflections recorded, 1851, for which $F_o^2 \geq 4.0\sigma(F_o^2)$ 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 12 reflections.

The structure was solved from Patterson and electron density calculations. Least-squares refinement of the positional and isotropic thermal parameters, using the block-diagonal approximation, yielded $R = 0.105$. Inclusion of anisotropic temperature factors for all atoms gave $R = 0.060$. In the final cycles six of the H atoms, namely those bonded to O(1), O(4) and O(6),

Table 1. *Fractional coordinates*

Estimated standard deviations are given in parentheses.

|	x	y	z
V	0.0000	0.0000	0.0000
N(1)	0.0775 (5)	0.0022 (5)	−0.2013 (5)
C(1)	0.1316 (5)	0.0062 (6)	−0.3076 (6)
S(1)	0.2122 (2)	0.0079 (2)	−0.4564 (2)
N(2)	0.1910 (5)	−0.0080 (5)	0.1077 (5)
C(2)	0.2995 (5)	−0.0156 (6)	0.1635 (6)
S(2)	0.4511 (2)	−0.0272 (2)	0.2435 (2)
N(3)	0.0914 (5)	0.2388 (5)	0.0486 (5)
C(3)	0.1395 (6)	0.3732 (6)	0.0697 (6)
S(3)	0.2105 (2)	0.5637 (2)	0.1071 (2)
Na(1)	0.5000	0.5000	0.5000
Na(2)	0.1975 (3)	0.5299 (4)	0.5815 (4)
O(1)	0.5951 (5)	0.3020 (5)	0.5105 (5)
O(2)	0.4271 (6)	0.2822 (7)	0.9649 (7)
O(3)	0.7907 (7)	0.2911 (7)	0.2120 (7)
O(4)	0.4163 (6)	0.4946 (6)	0.7453 (5)
O(5)	0.9616 (6)	0.3694 (7)	0.6094 (8)
O(6)	0.2383 (5)	0.3310 (5)	0.4172 (5)
H(11)	0.558 (6)	0.222 (7)	0.448 (7)
H(12)	0.607 (6)	0.282 (7)	0.591 (7)
H(41)	0.414 (6)	0.422 (7)	0.797 (7)
H(42)	0.462 (6)	0.580 (7)	0.814 (7)
H(61)	0.229 (6)	0.265 (7)	0.447 (7)
H(62)	0.203 (6)	0.296 (7)	0.350 (7)
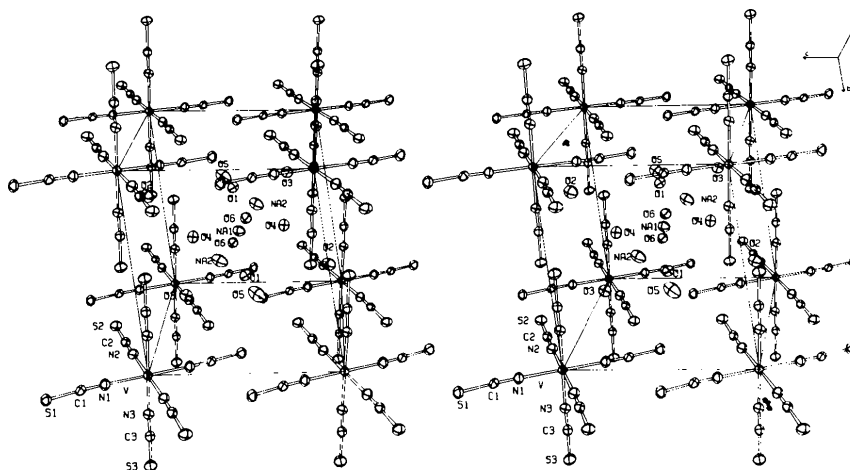
Fig. 1. Stereoscopic view of the structure. The thermal ellipsoids enclose 25% probability. The H atoms have been omitted.

were included with constant isotropic temperature factors $B = 5.0$ Å^2. The F_o values were weighted according to $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ (Cruickshank, 1970) with $a = 10.0$, $c = 0.017$ and $d = 0.0$. The scattering factors for Na, V, N, C, S and O were those of Doyle & Turner (1968) while scattering factors due to Stewart, Davidson & Simpson (1965) were employed for H. A final R of 0.053 was obtained for 176 parameters; when the 1109 unobserved reflections were included, $R = 0.091$. 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 0.4 e Å^{-3} with peaks in the vicinity of O(2), O(3) and O(5). It was not, however, possible to locate the H atoms bonded to these O 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); distances and angles, *DISTAN* (Zalkin); stereoscopic drawing, *ORTEP* (Johnson, 1965).

Discussion. The crystal structure of Na$_3$[V(NCS)$_6$].12H$_2$O is illustrated in Fig. 1. Bond lengths and angles within the [V(NCS)$_6$]$^{3-}$ ion are given in Table 2.

The configuration of ligands about V is octahedral, the thiocyanate groups being bonded to V through N, as expected (Norbury, 1975). The mean V–N distance, 2.044 (2) Å, is in good agreement with that found in

Table 2. *Bond lengths* (Å) *and angles* (°) *within the* [V(NCS)$_6$]$^{3-}$ *ion*

Estimated standard deviations are given in parentheses.

V–N(1)	2.039 (5)	N(3)–C(3)	1.154 (7)
V–N(2)	2.043 (4)	C(1)–S(1)	1.631 (5)
V–N(3)	2.051 (4)	C(2)–S(2)	1.626 (5)
N(1)–C(1)	1.145 (7)	C(3)–S(3)	1.636 (6)
N(2)–C(2)	1.156 (7)		
N(1)–V–N(2)	89.4 (2)	V–N(3)–C(3)	177.0 (4)
N(1)–V–N(3)	89.4 (2)	N(1)–C(1)–S(1)	177.8 (5)
N(2)–V–N(3)	90.1 (2)	N(2)–C(2)–S(2)	179.4 (5)
V–N(1)–C(1)	174.7 (4)	N(3)–C(3)–S(3)	177.6 (5)
V–N(2)–C(2)	177.4 (4)		

(NH$_4$)$_2$[VO(NCS)$_4$].5H$_2$O, 2.04 (3) Å (Hazell, 1963), and is considerably longer than the V–N distance in K$_3$[V(CN)$_5$NO].2H$_2$O, 1.66 (4) Å (Jagner & Vannerberg, 1970), and in K$_3$Na[V(CN)$_6$NO].2H$_2$O, 1.806 (6) Å (Jagner & Ljungström, 1978). Moreover, as expected, the V^{III}–N distance in [V(NCS)$_6$]$^{3-}$ is slightly longer than the corresponding Cr^{III}–N distance, 2.002 (6) Å, determined in [Ho(C$_5$H$_4$-NCOOH)$_3$(H$_2$O)$_2$][Cr(NCS)$_6$].2H$_2$O (Kay, Moore & Glick, 1972). The difference, 0.04 Å, would appear to be slightly, if not significantly, less than that, 0.07 Å, between V^{III}–C in K$_4$[V(CN)$_7$].2H$_2$O (Levenson & Towns, 1974) and Cr^{III}–C in K$_3$[Cr(CN)$_6$] (Jagner, Ljungström & Vannerberg, 1974). π contributions to the M^{III}–N or M^{III}–C bonds in all these complex ions are probably almost negligible. However, a smaller difference between V^{III}–N and Cr^{III}–N in [M(NCS)$_6$]$^{3-}$ could indicate a slight π-contribution to the M–N bond in [V(NCS)$_6$]$^{3-}$. This is supported by the linearity of the V–N–C and N–C–S linkages, the mean V–N–C and N–C–S angles being 176.4 (2) and 178.3 (2)°, respectively. The mean Cr–N–C angle in [Ho(C$_5$H$_4$NCOOH)$_3$(H$_2$O)$_2$][Cr(NCS)$_6$].-2H$_2$O is 164.3 (5)° (Kay, Moore & Glick, 1972), which

would be difficult to reconcile with metal to ligand back-bonding. The mean N—C and C—S distances in $Na_3[V(NCS)_6].12H_2O$, 1·152 (3) and 1·631 (2) Å, agree well with N—C and C—S distances found in N-bonded thiocyanato complexes (Norbury, 1975).

The water molecules appear to be loosely bound in the structure, the only short O···O contacts being those between O(2) and O(4), i.e. 2·951 (8) and 2·989 (8) Å. The positions of the H atoms bonded to O(4) are also consistent with hydrogen bonding. All other O···O contacts are greater than 3·10 Å. As is seen in Fig. 1, the thermal parameters of some of the O atoms are rather large. This could be due either to partial loss of water or to disorder in the positions of the loosely bound water molecules. It was not, however, considered to be in the interest of computer economy to investigate these points further, as it seemed unlikely that the geometry of the $[V(NCS)_6]^{3-}$ ion would be affected. Both Na ions are surrounded by a distorted octahedron of water molecules, the Na—O contacts ranging from 2·364 (4) to 2·462 (5) Å for Na(1) and from 2·279 (7) to 2·661 (7) Å for Na(2).

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Bis(pyridine)mercury(II) Bis(trifluoroacetate)

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Abstract. $Hg(C_5H_5N)_2(CO_2CF_3)_2$, monoclinic, $P2_1/c$, $a = 9·83$ (1), $b = 9·85$ (1), $c = 20·57$ (2) Å, $\beta = 115·8$ (1)°, $D_m = 2·13$, $D_c = 2·13$ g cm^{-3} with $Z = 4$. The structure has been determined from 1620 diffractometer-measured intensities (Mo $K\alpha$, $\lambda = 0·7107$ Å) and refined to $R = 0·067$. There is sevenfold coordination around Hg with two Hg—N bonds of 2·11 (2) and 2·13 (2) Å, the N—Hg—N angle is 170·2 (6)°. Five equatorial Hg—O bonds of 2·73 (2), 2·56 (2), 2·87 (2), 2·59 (1) and 2·64 (2) Å are formed to the trifluoroacetate anions, the cation being $Hg(C_5H_5N)_2^{2+}$.

Introduction. The title compound was obtained as the stable end-product of the reaction of pyridine with mercuric trifluoroacetate. Evaporation of excess pyridine yielded prismatic crystals which were stable in air but decomposed slowly on exposure to X-rays.

Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å) were used to obtain the cell dimensions and space group. Intensity measurements were made on a Stoe STADI-2 automatic two-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A crystal of dimensions 0·4 × 0·3 × 0·2 mm, set about a, was used; the limiting 2θ angle was 40°. Of the 2086 intensities measured, 1620 with $I > 3\sigma(I)$ were used for the structure determination. Absorption corrections and data reduction were carried out using the SHELX suite of programs (Sheldrick, 1976), the remainder of the calculations were done with the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Patterson maps were used to obtain the Hg position and a Fourier map phased on Hg gave the remainder of the non-H atoms. Least-squares refinement of all atomic positions, aniso-