Kinetics and Mechanism of the Equilibration Reaction between (2,2′,2″-Nitrilotriethoxy)nitrosylvanadate(1−) and Cyanide. Crystal Structures of Sodium (2,2′,2″-Nitrilotriethoxy)nitrosylvanadate(I)–Sodium Perchlorate Tetrahydrate and of Barium Cyano(2,2′,2″-nitrilotriethoxy)nitrosylvanadate(I) Pentahydrate†

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The reaction of triethanolamine, ammonium vanadate(V), and hydroxylamine in aqueous solution (pH 10) affords quantitatively a red nitrosyl complex (reductive nitrosylation), $Na[V(NO)\{N(C_2H_4O)_3\}]\cdot NaClO_4\cdot 4H_2O$, (**1**), which upon addition of cyanide forms a blue complex, $Ba[V(NO)(CN)\{N(C_2H_4O)_3\}]\cdot 5H_2O$, (**2**). The structures of these two compounds have been determined by single-crystal *X*-ray studies: (**1**), monoclinic, space group $P2_1/a$, with a = 12.234(3), b = 11.405(3), c = 12.478(4) Å, β = 93.56(3)°, and Z = 4, R = 0.089 from 2 104 reflections; (**2**), orthorhombic, space group $P2_1ab$, with a = 10.918(1), b = 11.604(3), c = 12.327(3) Å, and Z = 4, R = 0.047 for 3 285 reflections. The complex anion of (**1**) exhibits distorted trigonal-bipyramidal co-ordination (O_3N_2) about the vanadium atoms with a linear $\{V–N–O\}^4$ moiety. In contrast, the anion in (**2**) has distorted octahedral co-ordination (O_3N_2C) about the vanadium, involving the quadridentate ligand, a linear V–N–O group, and a cyanide. The rather long N–O distances in complexes (**1**) and (**2**) (average 1.253 Å) are in accord with low ν(N–O) stretching frequencies at 1 490 and 1 450 cm^{-1}. The $\{V–NO\}^4$ moiety of (**1**) is susceptible to electrophilic attack by protons, generating most probably a hydroxylamidovanadium(V) species. This process is reversible; in alkaline solutions (**1**) is regenerated. The kinetics of the equilibration reaction of complex (**1**) with cyanide have been measured by stopped-flow spectrophotometry at pH 11 [I = 2.0 mol dm^{-3} ($NaClO_4$)]. A rate constant, k_f = 1.12 dm^3 mol^{-1} s^{-1}, for the forward step and one, k_r = 0.61 s^{-1}, for the reverse have been determined at 20 °C.

In 1964 Hartkamp[1] reported a spectrophotometric method of high accuracy and good selectivity for the quantitative determination of vanadium in which vanadium(V) was treated with hydroxylamine and various tris(2-hydroxyalkyl)amines in alkaline solutions. Benes and co-workers[2,3] have shown that this reaction is equally well suited for quantitative determinations of H_2NOH. Wieghardt and Quilitzsch[4] subsequently recognized that these reactions produced air-stable, highly coloured nitrosyl complexes of vanadium(I) of the type $\{V–NO\}^4$ according to the nomenclature of Enemark and Feltham.[5] The stoicheiometry of the reactions is as depicted in equation (1). This is a further example of the smooth reductive

$$V^V + H_2NOH \longrightarrow V–N{=}O^{2+} + 3H^+ \qquad (1)$$

nitrosylation of vanadate(V) with hydroxylamine in alkaline solution in the presence of co-ordinating ligands.[6] Thus, $[V(NO)(CN)_5]^{3-}$, $[V(NO)(CN)_6]^{4-}$, $[V(NO)(H_2NO)(CN)_4]^{3-}$, and $[V(NO)(H_2NO)(pydca)(H_2O)]^-$ (pydca = pyridine-2,6-dicarboxylate) have been prepared using this method.[7–10] Recently, a report on the preparation of $[V(NO)_2(CN)_4]^{2-}$ and related dinitrosyl complexes *via* reductive nitrosylation with hydroxylamine has appeared.[11]

The mechanism of reaction (1) has been investigated in some detail.[6,12] It appears to involve the reversible interconversion of an O,N-co-ordinated hydroxylamidovanadate(V) species (Scheme) which undergoes an intramolecular two-electron redox reaction with concomitant deprotonation. A colourless hydroxylamido(1−)vanadium(V) complex $[VO(H_2NO)(pydca)(H_2O)]$ has been characterized by *X*-ray diffraction.[10,13] The susceptibility of the $\{V–NO\}^4$ moiety to electrophilic attack by protons, generating a hydroxylamido(1−)vanadium(V) complex, has also been demonstrated when 2,2′,2″-nitrilotris(2-propanol) is a quadridentate ligand.[4,12]

We here describe the preparation, *via* reductive nitrosylation of vanadate(V) with H_2NOH, and the crystal structures of sodium (2,2′,2″-nitrilotriethoxy)nitrosylvanadate(I)–sodium perchlorate tetrahydrate, (**1**), and of barium cyano(2,2′,2″-nitrilotriethoxy)nitrosylvanadate(I) pentahydrate, (**2**). The equilibration kinetics of the reaction of complex (**1**) with cyanide to give (**2**) have also been studied.

Results and Discussion

The reaction of ammonium vanadate(V), triethanolamine, and hydroxylamine in alkaline solution at 60 °C yields a deep red solution, from which upon addition of solid sodium perchlorate red crystals of $Na[V(NO)\{N(C_2H_4O)_3\}]\cdot NaClO_4\cdot 4H_2O$, (**1**), are obtained in good yield. The i.r. spectrum exhibits an intense band at 1 490 cm^{-1}, which is assigned to the stretching frequency of co-ordinated nitrosyl. This value is exceptionally low for a linear M–N–O moiety (see below) and suggests that the nitrosyl group should be susceptible to electrophilic attack.[14]

Aqueous solutions of complex (**1**) are stable in the presence of oxygen for at least 24 h in the range pH 8.8—11, but in acidic solutions under argon (pH 7—6.0) a colour change from red to

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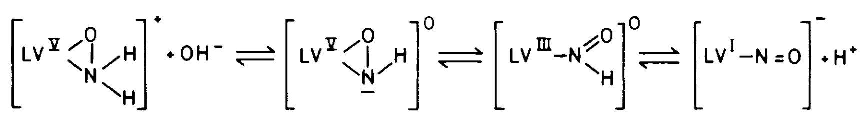
† *Supplementary data available* (No. SUP 56308, 7 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Transactions*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Scheme. L = $N(C_2H_4O)_3^{3-}$

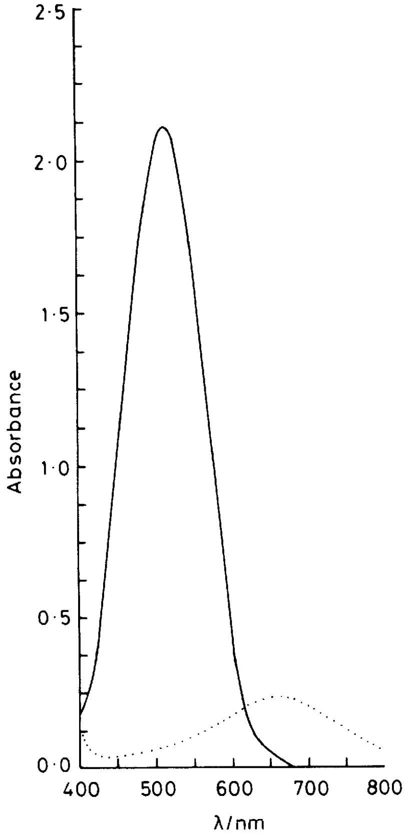


Figure 1. Electronic spectra of complex (**1**) (——, 2×10^{-3} mol dm^{-3} in 10^{-4} mol dm^{-3} NaOH) and (**2**) (· · · ·, 2×10^{-3} mol dm^{-3} in 2 mol dm^{-3} NaCN) at 20 °C (4-cm cell)

Table 1. Pseudo-first-order rate constants for the reaction of complex (**1**) (2×10^{-3} mol dm^{-3}) with CN$^-$ at I = 2.0 mol dm^{-3} ($NaClO_4$)

θ_c/°C	[CN$^-$]/mol dm^{-3}	$k_{obs.}$/s^{-1}
10	0.20	0.305
	0.50	0.43
	0.70	0.53
	1.00	0.62
20	0.20	0.88
	0.50	1.30
	0.70	1.57
	1.00	1.69
30	0.20	2.4
	0.40	2.7
	0.60	3.15
	1.00	4.3

Table 2. Summary of kinetic data for the reaction of complex (**1**) with CN$^-$ [I = 2.0 mol dm^{-3} ($NaClO_4$)]

θ_c/°C	k_f/dm^3 mol^{-1} s^{-1}	k_r/s^{-1}
10	0.41	0.22
20	1.12	0.61
30	2.38	1.91

$\Delta H_f^\ddagger = 60 \pm 4$ kJ mol^{-1}, $\Delta S_f^\ddagger = -38 \pm 12$ J K^{-1} mol^{-1}, $\Delta H_r^\ddagger = 75 \pm 4$ kJ mol^{-1}, $\Delta S_r^\ddagger = +8 \pm 12$ J K^{-1} mol^{-1}

yellow is observed. This colour change is reversible; re-adjustment of such solutions to pH 11 restores the original red solution. From concentrated solutions of complex (**1**) at pH 6 ($HClO_4$) a greenish yellow material was precipitated at 0 °C upon addition of sodium perchlorate. At room temperature this material decomposed rapidly with evolution of NO, even in the solid state. Elemental analyses were not very reproducible but confirmed the ratio V:N to be 1:2. In the i.r. spectrum of this material no band due to co-ordinated nitrosyl (or co-ordinated HNO[15]) was detected. The yellow precipitate reacts with gaseous ammonia whereupon the colour changes to red. The i.r. spectrum of this material again exhibited the original ν(NO) frequency of complex (**1**). Because of its rapid decomposition, even in the solid state, we have not been able to characterize this material further. We propose that the yellow material contains hydroxylamide(1 −), H_2NO^-, and the ligand 2,2′,2″-nitrilotriethoxy co-ordinated to a vanadium(V) centre. Similar results have been reported for an analogous system containing the ligand 2,2′,2″-nitrilotris(2-propoxy),[12] corroborating the proposed mechanism for the reductive nitrosylation of vanadate(V) with hydroxylamine (Scheme).[6]

When alkaline, aqueous solutions of complex (**1**) are treated with a large excess of sodium cyanide a colour change from red to blue is observed. Addition of barium chloride initiates the slow precipitation of blue crystals of $Ba[V(NO)(CN)\{N(C_2H_4O)_3\}]\cdot 5H_2O$, (**2**). In the i.r. spectrum NO and C≡N stretching frequencies are observed at 1 450 and 2 100 cm^{-1}, respectively. The ν(NO) wavenumber is 40 cm^{-1} less than that of complex (**1**). The electronic spectra of (**1**) and (**2**) in the visible region are quite different (Figure 1); most remarkable is the difference in intensity of the absorption maxima. The cyano-ligand in complex (**2**) is substitution labile and in alkaline solutions (pH 10) equilibrium (2) is rapidly established. The equilibrium constant K ($= k_f/k_r$) has been measured by spectrophotometry to be 8 ± 2 dm^3 mol^{-1} at 20 °C (I = 2.0 mol dm^{-3}).

$$(\mathbf{1}) + CN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (\mathbf{2}) \qquad (2)$$

Reaction (2) was followed by stopped-flow spectrophotometry by mixing solutions of complex (**1**) (pH 10) with solutions of sodium cyanide in large excess, I = 2.0 mol dm^{-3} ($NaClO_4$). The decrease in absorption at the 510 nm peak of complex (**1**) was used to monitor the equilibration. Pseudo-first-order rate constants, $k_{obs.}$, for the equilibration reaction are summarized in Table 1. Figure 2 shows the dependence of $k_{obs.}$ on [CN$^-$]. The rate equation is as in (3) where k_f is the rate constant for the formation of complex (**2**) and k_r that for its dissociation. Numerical values of k_f and k_r were evaluated (Table 2) from the slopes and intercepts in Figure 2 using a least-squares fitting routine. From the temperature dependence, log k against $1/T$, the respective activation parameters (Table 2) were calculated.

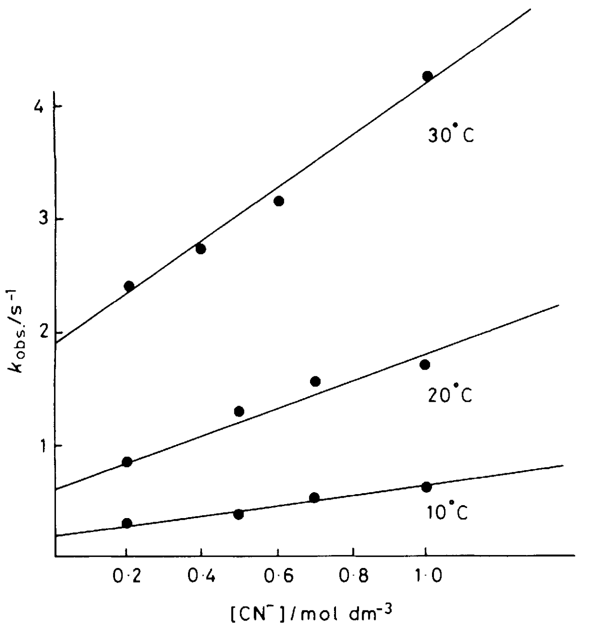


Figure 2. Dependence of pseudo-first-order rate constants, $k_{obs.}$, on $[CN^-]$ for the reaction of complex (**1**) with cyanide

The agreement between the spectrophotometrically determined equilibrium constant and the value obtained from kinetic data ($k_f/k_r = 1.8 \pm 0.5$ dm^3 mol^{-1}) is poor due to the relative large uncertainty in the determination of k_r (intercept, Figure 2).

$$k_{obs.} = k_f[CN^-] + k_r \qquad (3)$$

In the solid state the vanadium centre of complex (**1**) is in a trigonal-bipyramidal environment of the quadridentate ligand 2,2′,2″-nitrilotriethoxy and a co-ordinated nitrosyl (see below). Thus it is co-ordinatively and electronically (14-electron species) unsaturated; the addition reaction of (**1**) with cyanide leads then to an octahedral 16-electron species which is still co-ordinatively and electronically unsaturated, considering such known seven-co-ordinate species as $[V(NO)(CN)_6]^{4-}$. Since the absorption spectrum of complex (**1**) does not change between pH 8.8 and 11 we assume that (**1**) has the same structure in the solid state and in solution. [The diffuse-reflectance spectrum of (**1**) also exhibits a maximum at 510 nm.] Interestingly, the entropies of activation support the assignment of an addition mechanism for the reaction of complex (**1**) with CN^- (a negative value is observed), whereas the reverse reaction is very likely a dissociative process (a small $\Delta S_r^{\ddagger}$ is observed).

Compound (**1**) gave red plates which were not ideal for single-crystal *X*-ray structure determination but even so this was carried out and the structure refined to $R = 0.089$. Complex (**2**) gave better crystals, the structure of which was determined and refined to $R = 0.047$. Atomic co-ordinates and selected bond parameters for (**1**) are given in Tables 3 and 4, those for (**2**) in Tables 5 and 6. Their molecular structures are shown in Figures 3 and 4 respectively.

Crystals of complex (**1**) consist of sodium cations, the complex anion $[V(NO)\{N(C_2H_4O)_3\}]^-$, ClO_4^-, and water of crystallization. The vanadium centre is in a distorted trigonal-bipyramidal environment; the nitrogen atoms of the quadridentate ligand and of the co-ordinated nitrosyl are in axial positions, whereas three oxygens are in equatorial positions. This is to our knowledge the first $\{V\text{–}NO\}^4$ type complex with co-ordination number five; $[V(NO)(CN)_5]^{3-}$ [16] is six-co-ordinate (octahedral) and $[V(NO)(CN)_6]^{4-}$ [8] as well as $[V(NO)(H_2NO)(pydca)(H_2O)]^-$ [10] (pentagonal bipyramidal) are seven-co-ordinate 18-electron species.

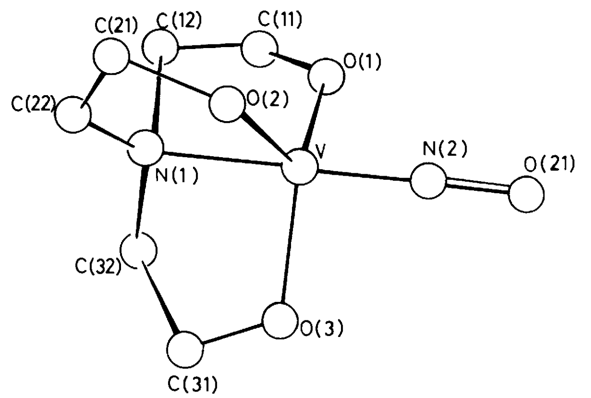


Figure 3. Structure of the anion in complex (**1**), $[V(NO)\{N(C_2H_4O)_3\}]^-$

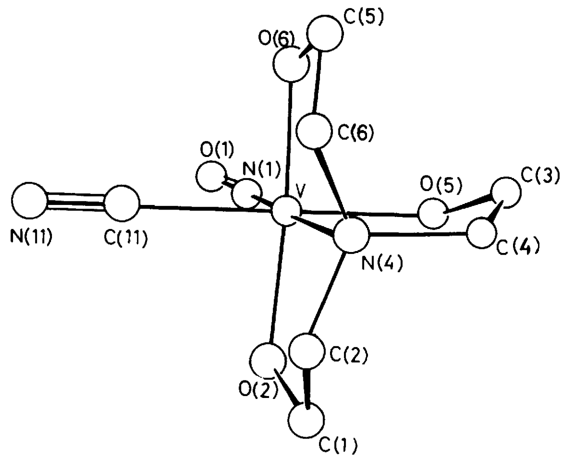


Figure 4. Structure of the anion in complex (**2**), $[V(NO)(CN)\{N(C_2H_4O)_3\}]^{2-}$

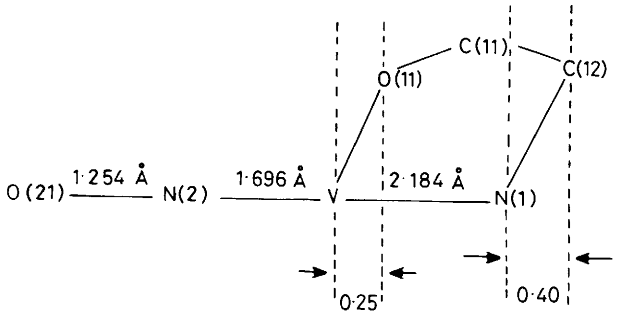


Figure 5. Schematic representation of a part of complex (**1**)

The N–O bond distance of the nitrosyl group is rather long [1.254(9) Å] and the V–N(2) bond length [1.696(7) Å] indicates a double bond. The V–N–O system is linear. The bonding of the nitrosyl in complex (**1**) may therefore be described as V=N=O. In contrast, V–N(1) is quite long [2.184(7) Å], indicating a considerable *trans* influence of the nitrosyl group. The sum of the three O–V–O angles is 354.7° and the vanadium centre is displaced by 0.25 Å from the plane defined by the oxygen donor atoms (Figure 5). Atom N(1) is displaced by 0.40 Å from the plane defined by the three carbon atoms bound to it [C(12),

Table 3. Atom co-ordinates (× 10^4) for $Na[V(NO)\{N(C_2H_4O)_3\}]\cdot NaClO_4\cdot 4H_2O$, (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
V	2 233(1)	−3 193(1)	−2 096(1)	Cl	4 056(3)	−2 773(3)	3 104(2)
O(1)	946(5)	−4 025(6)	−1 810(5)	Na(1)	8 519(3)	5 997(4)	774(3)
O(3)	2 129(6)	−1 552(2)	−2 338(5)	Na(2)	−4 942(3)	6 453(4)	625(3)
N(1)	1 510(6)	−3 264(7)	−3 739(5)	O(A)	2 886(11)	6 864(12)	2 868(11)
N(2)	2 789(6)	−3 130(7)	−817(5)	O(B)	4 398(10)	7 849(11)	2 252(10)
O(21)	3 185(5)	−3 070(6)	133(5)	O(C)	4 718(12)	6 273(14)	3 460(12)
C(11)	119(8)	−4 127(11)	−2 654(8)	O(D)	4 050(12)	−2 070(13)	3 996(12)
C(12)	565(13)	−4 055(16)	−3 718(10)	$O_w(1)$	280(5)	6 508(6)	215(5)
C(21)	3 170(10)	−4 447(12)	−3 798(9)	$O_w(2)$	−2 031(6)	5 037(6)	−863(5)
C(22)	2 363(13)	−3 678(15)	−4 402(10)	$O_w(3)$	−3 201(6)	6 219(7)	1 577(6)
C(31)	1 859(11)	−1 185(9)	−3 437(9)	$O_w(4)$	5 210(6)	−4 303(6)	−1 177(6)
C(32)	1 198(16)	−2 051(11)	−4 018(11)	O(2)	3 342(5)	−4 100(6)	−2 700(5)

Table 4. Selected bond parameters (lengths in Å, angles in °) for $Na[V(NO)\{N(C_2H_4O)_3\}]\cdot NaClO_4\cdot 4H_2O$, (**1**)

V–O(1)	1.892(7)	O(1)–V–O(2)	115.2(3)
V–O(2)	1.899(7)	O(2)–V–O(3)	121.1(3)
V–O(3)	1.899(6)	O(2)–V–N(1)	82.2(1)
V–N(1)	2.184(7)	O(1)–V–N(2)	97.7(3)
V–N(2)	1.696(7)	O(3)–V–N(2)	97.3(3)
O(1)–C(11)	1.42(1)	O(1)–V–O(3)	118.4(3)
O(2)–C(21)	1.43(1)	O(1)–V–N(1)	82.2(3)
N(2)–O(21)	1.254(9)	O(3)–V–N(1)	82.4(3)
O(3)–C(31)	1.45(1)	O(2)–V–N(2)	98.2(3)
C(11)–C(12)	1.47(2)	N(1)–V–N(2)	179.6(3)
C(21)–C(22)	1.49(2)	V–N(1)–C(12)	106.3(6)
C(31)–C(32)	1.44(2)	V–N(1)–C(32)	105.8(7)
C(12)–N(1)	1.47(2)	V–N(2)–O(21)	178.9(7)
C(22)–N(1)	1.45(2)	V–N(1)–C(22)	106.5(7)
C(32)–N(1)	1.47(2)		

C(22), C(32)]. Thus N(1) is sp^3-hybridized, in contrast to the structure of $P\{N(C_2H_4O)_3\}S$[17] where the nitrogen is in a trigonal-planar environment of the corresponding carbon atoms (sp^2). The conformation of the quadridentate ligand in complex (**1**) is very similar to that of free 2,2′2″-nitrilotriethanol in the solid state.[18]

Crystals of complex (**2**) consist of barium ions, the complex dianion $[V(NO)(CN)\{N(C_2H_4O)_3\}]^{2-}$, and water of crystallization. The vanadium centre is in a distorted octahedral environment of a quadridentate, chelating ligand, a co-ordinated nitrosyl and a cyano-group. The $\{V\text{–}N\text{–}O\}^4$ moiety is linear and the corresponding V–N and N–O bond distances are very similar to those in complex (**1**), indicative of V=N=O. The V–N bond of the chelating ligand is also *trans* with respect to the nitrosyl group and within experimental error identical to that observed in (**1**). The V–O bond distances are somewhat longer than in complex (**1**), most probably due to steric crowding in going from five- to six-co-ordination. The cyano-group is weakly bound to vanadium; the V–C bond distance [2.172(6) Å] is in excellent agreement with those in $[V(NO)(CN)_5]^{3-}$ (2.17 Å).[16] The bond angles O(2)–V–O(5) and O(5)–V–O(6) are 95.1(3) and 93.0(3)°, respectively. They are considerably smaller than those in complex (**1**), in agreement with a distorted trigonal-planar arrangement of the oxygen donor atoms in (**1**) and distorted square planar (O_3C) in (**2**).

The structures of complexes (**1**) and (**2**) clearly show that the addition of cyanide to (**1**) may be accomplished by a small amount of compression of the O–V–O bond angles in (**1**).

Experimental

Preparations.—$Na[V(NO)\{N(C_2H_4O)_3\}]\cdot NaClO_4\cdot 4H_2O$, (**1**). This was prepared by a modification of the procedure described by Hartkamp.[1] Ammonium vanadate(V) (1.2 g), triethanolamine (1.6 g), hydroxylammonium chloride (1.3 g), and sodium hydroxide (2 g) were dissolved in water (70 cm^3) at 60 °C with stirring. To the deep red solution benzene (200 cm^3) was added and the volume was reduced to 50 cm^3 by evaporation at 90 °C. Sodium perchlorate (10 g) was added and the solution was allowed to stand at room temperature for 12 h, after which the red crystals of complex (**1**) were filtered off (yield 3.2 g, 70%) (Found: C, 16.4; H, 4.6; N, 6.5; V, 11.4; ClO_4, 22.0. $C_6H_{20}N_2Na_2O_{12}V$ requires C, 16.2; H, 4.5; N, 6.3; V, 11.45; ClO_4, 22.4%). I.r. (KBr disc): 1 490vs cm^{-1}, ν(NO). Electronic spectrum: $\lambda_{max.}$ (H_2O) 511 nm (ε 264 dm^3 mol^{-1} cm^{-1}).

$Ba[V(NO)(CN)\{N(C_2H_4O)_3\}]\cdot 5H_2O$, (**2**). Ammonium vanadate(V) (1.2 g), triethanolamine (1.6 g), hydroxylammonium chloride (1.3 g) and sodium hydroxide (3.0 g) were dissolved in water (50 cm^3) at 60 °C. To the deep red solution were added sodium cyanide (8 g) and barium chloride (2 g) whereupon a deep blue solution was obtained which was allowed to stand under a nitrogen atmosphere for 6 d. Blue crystals were filtered off and air-dried (yield 2.5 g, 50%) (Found: C, 17.6; H, 4.7; N, 9.0. $C_7H_{22}BaN_3O_9V$ requires C, 17.5; H, 4.6; N, 8.8%). I.r. (KBr disc): 2 100s (CN) and 1 450s cm^{-1} (NO). Electronic spectrum: $\lambda_{max.}$ (4 mol dm^{-3} KCN): 659 nm (ε 29 dm^3 mol^{-1} cm^{-1}).

Reaction of Complex (**1**) *with Protons.*—An aqueous solution (50 cm^3) of complex (**1**) (2 g) and $NaClO_4$ (10 g) was cooled to 0 °C under argon. Perchloric acid (1 mol dm^{-3}) was added dropwise with stirring and cooling until the pH was 6, during which time the colour changed from red to greenish yellow. A greenish yellow material precipitated, which was rapidly filtered off (yield: 0.5 g) (Found: C, 20.7; H, 5.8; N, 7.6; ClO_4, 14.5. $[\{V(H_2NO)[N(C_2H_4O)_3]\}_2OH]ClO_4\cdot 7H_2O$ (tentative formula) requires C, 20.55; H, 6.2; N, 8.0; ClO_4, 14.2%).

Spectrophotometric Determination of the Equilibrium Constant.—Compound (**1**) was dissolved in aqueous solutions of KCN [0.05—1.0, $I = 2.0$ mol dm^{-3} ($NaClO_4$)] and the absorption at 510 and 660 nm measured at 20 °C. The molar absorption coefficients of (**1**), ε_1, and (**2**), ε_2, at these wavelengths were determined from a 0.001 mol dm^{-3} KOH solution containing (**1**) and 4 mol dm^{-3} KCN containing (**2**). For equilibrium (1) the expression (4) can be derived. A plot of $(\varepsilon_1 - \varepsilon_{obs.})^{-1}/(\varepsilon_1 - \varepsilon_2)^{-1}$ *vs.* $[CN^-]^{-1}$ was linear; *K* was determined as 8 ± 2 dm^3 mol^{-1} from the slope, using a least-squares procedure.

$$(\varepsilon_1 - \varepsilon_{obs.})^{-1}/(\varepsilon_1 - \varepsilon_2)^{-1} = 1 + (K[CN^-])^{-1} \qquad (4)$$

Kinetic Measurements.—The kinetics of the equilibration reaction between complex (**1**) and CN^- were measured by

Table 5. Atom co-ordinates (× 10^4) for $Ba[V(NO)(CN)\{N(C_2H_4O)_3\}]\cdot5H_2O$, (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ba	5 000	4 282(1)	560(1)	C(4)	7 770(8)	5 580(5)	4 388(5)
V	2 833(1)	635(1)	2 234(1)	C(5)	10 036(10)	4 265(5)	3 568(5)
N(1)	2 838(5)	591(4)	860(4)	C(6)	9 056(7)	3 821(6)	4 309(5)
O(2)	1 133(4)	975(4)	2 464(4)	N(11)	8 189(6)	1 525(5)	2 134(5)
C(11)	3 077(5)	2 493(5)	2 207(4)	O(1)	7 848(5)	4 420(4)	−155(3)
N(4)	2 876(6)	634(4)	4 006(4)	$O_w(1)$	5 212(5)	6 343(4)	1 911(4)
O(5)	2 666(5)	−1 028(3)	2 488(4)	$O_w(2)$	2 866(7)	5 823(4)	2 837(5)
O(6)	4 618(4)	607(4)	2 483(4)	$O_w(3)$	3 174(6)	8 024(4)	530(4)
C(1)	5 734(6)	4 025(6)	3 561(5)	$O_w(4)$	693(5)	6 241(4)	1 579(5)
C(2)	6 777(7)	3 676(6)	4 313(5)	$O_w(5)$	621(6)	3 328(6)	637(4)
C(3)	8 118(8)	6 420(5)	3 497(5)				

Table 6. Selected bond parameters (lengths in Å, angles in °) for $Ba[V(NO)(CN)\{N(C_2H_4O)_3\}]\cdot5H_2O$, (**2**)

V–N(1)	1.695(5)	V–O(5)	1.963(4)
V–O(2)	1.919(4)	V–O(6)	1.973(5)
V–C(11)	2.172(6)	N(1)–O(1)	1.251(7)
V–N(4)	2.185(5)	C(11)–N(11)	1.150(8)
N(1)–V–O(2)	99.0(3)	C(11)–V–N(4)	90.7(3)
N(1)–V–C(11)	90.8(3)	C(11)–V–O(5)	171.8(5)
N(1)–V–N(4)	176.9(4)	C(11)–V–O(6)	84.1(3)
N(1)–V–O(5)	97.5(3)	N(4)–V–O(5)	80.9(2)
N(1)–V–O(6)	98.7(3)	N(4)–V–O(6)	79.8(3)
O(2)–V–C(11)	85.2(3)	O(5)–V–O(6)	93.0(3)
O(2)–V–N(4)	82.7(3)	V–C(11)–N(11)	176.0(6)
O(2)–V–O(5)	95.1(3)	V–N(1)–O(1)	178.0(7)
O(2)–V–O(6)	159.4(5)		

stopped-flow spectrophotometry (the instrument was interfaced to a PET 4001 Commodore computer for data acquisition and analysis). The reaction was followed at 510 nm using pseudo-first-order conditions with $[CN^-]$ in large excess over complex (**1**) (2×10^{-3} mol dm^{-3}) and $I = 2.0$ mol dm^{-3} ($NaClO_4$). All solutions were adjusted to pH 10 with NaOH.

Pseudo-first-order rate constants were calculated by using a least-squares program[19] where the absorption at the beginning and after the completed reaction were treated as variables. Semilogarithmic plots of ln ($A_t - A_\infty$) were linear for at least four half-lives. The reproducibility of replicate runs was better than 8% for all reactions.

X-Ray Structure Determinations.—*Crystal data.* $C_6H_{20}N_2Na_2O_{12}V$, (**1**). $M = 444.6$, monoclinic, $a = 12.234(3)$, $b = 11.405(3)$, $c = 12.478(4)$ Å, $\beta = 93.56(3)°$, $U = 1\,737.6(8)$ Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.699$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.11$ cm^{-1}, $F(000) = 911.8$.

$C_7H_{22}BaN_3O_9V$, (**2**). $M = 480.6$, orthorhombic, $a = 10.918(1)$, $b = 11.604(3)$, $c = 12.327(3)$ Å, $U = 1\,561.7(9)$ Å^3, space group $P2_1ab$, $Z = 4$, $D_c = 2.06$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 28.4$ cm^{-1}.

Data collection.—A Siemens-Stoe AED II automatic four-circle diffractometer was used with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and the θ—2θ scan mode; 2 104 unique reflections were measured for compound (**1**) and 3 285 for compound (**2**) with $I \geqslant 2.5\sigma(I)$ ($3 \leqslant 2\theta \leqslant 70°$) and these were used in the structure solutions and refinements. Empirical absorption and Lorentz polarization corrections were applied.

Structure solutions and refinement. The structures were solved and refined using the SHELXTL program system.[20] The positions of the V atoms of compounds (**1**) and (**2**) and of the Ba atoms of (**2**) were located from Patterson syntheses. Subsequent Fourier syntheses revealed the positions of all non-hydrogen atoms. Idealized positions of the H atoms bound to C atoms of the ligand were calculated [on the basis of d(C–H) 0.97 Å and sp^3-hybridized C atoms] and included in the refinement cycles with a fixed isotropic thermal parameter. No hydrogens were located for molecules of water of crystallization from final Fourier difference maps and were not included. The full-matrix least-squares refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms [except O atoms of ClO_4^- anions in (**1**), which were refined with isotropic thermal parameters] and with unit weights, and the final R factors were 0.089 for (**1**) and 0.047 for (**2**).

All computations were made on a NOVA 3 (General Data) computer.

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