$d_{yz})^2(d_{z^2})^1$, which should not contribute to the EFG. The alternative ^4E orbital doublet configuration $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$ should produce a large negative contribution to the EFG. Both of these predictions ignore covalency. In iron(II) phthalocyanine, a square-planar $S = 1$ complex, the contribution to ΔE_Q from covalency has been estimated to be +3.8 mm s^{-1}.[28] It would require a slightly smaller covalency correction (~+3.5 mm s^{-1}) to account for the observed splittings in **1** and **2** if the ground state is the $|xy\rangle$ singlet.[29] The $|xz, yz\rangle$ ground state would seem to require an impossibly large covalency correction to give the observed ΔE_Q values.

Mössbauer spectra of high-spin iron(III) porphyrin complexes invariably show asymmetric line broadening at temperature above 4.2 K owing to slow spin relaxation in higher lying Kramers doublets.[10,20,30] The absence of any relaxation broadening in the zero-field spectra of **1** and **2** suggests fast spin relaxation within both $|\pm^1/_2\rangle$ and $|\pm^3/_2\rangle$ doublets, since it is unlikely that the crystal field splitting parameter D is so large that only the $|\pm^1/_2\rangle$ doublet is occupied at 295 K.[31]

Although the zero-field spectra of **1** and **2** are quite similar, Mössbauer measurements at 4.2 K in applied magnetic fields of 5.0 T revealed pronounced differences. The spectrum of **1** under these conditions approximated to the triplet–doublet pattern typical of diamagnetic complexes, with an effective magnetic field at the ^{57}Fe nucleus of about 3.4 T (estimated from the triplet splitting). This suggests that electronic spin relaxation in **1** is very fast even in the presence of a large applied field. On the other hand, **2** gave a complex but well-resolved hyperfine-split pattern with an effective field, estimated from the total splitting of the spectrum, of about 24 T. (This is similar to the hyperfine field of 27 T found for a tetraaza iron(III) complex with $S = {}^3/_2$ ground state.[7]) Thus, although in zero field at 4.2 K spin relaxation in **2** is fast compared to the nuclear precession frequency, it is nevertheless slow enough that an applied field of 5.0 T induces a large magnetization. These results appear to implicate spin–lattice rather than spin–spin relaxation as the dominant relaxation mechanism in these complexes, since the mean Fe–Fe separation in **2** is probably a bit less than in **1** (certainly no greater), and this would tend to make spin–spin relaxation faster in **2** rather than slower. This is another indication of significant structural differences between the two complexes.

Attempts to obtain EPR spectra have thus far been hampered by the very fast electronic relaxation. No signal was observed at 295 K for a polycrystalline sample of **2**, and even at 78 K the signals were extremely broad (~500–600 G) so that no accurate assignments could be made. However, the signals were centered at g values of approximately 2 and 4, consistent with a quartet ground state. We plan to carry out single-crystal EPR measurements at 4.2 K in an effort to obtain g values for the complexes.

It should be possible to prepare further examples of $S = {}^3/_2$ iron porphyrins using other weak anions such as BF_4^-, PF_6^-, etc., and work in this direction is in progress.

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Potassium Hexaisothiocyanatovanadate(II). Preparation and Characterization of a New Vanadium(II) Compound

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Vanadium(II) has been scarcely investigated until now. Further knowledge on its coordination chemistry should be of interest as a counterpart to the well-known chemistry of isoelectronic chromium(III). In particular, a comparison between the two d^3 ions should be revealing under theoretical aspects. Binary complexes are desirable in this connection because their simplicity facilitates interpretation.

Until now no vanadium(II)–hexathiocyanato compound was known. The system V(II)/SCN$^-$ has been subjected to a few studies. The most detailed and recent ones[1-3] are concerned with the kinetics and thermodynamics of formation of $[V(NCS)(H_2O)_5]^+$. Polarographic[4-6] and extraction studies[7] suggest the existence of further unspecified thiocyanato complexes in aqueous $V(II)/SCN^-$ solutions. In two early works, Uzumasa[8] reported a UV absorption at 350 nm for a $V(II)/SCN^-$ solution, and Bongiovanni[9] obtained deep violet and green solutions by adding HSCN or $Ba(SCN)_2$ to VCl_2 or VSO_4 in H_2O and suggested that the green color resulted from oxidation to V(III).

We succeeded for the first time in isolating a thiocyanato-vanadium(II) complex, obtaining a solid compound of composition $K_4[V(NCS)_6]\cdot C_2H_5OH$.

Experimental Section

Due to air sensitivity of V(II), working under N_2 gas and use of deoxygenated solvents were necessary.

Preparations. $VSO_4\cdot 6H_2O$ was prepared by the procedure of Brauer.[10] To obtain $K_4[V(NCS)_6]\cdot C_2H_5OH$, 2 g of $VSO_4\cdot 6H_2O$ was dissolved in a solution of 3 g of KSCN in 10 ml of H_2O. Ethanol (200 ml) was added, and the precipitated K_2SO_4 was filtered off. The filtrate was treated with 8 ml of saturated aqueous KSCN (9.7 M). The gradually forming $K_4[V(NCS)_6]\cdot C_2H_5OH$ was collected and washed with ethanol and peroxide-free ether. A 3.2-g (70%) amount of pure $K_4[V(NCS)_6]\cdot C_2H_5OH$ was obtained. Anal. Calcd: V, 8.5; K, 26.0; N, 14.0; C, 16.0; S, 32.0; H, 1.0. Found: V, 8.4; K, 26.0; N, 14.1; C, 15.7; S, 32.6; H, 0.8. The oxidation number was 2.01.

Analytical Work. C, H, N, and S have been determined by microanalytical standard methods,[11] and K was determined with sodium tetraphenylborate. For the V analysis the substance was disintegrated by treating it with concentrated HNO_3. The initially violent reaction was controlled by cooling below 10 °C and completed by heating to the boiling point. The further procedure followed the method of Treadwell[12] determining V gravimetrically as V_2O_5. Redox titration was performed iodometrically. A weighed sample of $K_4[V(NCS)_6]\cdot C_2H_5OH$ was dissolved in 2 N H_2SO_4 and treated with a known amount of 0.1 N I_2 solution, and the excess of iodine back-titrated with $Na_2S_2O_3$. We found that under these conditions V(II) is oxidized to V(III) and on quick working the slow oxidation of SCN^- can be neglected.

Apparatus. IR spectra were recorded as KBr pellets on a Perkin-Elmer SP 621; far-infrared spectra, as Nujol mulls between polyethylene foils on a Beckmann IR 11.

Raman measurements have been carried out using spinning equipment on a Coderg PH 1 spectrometer under excitation with the 15 802-cm^{-1} line of a He–Ne laser (OIP Gent) and with the 19 430-cm^{-1} line of an Ar–Kr laser (Coherent Radiation 53 MG).

UV spectra have been measured on a Leitz-Unicam SP 800. For diffuse-reflectance measurements commercial sample holders were covered with a quartz slide after filling and sealed with stopcock grease.

Magnetic measurements were performed by using polycrystalline samples at room temperature by the Faraday method.[13] Diamagnetic corrections were calculated from constants listed by Haberditzl.[13]

The EPR spectra were taken on a Bruker X-band spectrometer, Type B-ER 418. The magnetic field was determined with a proton resonance gaussmeter, and microwave frequency was measured with a Dana EiP Autohet Counter, Model 351 D.

Results and Discussion

For the preparation of potassium hexathiocyanatovanadate(II) from $VSO_4\cdot 6H_2O$ and KSCN as described in the Experimental Section a two-step reaction via a mixed aquo–thiocyanato compound was successful. Interfering hydrolysis was avoided by completing the reaction in ethanolic solution, and K_2SO_4 formed as a by-product could be easily removed.

Properties. $K_4[V(NCS)_6]\cdot C_2H_5OH$ is a deeply colored bluish green solid. Like other V(II) compounds it has considerable reducing properties and is readily oxidized by O_2. In the presence of air conversion into related V(III) compounds indicated by a change in color from green over yellow to brown-red takes place within a few minutes. The alcohol of crystallization is rather strongly bonded and cannot be removed by drying in vacuo at 50 °C for several hours.

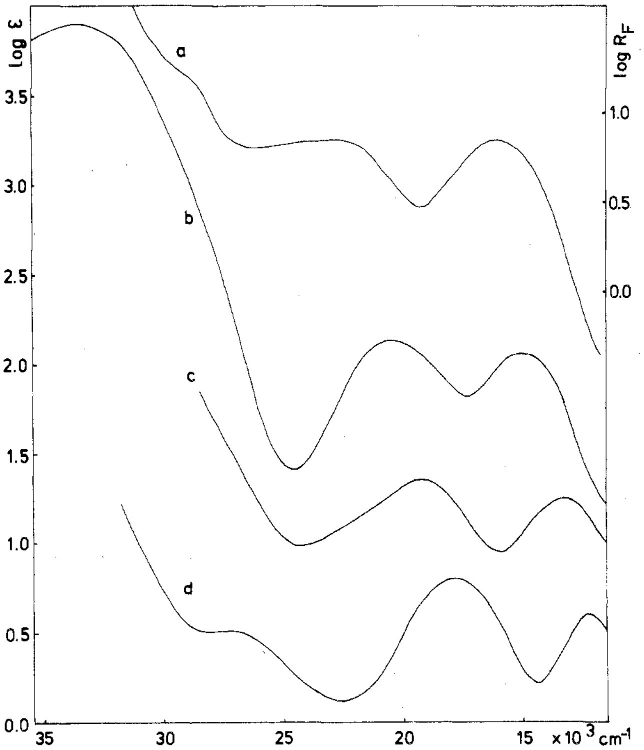

Figure 1. Electronic spectra of $K_4[V(NCS)_6]\cdot C_2H_5OH$: (a) diffuse-reflectance spectrum; ordinate calibrated in R_f values of the Kubelka–Munk function;[14] (b) spectrum in saturated aqueous KSCN solution; (c) spectrum in H_2O; (d) spectrum of $[V(H_2O)_6]^{2+}$ in 2 N H_2SO_4.

A conspicuous feature of the hexathiocyanatovanadate(II) is its kinetic labile behavior. It is illustrated by the immediate hydrolysis that occurs, when $K_4[V(NCS)_6]\cdot C_2H_5OH$ is dissolved in water leading to a violet solution. In the UV spectrum of this solution the ligand field bands occupy an intermediate position between those of the hexathiocyanato and the hexaaquo ion. Both band positions and extinction coefficients in the UV spectrum depend on the SCN^- concentration present in solution reflecting mobile equilibria involving the series of aquo–thiocyanato complexes $[V(NCS)_n(H_2O)_{6-n}]^{(n-2)-}$. Bridged polynuclear species might play some role too. Figure 1 exemplifies the observed relation.

Though the existence of mixed forms must be assumed, it has not been possible to determine separate band positions corresponding to definite compounds. Actually there will be always a mixture of different species giving rise to a pseudoband out of components whose splittings are not marked enough to be resolved. Therefore splittings resulting from symmetry lowering cannot be detected either. This is in accordance with the statements of the principle of the average environment.[15]

Even in aqueous solutions saturated in KSCN, $[V(NCS)_6]^{4-}$ may not be the predominant species. This can be inferred from the blue-violet color of these solutions and a difference of 1000 cm^{-1} in relation to the band positions of the solid in the UV spectrum (see Table III). Still NCS^- coordination appears to be preferred throughout over H_2O coordination, for only an excess of H_2O over SCN^- produces noticeable hydrolysis.

In solvents like dimethylformamide and dimethyl sulfoxide solutions are purple-red, apparently due to solvolysis. In other common solvents like ethanol, acetone, and acetonitrile $K_4[V(NCS)_6]\cdot C_2H_5OH$ is practically insoluble. Gradually, however, slow dissolution proceeds under decomposition of the complex.

Vibrational Spectra. IR, far-infrared (far-IR), and Raman-measurements have been performed between 4000 and

Table I. Vibrational Bands of $K_4[V(NCS)_6]\cdot C_2H_5OH$[a]

Wavenumber, cm^{-1}	Assignment	Origin
2107	ν_1 A_{1g} $\nu_{C\equiv N}$	Raman spectrum
781	ν_2 A_{1g} ν_{C-S}	
405	ν_7 F_{1g} $\delta_{N\equiv C-S}$	
2103 vs	ν_9 F_{1u} $\nu_{C\equiv N}$	IR spectrum
769 m	ν_{10} F_{1u} ν_{C-S}	
475 w	ν_{11} F_{1u} $\delta_{N\equiv C-S}$	
307 m	ν_{12} F_{1u} ν_{V-N}	
140 s, br	F_{1u} [$\delta_{V-N\equiv C}$, δ_{N-V-N}, lattice?]	Far-IR spectrum
155 sh		
180 sh		

[a] Ethanol bands omitted.

Table II. Ligand Field Parameters of V(II) Complexes[a]

Complex	$\Delta \equiv 10Dq$, cm^{-1}	B_{35}, cm^{-1}	Ref
$CsCaCl_3/VCl_2$[c]	7 200	610	27
$V(H_2O)_6^{2+}$	12 350	680	20
$K_4[V(NCS)_6]\cdot C_2H_5OH$	16 100	600	This work
$[V(iz)_6]Br_2$[b]	16 100	680	21
$[V(en)_3]Cl_2\cdot H_2O$	15 600	580	22
$K_4[V(CN)_6]$	22 300	484	23

[a] The compounds are arranged according to the position of ligands in the spectrochemical series. [b] iz = imidazole. [c] V(II) doped into crystals of $CsCaCl_3$.

Table III. UV Bands of $K_4[V(NCS)_6]\cdot C_2H_5OH$[a]

	Wavenumber, cm^{-1}	Extinction coeff, M^{-1} cm^{-1}	Assignment
Diffuse-	16 100		$^4A_{2g} \rightarrow {}^4T_{2g}$
reflectance	22 200		$^4A_{2g} \rightarrow {}^4T_{1g}$
spectrum	29 000		Charge transfer
Spectrum in	15 150	115	$^4A_{2g} \rightarrow {}^4T_{2g}$
satd aq	20 950	136	$^4A_{2g} \rightarrow {}^4T_{1g}$
KSCN soln	33 000	7900	Charge transfer

[a] $10Dq = 16\ 100\ cm^{-1}$; $B_{35} = 600\ cm^{-1}$; $\beta_{35} = 0.78$.

70 cm^{-1}. The results are listed in Table I. In analogy to the known hexacoordinated thiocyanato complexes an approximate octahedral symmetry can be assumed.[18] This is supported by the vibrational data. Twenty fundamentals are to be expected, of which six are IR and nine Raman active. All IR-active modes predicted to occur above 200 cm^{-1} have been found and assigned. Concerning the observed far-IR vibrations, assignment is difficult. Usually the one broad main far-IR absorption typical for all hexaisothiocyanato complexes is regarded as bearing essentially $\delta_{M-N\equiv C}$ character, while δ_{N-M-N} is supposed to fall below 50 cm^{-1}.[16] From luminescence studies on $Cr(NCS)_6^{3-}$ Flint,[17] however, recently deduced evidence in favor of an interpretation of this band as a lattice mode. Therefore lacking additional data, we prefer to leave the assignment open.

Because of the intense color of the compound the observed Raman spectrum was weak and only the three inner ligand vibrations could be detected. They are assigned and listed in Table I.

The positions of the inner ligand bands in thiocyanato complexes allow distinction between N or S coordination.[18] The inner ligand bands of $K_4[V(NCS)_6]\cdot C_2H_5OH$ furnish uniform evidence in favor of the NCS^- attached at nitrogen as in most thiocyanato complexes of the metals of the first transition series.

Furthermore the frequencies found suggest only weak bonding forces between V(II) and NCS^-. In an N-bonded NCS^- complex the relative contribution of the two canonical structures

$$:N\equiv C-\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:^- \leftrightarrow {}^-\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}=C=\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}$$

to the real electronic state of the ligand depends on the strength of the bonding interaction between NCS^- and the central atom, a strong interaction increasing the significance of the right canonical structure. Therefore high C≡N and low C—S frequencies as in the case of $V(NCS)_6^{4-}$ are indicative of a weak V—N bond. The low-lying V—N stretching mode is consistent with this interpretation.

Ligand Field Parameters. The observed VIS and UV spectra can be easily interpreted on the basis of the ligand field terms of a hexacoordinated octahedral d^3 ion. The energy of the first transition yields $\Delta \equiv 10Dq = 16\,100\ cm^{-1}$, and from the energy separation between the two first bands the Racah parameter B_{35} can be estimated to 600 cm^{-1}.[19]

Table II presents these values together with the ligand field parameters of other binary V(II) complexes. As can be seen the obtained values for $K_4[V(NCS)_6]\cdot C_2H_5OH$ correspond fairly well to the position of SCN^- in the spectrochemical[15,20] and nephelauxetic[15,20] series. Especially the relationship between the N-coordinated compounds is obvious.

The resulting nephelauxetic ratio $\beta_{35} = 0.78$ confirms the early position of V(II) in the nephelauxetic series of central ions. Moreover, considering the hexathiocyanato complexes of Mn^{2+} and Ni^{2+}, which are neighbors of V(II) in the nephelauxetic series of cations as given by Lever,[20] this value fits well between $\beta_{35} = 0.91$ for $Mn(NCS)_6^{4-}$ [24] and $\beta_{35} = 0.65$ for $Ni(NCS)_6^{4-}$.[25]

The third spin-allowed transition should occur at about 33 000 cm^{-1}, but it is obscured by charge-transfer absorption in this region. All observed UV bands are listed in Table III.

Magnetic Measurements and EPR Spectra. The experimentally found magnetic moment of 3.83 μ_B is in agreement with the expected spin only value of 3.87 μ_B for three unpaired electrons.

The EPR spectrum of a polycrystalline sample showed a symmetrical signal at $g = 2.014$ (line width 207 G). In saturated aqueous KSCN an eight-line spectrum was observed at $g = 1.985$ with an isotropic hyperfine splitting $A_{iso} = 78.6$ G. The found high coupling with the V core and the absence of superhyperfine coupling with the ^{14}N core of NCS^- both indicate that interaction between the t_{2g} electrons of V and antibonding π orbitals of the ligands must be weak,[26] i.e., that metal to ligand back-bonding is not important.

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Properties of the Reaction Intermediate Formed during Oxidation of Vanadium(IV) by Permanganate Ion

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While studying the kinetics of the oxidation of the vanadium(IV) ion, VO^{2+}, by the permanganate ion, MnO_4^-, in perchlorate media by spectrophotometric stopped-flow techniques, the formation of a reaction intermediate absorbing near 410 nm with an absorption coefficient of about 160 M^{-1} cm^{-1} was observed.[1] In an attempt to learn more about this intermediate, the kinetics of its reaction with VO^{2+} were studied in detail.

Experimental Section

The preparation of the reactants and experimental methods of determining the kinetics have been previously described.[1] The kinetics were studied at 410 nm, the absorption maximum of the intermediate. The pseudo-first-order rate constants were determined graphically from plots of log (absorbance) vs. time.

Results and Discussion

The stopped-flow traces obtained at 410 nm show a rapid increase in absorbance followed by a slow decay to an absorbance characteristic of products (Figure 1). The absorbance reaches a maximum value at a reaction time labeled t_{max}. Using initial rate data from λ 410 nm, it was shown that the rate of formation of the intermediate (reaction I, Figure 2) is about equal to the rate of disappearance of MnO_4^- obtained at 526 nm (k_1 = 105 M^{-1} s^{-1}, $[H^+] = \mu = 1.00$ M, T = 25.0 °C). No attempt was made to study the formation reaction in detail at 410 nm because of the low quality of the traces at the beginning of the reaction. Under pseudo-first-order reaction conditions, plots of log ($A_t - A_\infty$) vs. time indicated that the decay of the intermediate consisted of two simultaneous reactions; a faster reaction, reaction II, and a slower process, reaction III, Figure 2. The kinetics of reaction II were determined from log (absorbance ($A_t - A_\infty$)) values vs. time plots by extrapolating the straight-line portion of reaction III back to t_{max} and subtracting the absorbance value from the experimental ($A_t - A_\infty$) absorbance values at each time interval. The rate constants obtained for reactions II and III are shown in Table I.

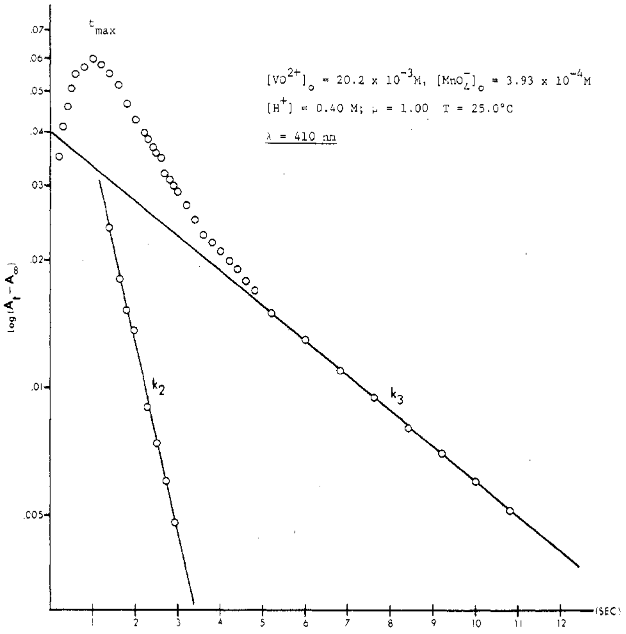

Figure 1. Plot of log ($A_t - A_\infty$) vs. time at λ 410 nm.

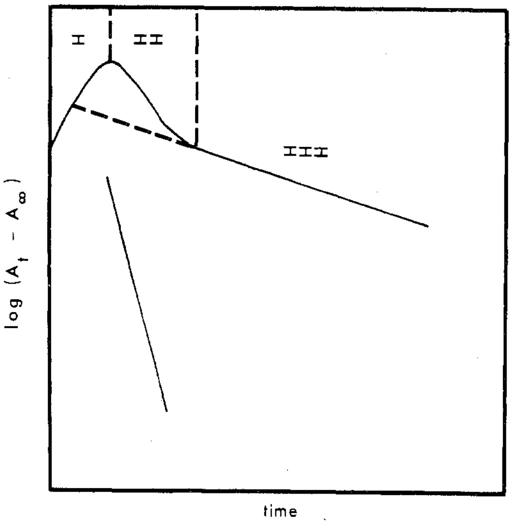

Figure 2. Representative diagrams of kinetic processes at 410 nm.

The near constancy of the second-order rate constant for the more rapid process indicates that this reaction is first order in each reactant. The second-order rate constants for reaction II were found to be independent of H^+ concentration (Table II) and were unaffected by addition of vanadium(V), VO_2^+.

The rate constant of reaction III was determined from the straight-line portion of a log (absorbance) vs. time plot at long reaction times and the data obtained are summarized in Table I. This process was found to be a third-order reaction with a second-order dependence on VO^{2+} and the rate was independent of added VO_2^+. Over a hydrogen ion concentration range of 0.10–1.00 M, the reaction was found to be inversely dependent on the H^+ concentration (Table II). This relationship is of the form $k_3 = k_{30} + k_{3H}(1/[H^+])$ and a least-squares treatment of these data yields a value of 223 M^{-2} s^{-1} for k_{30} and 150 M^{-1} s^{-1} for k_{3H}.

Although previous studies of the oxidation of VO^{2+} by MnO_4^- in $HClO_4$ with excess MnO_4^{2-} or in H_2SO_4[3] were

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