is not settled by the experimental evidence offered by this work. A comparison with kinetic data for reduction by Ru(NH$_3$)$_6^{2+}$ might be useful since a linear rate correlation on the log–log scale for the outer-sphere reduction of Co(III) centers by Ti(III) and Ru(NH$_3$)$_6^{2+}$ has been recently shown.[6]

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Registry No. Co(EDTA)$^-$, 15136-66-0; Co(HEDTA)OH$_2$, 54713-24-5; Co(HEDTA)Cl$^-$, 54735-69-2; Ti^{3+}, 22541-75-9.

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A Kinetic Study of Anation of Thiocyanate and Azide to Aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV) and the Aquation of the Product in Aqueous Solution. A Direct Basal Site Substitution

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Substitution reactions between water in aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV), VO(pmida)H$_2$O [(4–8) $\times 10^{-4}$ M, M = mol dm^{-3}], and NCS$^-$ (0.02–0.31 M) and N$_3^-$ (0.02–0.4 M) have been kinetically studied by the stopped-flow method in aqueous solutions of pH 3.2–4.7 and 3.6–4.9 at ionic strength 1.0, respectively. The pseudo-first-order rate constant k_0 is expressed by $k_0 = k_b + k_f[X^-]$ (X$^-$ = NCS$^-$ or N$_3^-$), where k_b and k_f stand for the first- and second-order rate constants of the aquation of VO(pmida)X$^-$ and the anation of X$^-$ to VO(pmida)H$_2$O, respectively. The rate constants and activation parameters are as follows: k_b and k_f are 0.061 and 0.13 s^{-1} and 0.26 and 3.7 M^{-1} s^{-1} at 25 °C for NCS$^-$ and N$_3^-$, respectively; the corresponding $\Delta H^‡$ and $\Delta S^‡$ are 61.4, 63.5, 48.9, and 47.2 kJ mol^{-1} and −61, −47, −90, and −75 J mol^{-1} K^{-1}. These reactions must reflect a direct basal site substitution of the oxovanadium(IV) complex and seem to proceed via an associative mechanism.

Introduction

The substitution reaction of oxovanadium(IV) complexes includes various rapid processes at varying coordination sites and has been investigated mainly by NMR, ESR, and stopped-flow spectrometry.[1-11] The mechanisms of these reactions are different from one another and cannot be directly compared. The exchange of solvent molecules between the coordination site and the bulk solvent is claimed to have a first-order rate constant $>10^7$ s^{-1},[1-3] whereas that at the basal site is $\approx 10^3$ s^{-1} at room temperature.[1,2,5,6] On the other hand, chelation of a bidentate ligand is much slower ($\approx 10^1$ s^{-1} at 25 °C[11,12]).

The substitution at the basal site can proceed either by a direct substitution or by an intramolecular process from the apical site. For discriminating these two processes we have synthesized the new compound aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV), VO(pmida)H$_2$O, in the crystalline state and elucidated the structure by X-ray crystallography,[13] to find that the trans site to the oxo ligand is occupied by the tertiary amine (Figure 1). So far as this structure is maintained in solution, the replacement of the aqua ligand by a unidentate ligand can proceed only by a direct substitution. We have found that addition of thiocyanate or azide ions into the aqueous solution results in the replacement of coordinated water, and the rate can be measured by a stopped-flow technique at room temperature (X$^-$ = NCS$^-$ or N$_3^-$).

$$\mathrm{VO(pmida)H_2O + X^- \rightleftharpoons VO(pmida)X^- + H_2O} \quad (1)$$

This paper deals with the result of kinetic studies and the discussion of the reaction mechanism.

Experimental Section

Materials. The complex [VO(pmida)H$_2$O]·2H$_2$O was synthesized by a given method,[13] and the purity was checked by IR and UV spectra, elemental analysis of carbon, hydrogen, and nitrogen, and the pK_a measurement (6.4 at 25 °C and I = 1.0). Ammonium oxo((2-pyridylmethyl)iminodiacetato)thiocyanatovanadium(IV), NH$_4$[VO(pmida)(NCS)], was prepared by mixing the aqua complex with a large excess of ammonium thiocyanate in aqueous solution and setting aside for 24 h. The violet crystals were washed with a mixture of ethanol and water and then ethanol and air-dried. Anal. Calcd for C$_{11}$H$_{14}$N$_4$O$_5$V: C, 36.17; H, 4.03; N, 15.68. Found: C, 36.17; H, 3.84; N, 15.34. Infrared absorption [$\bar{\nu}$(C–S) 772, $\bar{\nu}$(C–N) 2098 cm^{-1}] supported the coordination of NCS$^-$ by the nitrogen atom. Attempts to prepare a crystalline azido complex have turned out unsuccessful.

The ionic strength was adjusted with commercial Special Grade sodium perchlorate and lithium perchlorate. The latter was prepared from the carbonate and perchloric acid and doubly recrystallized. Sodium thiocyanate was recrystallized from aqueous ethanol, and the concentration of the aqueous solution was determined by titration with mercury(II) nitrate with iron(III) ions as indicator.[14] Sodium azide was recrystallized from aqueous ethanol. Lithium azide was prepared by adding a calculated amount of barium azide solution to a lithium sulfate solution. The suspension was centrifuged, filtered, and treated with ethanol to obtain colorless crystals, which were recrystallized

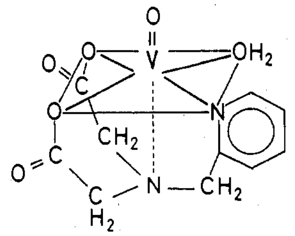

Figure 1. Crystal structure of VO(pmida)H_2O. Bond lengths (in Å) are V=O = 1.59, V—N (apical) = 2.29, V—N (basal) = 2.10, V—OH_2 = 2.02, V—O (cis to water) = 1.98, V—O (trans to water) = 2.00.

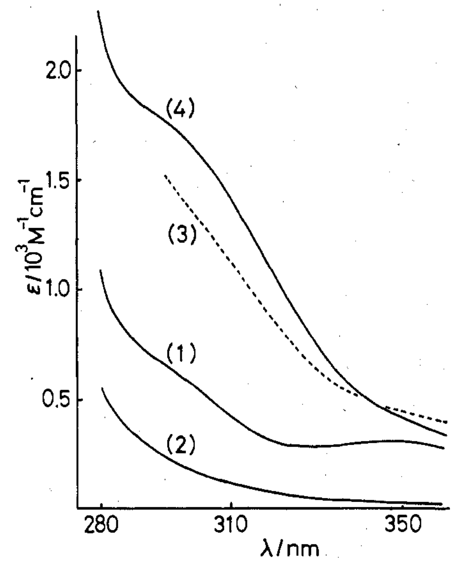

Figure 2. Ultraviolet absorption spectra of VO(pmida)H_2O in aqueous solution containing various reagents: (1) no reagent added at pH 4.5, (2) in 0.5 M acid, (3) after equilibration in 0.33 M N_3^- solution, (4) after equilibration in 0.39 M NCS^- solution.

from aqueous ethanol. Aqueous hydrazoic acid was prepared by ion exchange of aqueous sodium azide on Amberlite IR-120 (H^+ form). The acid concentration was determined by alkalimetric titration and the azide concentration by back-titration with cerium(IV) and iron(II) solution. Perchloric acid (Wako Chemical Co., Special Grade) was used without further purification.

The ultraviolet absorption spectra of related compounds are shown in Figure 2.

Measurement of the Formation Constant. The equilibrium constant expressed by formula 2 was determined spectrometrically at 310 nm

$$K = [\mathrm{VO(pmida)X^-}]/[\mathrm{VO(pmida)H_2O}][\mathrm{X^-}] \qquad (2)$$

for both thiocyanate and azide in the pH regions from 3.0 to 4.7 and from 4.27 to 4.93, respectively, in the presence of 0.06–0.31 M NCS^- and 0.027–0.27 M N_3^-. For the azide system a mixture of HN_3 and NaN_3 or LiN_3 was used and the concentration of N_3^- was calculated from the given concentrations and the pK_a (4.38 at 25 °C, I = 1.0). The contribution of UV absorption of HN_3 in the reaction mixtures was corrected with an authentic solution. The measured absorbance A is expressed by eq 3, where A_0 is the absorbance of the solution

$$A = \frac{(\epsilon_0 - \epsilon_x)}{\epsilon_x} \frac{1}{K} \frac{(A - A_0)}{[\mathrm{X^-}]} + [\mathrm{VO}]_t\epsilon_x \qquad (3)$$

in the absence of X^-. The $[VO]_t$ is the total concentration of the complex (7.8×10^{-4} M), ϵ_x the molar absorption coefficient of the formed complex calculated from Figure 3 (1945 and 1420 M^{-1} cm^{-1}, for NCS^- and N^{3-}, respectively), and ϵ_0 is that of the aqua complex (384 M^{-1} cm^{-1} at 310 nm). The K is known from the slope of the diagram of A vs. $(A - A_0)/[X^-]$ (Figure 3). Measurements at different wavelengths gave the same values.

Kinetic Runs. The rate was measured by plotting the absorbance at 310 nm by the stopped-flow technique in the pH regions 3.2–4.7 and 3.6–4.9 for NCS^- and N_3^-, respectively. The change in absorption pattern was also examined by the rapid scan spectroscopy in the range from 280 to 350 nm. In the presence of more than a 20-fold excess of X^-, the change in absorption corresponded to that between the aqua complex and the equilibrated mixture of reaction 1. The pH was adjusted with perchloric acid and azide–hydrazoic acid buffer for the NCS^- and N_3^- systems, respectively. Acetate ions affected the rate of anation, although they gave only little influence upon the spectra.

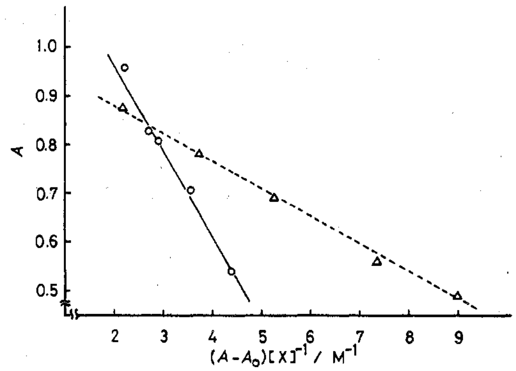

Figure 3. Spectroscopic determination of the equilibrium constant at 25 °C and I = 1.0 ($NaClO_4$): -○-, [NCS^-] = 0.06–0.31 M; --△--, [N_3^-] = 0.027–0.27 M.

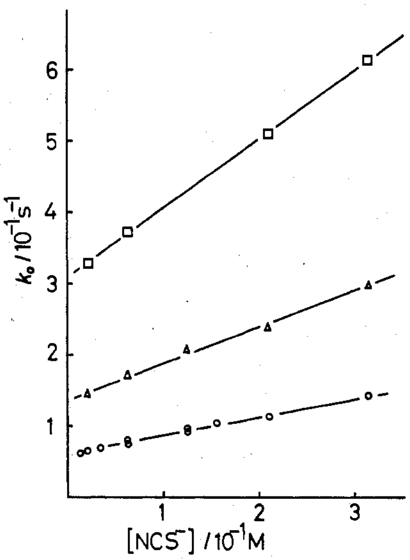

Figure 4. Dependence of the first-order rate constant k_0 upon the concentration of thiocyanate (I = 1.0, $NaClO_4$): (-○-) 25 °C, pH 3.2–4.7; (-△-) 35 °C, pH 4.1; (-□-) 45 °C, pH 4.1.

In the time scale from 5 ms to 200 s, only one change of the absorbance was observed in the range from 5 to 200 s. First-order plots of log $(A_\infty - A_t)$ against time gave straight lines until the reaction reached 90% completion under the given experimental conditions. The first-order rate constant k_0 was obtained from the slope. On examinations by use of different time scales of the apparatus the reproducibility was satisfactory within an error ±3%. The data were treated by the least-squares method.

In more than 0.1 M acid solution the aqua complex undergoes acid hydrolysis to liberate pmida ligand.[15] In the pH region 1–3, the increase in absorbance at 310 nm was similarly observed and the same kinetic treatment was made. However, reaction 1 was involved by some other reaction, and the discussion was mainly made in the said pH range.

The absorption spectra were recorded by a Hitachi 124 double beam spectrometer and a Hitachi 323 recording spectrometer. Kinetic runs were performed in a thermostated cell of a Union Giken RA 601 stopped-flow spectrometer with a data processor and an X-Y recorder. The pH was measured with a Metrohm Herisau pH/meter E 300B.

Results

The observed first-order rate constant k_0 increases linearly with increase in the concentrations of NCS^- and N_3^-. When

Table I. The k_b and k_f Values for the Thiocyanate and the Azide System at Various pH Values at 25 °C ($I = 1.0$)

X^-	pH	k_b/s^{-1}	$k_f/M^{-1}\ s^{-1}$
NCS^-	4.7	0.060 ± 0.003	0.290 ± 0.033
	4.1	0.061 ± 0.003	0.256 ± 0.023
	3.2	0.056 ± 0.011	0.277 ± 0.050
	2.0	0.10 ± 0.01	0.368 ± 0.045
	1.3	0.28 ± 0.02	0.444 ± 0.112
	0.8	90 ± 7	780 ± 30
N_3^-	4.93	0.11 ± 0.04	3.95 ± 0.20
	4.76	0.14 ± 0.02	3.75 ± 0.21
	4.27	0.18 ± 0.07	3.25 ± 0.56

the forward and backward reaction rate constants of reaction 1 are expressed by k_f and k_b, respectively, the following equation is obtained. (See Figures 4 and 5.)

$$d[\text{product}]/dt = k_o[\text{VO}]_t = (k_b + k_f[X^-])[\text{VO}]_t$$

These first- and second-order rate constants remain unchanged in the pH regions 3.2–4.7 and 3.6–4.9, for the NCS^- and N_3^- systems, respectively (Table I). The k_b and k_f values and the activation parameters obtained by the measurements at 25–45 °C are summarized in Table II together with other data of related reactions.

Below pH 3.2 the rate constants for the NCS^- system increase. At pH 0.8 the rate is greater than that at pH 3.2 by ca. 1000 times and is similar to that of substitution of NCS^- for $[VO(H_2O)_5]^{2+}$.[4] Clearly aquation of $[VO(\text{pmida})H_2O]$ takes place. The apparently enhanced rate of substitution at pH 1–3, where the product seems to be mostly $[VO(\text{pmida})NCS]^-$, may reflect proton catalysis upon reaction 1.

Ionic strength gave little effect on the rate in the range from 0.5 to 1.0. Acetate decreased the rate of anation of NCS^- (e.g., k_f is 0.103 $M^{-1}\ s^{-1}$ in the presence of 0.16 M acetate at pH 4.7) but not the aquation. Attempts have been made to carry out similar kinetic studies with chloride, bromide, acetate, chloroacetate, thiourea, nitrate, and glycinate, but the changes in the absorption pattern on the reaction were too small to enable kinetic studies. Nitrite oxidized vanadium(IV) with evolution of gas, and the result will be reported elsewhere.

Discussion

Direct Basal Substitution. The absorption spectrum of the aqua complex remains unchanged for 1 month at pH 3.0–4.9, and the pattern is very similar to that of the crystals measured by the reflection method. Although this method enables the observation of the absorption peak positions only in the region from 340 to 700 nm, both the solid and the aqueous solution gave common peaks at ca. 352 and 570 nm. The latter peak is so sensitive to the environment of oxovanadium(IV) ions as to be useful for measuring the adduct formation constants with Lewis bases including donor solvent molecules.[17] Presence of a common peak at this wavelength provides support for the same structure between solid and aqueous solution.

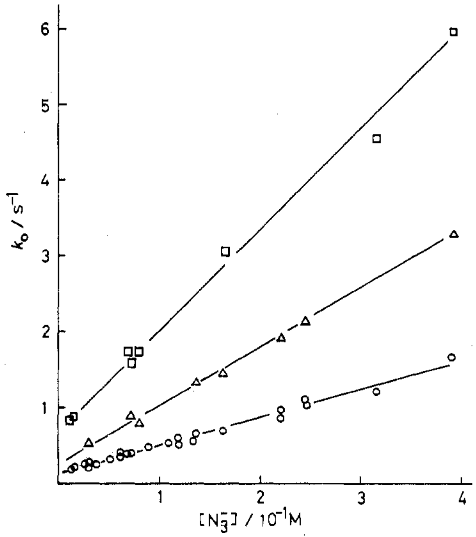

Figure 5. Dependence of the first-order rate constant k_o upon the concentration of azide (I = 1.0, $NaClO_4$ or $LiClO_4$): –○–, 25 °C; –△–, 35 °C; –□–, 45 °C (ratio $[NH_3]/[N_3^-]$ = 0.28–6.0).

The equilibrium constants (eq 2) measured by the spectroscopic method (4.4 and 14 M^{-1} at 25 °C, I = 1.0) are similar to those obtained from the kinetic data (4.2 and 29 M^{-1} under the same condition for NCS^- and N_3^-, respectively). Absence of spectral change other than that involved in the present kinetic study verifies that only reaction 1 takes place in the present systems under the given experimental conditions. On the basis of these observations we conclude that the kinetic data of the present study in Table II represent direct basal site ligand substitution of oxovanadium(IV) complexes.

Substitution at the basal site of oxovanadium(IV) complexes has been studied for several systems (Table II), and the measured first-order rate constants center around $10^3\ s^{-1}$ at room temperature. These values are remarkably greater than the rate constants determined during this work. Although such

Table II. Rate Constants and Activation Parameters for Various Substitution Reactions of Oxovanadium(IV) Complexes

systems	method	t/°C	k/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	ref	category
$[VO(acac)_2]$-py[a] in benzene formation	ESR	18	10^9			10	1
dissoc	ESR	18	1.3×10^7			10	1
$[VO(H_2O)_5]^{2+}$-H_2O in H_2O	^{17}O NMR	25	520	57.2	-6.3	1, 2	2
		25	10^{11}			1, 2	1
		25	10^9			3	1
$[VO(H_2O)_5]^{2+}$-NCS^- in H_2O[b]	p jump	25	11500 M^{-1}	45.1	-16	4	2
$[VO(dmf)_5]^{2+}$-DMF in DMF[c]	^{1}H NMR	25	570	30.3	-90	5	2
$[VO(CH_3CN)_5]^{2+}$-CH_3CN	^{1}H NMR	25	2800	29.4	-84	6	2
$[VO(gly)_2]$-Hgly exchange[d]	^{1}H NMR	25	360	33.4	-84	8	2
$[VO(gly)(H_2O)_4]^+$ in H_2O (chelation)	t jump	25	37			11	5
	stopped flow	25	35			11	5
$[VO(H_2O)_5]^{2+}$-oxo exchange	^{18}O label	0	2.98×10^{-5}			16	4
$[VO(acac)_2]$-Hacac in DCE[e]	^{14}C label	-33	0.37[f]	47.6	-61.9	12	5
$[VO(pmida)(H_2O)]$ vs. NCS^- aquat	stopped flow	25	0.061	61.4 ± 3.3	-61 ± 10	this work	3
anat	stopped flow	25	0.26 M^{-1}	48.9 ± 1.7	-90 ± 9	this work	3
$[VO(pmida)H_2O]$ vs. N_3^- aquat	stopped flow	25	0.13	63.5 ± 13	-47 ± 42	this work	3
anat	stopped flow	25	3.7 M^{-1}	47.2 ± 6	-75 ± 20	this work	3

[a] $acac^-$, enolate anion of acetylacetone; py, pyridine. [b] Formation of monothiocyanato complex. [c] DMF, *N,N*-dimethylformamide. [d] gly^-, glycinate anion. [e] DCE, 1,2-dichloroethane. [f] k_{ex} value at −33 °C; the observed first-order rate constant k_o is expressed by $k_o = k_{ex}K_L[\text{Hacac}]$, where K_L is the formation constant of the adduct $[VO(acac)_2]\cdot$Hacac. The k_{ex} value is converted into that at 25 °C, 63 s^{-1}.

a rate constant depends on the nature of the ligands and on the other experimental conditions, the difference by a factor 10^3 to 10^4 seems too large to be ascribed to those conditions. We tend to consider that the claimed basal site substitution rates might reflect those of an intramolecular process in which the incoming ligand first interacts at the apical site very rapidly and rearranges to the basal site. If such a consideration were appropriate, the kinetic data in Table II could be classified into five categories: (1) very rapid substitution at the apical site, (2) fairly rapid intramolecular rearrangement from the apical to the basal site, (3) rather slow direct basal substitution elucidated first by the present study, (4) very slow exchange of the oxo ligand,[16] and (5) slow chelate formation of a bidentate ligand coordinated as a unidentate (both ends of the bidentate are at the basal site after chelation). According to this view, the magnitude of regioselectivity between the trans (apical) and the cis (basal) site of oxo ligand of vanadium(IV) on ligand substitution reaches the order of 10^9.

Garner et al. found that the substitution of the halide ion for the triphenylphosphine oxide in octahedral *mer*-trichlorooxo-*cis*(*O*,*O*)-bis(triphenylphosphine oxide)molybdenum(V) in dichloromethane proceeded in two steps with rate constants of 40 and 1.5 s^{-1} at room temperature. The first and second steps were reckoned to correspond to the substitutions at the apical site followed by the rearrangement to the basal site.[18] Square-pyramidal tetrachlorooxomolybdenum(V) undergoes addition reaction with thiocyanate to give an octahedral $MoOCl_4(NCS)^{2-}$ with a rate constant of 2 s^{-1}. This rate was considered to be too small to represent the addition rate at the apical site and indicate the rate of isomerization of the rapidly formed apical adduct to the final product having NCS^- at the basal site.[18] These results suggest that a two-step mechanism is probable for the complexes of d^1 transition-metal ions containing an oxo ligand, and the trans site is very much labilized. The apparently very large regioselectivity of oxovanadium(IV) complexes as compared with that of oxomolybdenum(V) complexes might be due to the very rapid substitution at the apical site.

Reaction Mechanism. The rather low activation enthalpies and large negative activation entropies of the present reactions suggest an association path of substitution. Azide ions give larger k_f's than thiocyanate ions do by 1 order of magnitude. Such a difference may reflect the facts that azide is a stronger Lewis base than thiocyanate and that both ends of the linear N_3^- can interact with vanadium(IV) as nucleophile. (All the known thiocyanato complexes of vanadium(IV) have V–N bonding). These considerations also support the participation of an associative rate-determining step. Since the trans side of the oxo ligand is blocked by the tertiary amine and the three chelate rings of $pmida^{2-}$, the nucleophilic interaction of NCS^- or N_3^- would come from the front side of the oxo ligand. Little influence of the ionic strength upon the rate may reflect the absence of electric charge of the substrate complex $[VO(pmida)H_2O]$.

The difference in the aquation rate constants k_b's between the thiocyanato and the azido complex is much smaller. If the ease of break of the V–N bond were responsible for determining the rate of aquation, the more basic azide would be liberated with much more difficulty, and the difference should be larger. Thus an associative interaction of a water molecule in the second coordination sphere of $[VO(pmida)X]^-$ seems to be responsible for the rate-determining step of the aquation. Slightly larger k_b for the azido complex than that for the thiocyanato complex may be accounted for by considering that the water molecule loosely bound in the second sphere can make a hydrogen bonding with a basic azido ligand so that the effective basicity of the incoming water molecule is increased to some extent. On the basis of all these observations and considerations, we conclude that reaction 1 proceeds via an associative interchange mechanism in both directions.

In the pH region from 1.3 to 2.0 thiocyanate ions react with $[VO(pmida)H_2O]$ to give the same product $[VO(pmida)NCS]^-$, at a greater rate than above pH 4.2. The acid hydrolysis of $[VO(pmida)H_2O]$ to lose the pmida ligand is observed below pH 0.8, and a marked acid catalysis is noticed. At pH 1.3–2.0 one of the acetate branches of $pmida^{2-}$ may be protonated (although not necessarily dissociated), and the overall positive charge may facilitate the nucleophilic attack of anions to increase the observed rate constants.

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Registry No. $VO(pmida)H_2O$, 67904-95-4; NCS^-, 302-04-5; N_3^-, 14343-69-2; $NH_4[VO(pmida)(NCS)]$, 67938-35-6.

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