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Preparation and Properties of Vanadium (III) Complexes with L-Cysteinate and D-Penicillaminate

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The coordination geometry of bis(L-cysteinato) vanadate(III) was determined by single-crystal X-ray crystallography. The vanadium(III) center coordinates octahedrally two tridentate L-cysteinate ligands via *trans* S, *cis* O, and *cis* N atoms. Bis(D-penicillaminato) vanadate(III) was characterized so as to adopt a similar *trans*(S) configuration based on its electronic spectrum. The coordination chemistry of the two complexes in solution was examined on the basis of the ligand-to-metal charge-transfer band. One of the two V(III)–S bonds of each complex is easily cleaved in solution.

Certain species of ascidians have been known to accumulate vanadium selectively and intensively. Michibata et al.[1)] have shown that the concentration of vanadium in the blood cells of Ascidia gemmata is as high as 150 mmol, exceeding 10^6-times that in sea water. They have also suggested that the vanadium ion in blood cells in mainly in the III oxidation state. We consider the puzzling role of the high concentration of vanadium(III) ions in ascidians, and, the coordination chemistry of vanadium(III) complexes with amino acids (fundamental biochemical compounds) to be of importance. Vanadium(III) complexes with some amino acids, such as aspartic and glutamic acids as well as methionine,[2)] glycine,[3)] serine, threonine, and leucine,[4)] have been reported without good characterization. The difficulty to prepare vanadium(III) complexes with amino acids mainly results from the fact that aminoacidato vanadium(III) complexes are generally hydrolyzed in the 4—7 pH range. Konstantatos et al.,[5)] however, have pointed out that the vanadium(III) complex with cysteine is moderately stable in neutral, and even in weakly alkaline solutions, though they did not isolate the complex. We describe here the preparation, structure, and some properties of vanadium(III) complexes with L-cysteinate ($^-SCH_2CH(NH_2)COO^-$; L-cys) and D-penicillaminate ($^-SC(CH_3)_2CH(NH_2)COO^-$; D-pen).

Experimental

General Procedure. All manipulation was carried out under an argon atmosphere using standard Schlenck techniques or in a nitrogen-filled dry box. Argon gas was purified by passage through a gas-purification column (Gasclean, Nikka Seiko Co.) before use.

Na[V^{III}(L-cys)$_2$]·2H$_2$O. Vanadium(III) chloride (0.79 g, 5 mmol) and L-cysteine monohydrochloride monohydrate (2.63 g, 15 mmol) were dissolved in 7 cm^3 of deaerated and argon-saturated water. This initial solution was deep green. The pH of the solution was increased by the addition of 3 mol dm^{-3} NaOH with stirring. At pH 5—6, a geen-brown precipitate appeared. After stirring for 30 min at pH 7, most of the precipitate redissolved, giving a brown solution. The undissolved material was filtered off. After the volume of the filtrate was reduced to half in vacuo, 2 cm^3 of dioxane was added. Allowing the solution to stand in a refrigerator for several hours yielded brown columnar crystals. Crystals of appropriate size for X-ray crystallography were obtained by slow evaporation over $CaCl_2$. Yield; 0.50 g. Found: C, 20.78; H, 4.03; N, 8.03%. Calcd for $C_6H_{14}N_2O_6S_2NaV$: C, 20.71; H, 4.02; N, 8.05%.

K[V^{III}(D-pen)$_2$]·2H$_2$O. This compound was prepared in the manner similar as that of Na[V^{III}(L-cys)$_2$]·2H$_2$O using D-penicillamine (1.4 g, 15 mmol) and KOH. The volume of the reaction mixture was reduced by half. The solution was allowed to stand in a refrigerator for several hours, after which fine yellow needles appeared. Yield; 0.57 g. Found: C, 28.55; H, 5.10; N, 6.56%. Calcd for $C_{10}H_{22}N_2O_6S_2KV$: C, 28.57; H, 5.29; N, 6.67%.

Measurements. UV-vis spectra were obtained using a JASCO Ubest-50 spectrophotometer. Diffuse reflectance spectra were obtained for complexes diluted with MgO (1 : 1 weight ratio). Electrochemical measurements were carried out with a CV-1B apparatus [Bioanalytical Systems, Inc. (BAS)] using a platinum-disk working electrode (BAS, PTE). An aqueous Ag/AgCl/NaCl (3 mol dm^{-3}) electrode (BAS, RE-1) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22°C in *N,N*-dimethylformamide (DMF) with 0.1 mol dm^{-3} $[(C_2H_5)_4N][ClO_4]$ as the supporting electrolyte and complex concentrations of 1.0 mmol dm^{-3}.

Crystallography. X-Ray Data Collection. Unit cell parameters and intensity data for the single crystal (ca. 0.20×0.25×0.30 mm^3) were measured on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073Å). The unit-cell parameters were determined by least-squares refinements from 25 reflections with $16<2\theta<20°$. Systematic absences led to space groups of $P3_1$ (No. 144), $P3_2$ (No. 145), $P3_112$ (No. 151), $P3_121$ (No. 152), $P3_212$ (No. 151), and $P3_221$ (No. 154). Of these groups, space-group $P3_1$ was determined based on a solution of the structure and the absolute configuration of the asymmetric carbon atom in L-cysteinate. Crystal data: $C_6H_{14}N_2O_6S_2NaV$, M=348.25, trigonal, space group $P3_1$ (No. 144), a=18.620(2) Å, c=9.604(1) Å, U=2883.8(8) Å^3

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j.$$

Atom	x	y	z	B_{eq}
V1	0.85698(8)	0.72925(9)	0.280	1.39(3)
S11	0.9496(2)	0.7218(2)	0.4482(3)	2.41(5)
S12	0.7517(1)	0.7057(2)	0.1141(2)	2.14(5)
O11	0.8474(4)	0.8149(4)	0.4007(7)	1.7(1)
O12	0.8285(5)	0.8372(5)	0.6217(8)	3.7(2)
O13	0.9443(4)	0.8117(4)	0.1521(7)	2.2(1)
O14	0.9797(7)	0.8323(7)	−0.0727(8)	4.8(2)
N11	0.7672(5)	0.6517(5)	0.4307(8)	1.9(2)
N12	0.8780(6)	0.6530(5)	0.1400(9)	2.7(2)
C11	0.8254(6)	0.7882(6)	0.5259(9)	2.6(2)
C12	0.8032(6)	0.7028(7)	0.5573(8)	2.0(2)
C13	0.8800(8)	0.6997(8)	0.598(1)	3.0(3)
C14	0.9437(6)	0.7870(7)	0.026(1)	2.3(2)
C15	0.8836(6)	0.6961(7)	0.0035(9)	2.4(2)
C16	0.7987(6)	0.6816(9)	−0.0320(9)	3.4(3)
V2	0.5971(1)	0.7993(1)	0.6234(1)	1.71(3)
S21	0.6268(2)	0.9079(2)	0.7856(2)	2.08(5)
S22	0.6035(2)	0.7056(2)	0.4597(3)	3.25(6)
O21	0.5077(5)	0.7179(5)	0.7546(7)	2.6(2)
O22	0.4856(7)	0.6930(7)	0.979(1)	4.4(3)
O23	0.5181(4)	0.8139(4)	0.4964(6)	1.8(1)
O24	0.5012(6)	0.8309(6)	0.2703(8)	3.7(2)
N21	0.6653(6)	0.7696(5)	0.7694(9)	2.2(2)
N22	0.6797(5)	0.8891(7)	0.4735(8)	2.6(2)
C21	0.5317(7)	0.7206(7)	0.882(1)	2.5(2)
C22	0.6244(7)	0.7719(7)	0.9030(9)	2.4(2)
C23	0.6482(7)	0.8607(7)	0.937(1)	2.5(2)
C24	0.5449(6)	0.8333(6)	0.3684(9)	1.9(2)
C25	0.6318(7)	0.8548(6)	0.3431(9)	2.2(2)
C26	0.6342(9)	0.7750(8)	0.306(1)	3.9(3)
V3	0.93820(9)	0.47629(9)	0.6113(2)	1.42(3)
S31	0.9590(2)	0.5811(2)	0.7770(3)	2.61(5)
S32	0.9479(2)	0.3876(1)	0.4421(2)	2.06(5)
O31	0.8593(4)	0.3882(5)	0.7389(6)	2.2(1)
O32	0.8466(5)	0.3550(5)	0.9679(8)	2.9(2)
O33	0.8444(5)	0.4778(5)	0.5054(7)	3.7(2)
O34	0.8103(6)	0.4940(7)	0.2940(9)	4.1(2)
N31	1.0198(6)	0.4625(5)	0.7482(7)	2.0(2)
N32	1.0034(5)	0.5634(5)	0.4535(7)	1.5(2)
C31	0.8865(6)	0.3912(6)	0.8648(9)	2.0(2)
C32	0.9793(6)	0.4535(6)	0.8837(8)	1.9(2)
C33	0.990(1)	0.5368(7)	0.921(1)	3.6(3)
C34	0.8637(7)	0.5012(7)	0.376(1)	2.5(2)
C35	0.9516(6)	0.5283(7)	0.3316(9)	2.2(2)
C36	0.9564(8)	0.4508(7)	0.2883(9)	3.0(2)
Na1	0.7317(3)	0.3670(4)	0.6260(5)	3.4(1)
Na2	0.9659(4)	0.9349(4)	0.2753(6)	4.0(1)
Na3	0.3886(4)	0.7399(4)	0.1033(6)	4.5(2)
O1W	0.6434(6)	0.3652(6)	0.4565(9)	4.7(2)
O2W	0.1639(9)	0.6022(8)	0.251(1)	5.9(4)
O3W	0.859(1)	0.9317(8)	0.111(1)	6.3(4)
O4W	0.9811(9)	1.038(1)	0.440(1)	6.5(4)
O5W	0.3668(8)	0.6419(7)	0.279(1)	4.7(3)
O6W	0.7359(7)	0.4748(7)	0.793(1)	4.3(3)

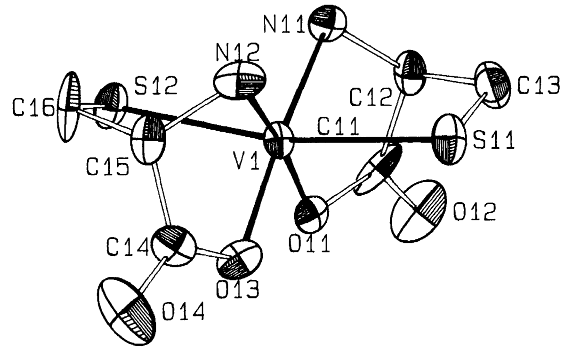


Fig. 1. Perspective drawing of [V^{III}(L-cys)$_2$]$^-$ (V(1) species) with the numbering scheme of atoms.

Table 2. Bond Distances (Å) and Angles (degree) of Interest in Na[V^{III} (L-cys)$_2$]·2H$_2$O and Na[Cr^{III}(L-cys)$_2$]·2H$_2$O$^{a)}$

	Na[V^{III}(L-cys)$_2$]	Na[Cr^{III}(L-cys)$_2$]
M–S	2.395	2.416
M–N	2.132	2.062
M–O	2.022	1.981
S–C	1.84	1.829
C–C(S)	1.53	1.521
C–C(O)	1.50	1.518
C–N	1.48	1.484
C–O	1.30	1.291
C=O	1.22	1.231
S–M–O	90.5	89.33
S–M–N	81.6	82.83
O–M–N	77.7	79.59
S–M–S′	167.4	174.6
S–M–O′	98.1	94.33
S–M–N′	91.2	93.95
O–M–O′	94.4	94.15
N–M–N′	110.3	106.8
O–M–N′	171.9	173.13

a) Ref. 8.

$Z=9$, $D_c=1.80$ g cm^{-3}, $F(000)=1602$, $\mu=11.1$ cm^{-1}, and room temperature.

The intensity data were collected using the ω–2θ scan mode up to $2\theta=56°$ ($h,k\leq24$ and $l\leq12$) with a scan width $(0.7+0.350\tan\theta)°$; the scan rate was varied from 1 to 5° min^{-1} (on ω). As a check on the crystal and electronic stability, three representative reflections were measured every 120 min of X-ray exposure time, and a linear decay correction was applied (correction factor on I, 1.000 to 1.006). The orientation (for the same three reflections) was monitored after every 200th scan. The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of psi-scans was applied (min. and max. transmission factors, 0.95 to 1.00). A total of 4491 independent reflections with $F_o>5\sigma(F_o)$ of the unique 4800 reflections were considered, as "observed" and used for a structure determination.

Determination of Crystal Structure. The vanadium and donor atom positions were determined by direct methods. The remaining non-hydrogen atom positions were found by successive difference Fourier techniques to give a

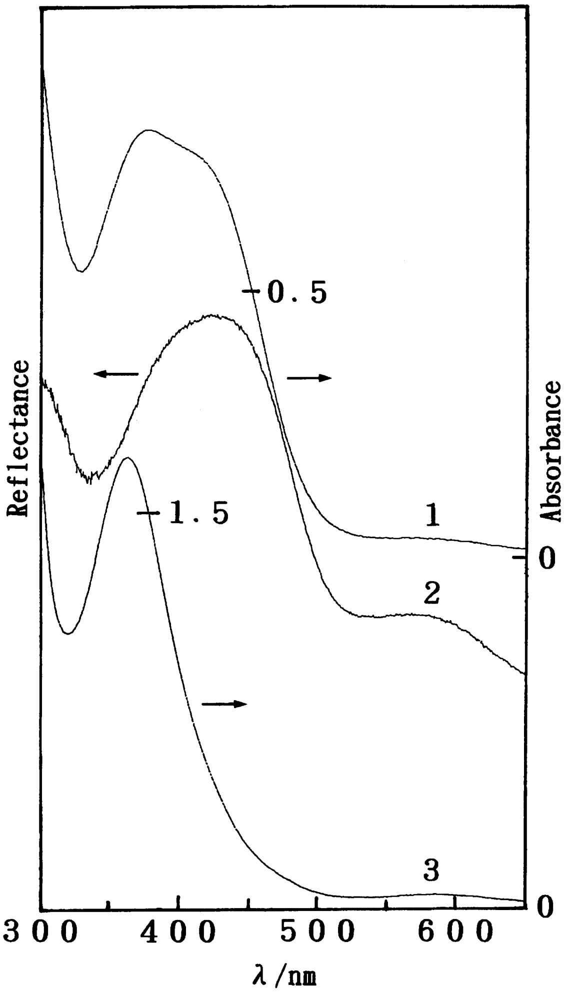


Fig. 2. Electronic absorption spectra and diffuse reflectance spectrum of bis(L-cysteinato)vanadate (III). (1) Absorption spectrum in water: concentration, [complex]=5.0×1.0^{-3} mol dm^{-3}, [cys]=0.12 mol dm^{-3}, 1 mm cell; (2) diffuse reflectance spectrum (complex : MgO = 1 : 1); (3) absorption spectrum in DMF: concentration, [complex] = 1.0×10^{-3} mol dm^{-3}, 1 cm cell.

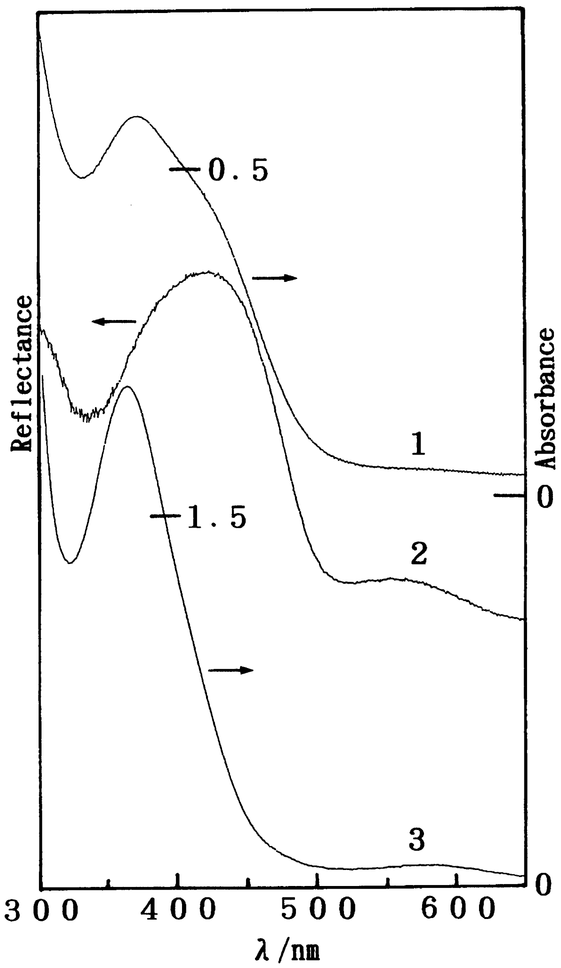


Fig. 3. Electronic absorption spectra and diffuse reflectance spectrum of bis(D-penicillaminato)vanadate(III) (1) absorption spectrum in water: concentration, [complex] = 5.0×10^{-3} mol dm^{-3}, 1 mm cell; (2) diffuse reflectance spectrum (complex : MgO = 1 : 1); (3) absorption spectrum in DMF: concentration, [complex]=1.0×10^{-3} mol dm^{-3}, 1 cm cell.

trial structure. The structure was refined by a full-matrix least-squares process on F using anisotropic thermal parameters for the non-hydrogen atoms and their corrections for anomalous dispersion. The hydrogen atoms were not included in the calculation. The final refinement gave R=0.092, R_w=0.083 [$w= 4F_o^2/\sigma^2(F_o)^2$], and $\Delta_{\max}$=0.02σ. The final difference Fourier synthesis ($\Delta\rho_{\max}$) indicated no significant peaks larger than 1.0 eA^{-3} (except some peaks at around the V3, S31, O1W atoms). All of the calculations were performed on a VAX computer using the crystallographic package of MOLEN.[6] The atomic positional parameters are given in Table 1.[7]

Results and Discussion

Solid State Structure of Na[V^{III}(L-cys)$_2$]·2H$_2$O. The solid state structure of Na[V^{III}(L-cys)$_2$] was determined by X-ray crystallography. There are three crystallographically independent complex anions in a unit cell. Each complex anion has very similar geometrical parameters to each other. Figure 1 shows a perspective view of the complex anion (**1**). The complex anion comprises a vanadium(III) center and two L-cysteinate ligands, being tridentate via *trans* S atoms and *cis* O and N atoms.

The bond lengths and angles of interest are compared with those found for *trans(S)*-[Cr^{III}(L-cys)$_2$]$^{-}$[8] in Table 2. The bond lengths in the present vanadium(III) complex correlate well to the corresponding lengths in the chromium(III) complex. The long Cr–S bond lengths have been attributed to the trans influence of the coordinated S atoms. This is also the case for the present vanadium(III) complex.

Solid State Structure of K[V^{III}(D-pen)$_2$]·2H$_2$O. The coordination geometry of [V^{III}(D-pen)$_2$]$^-$ could not

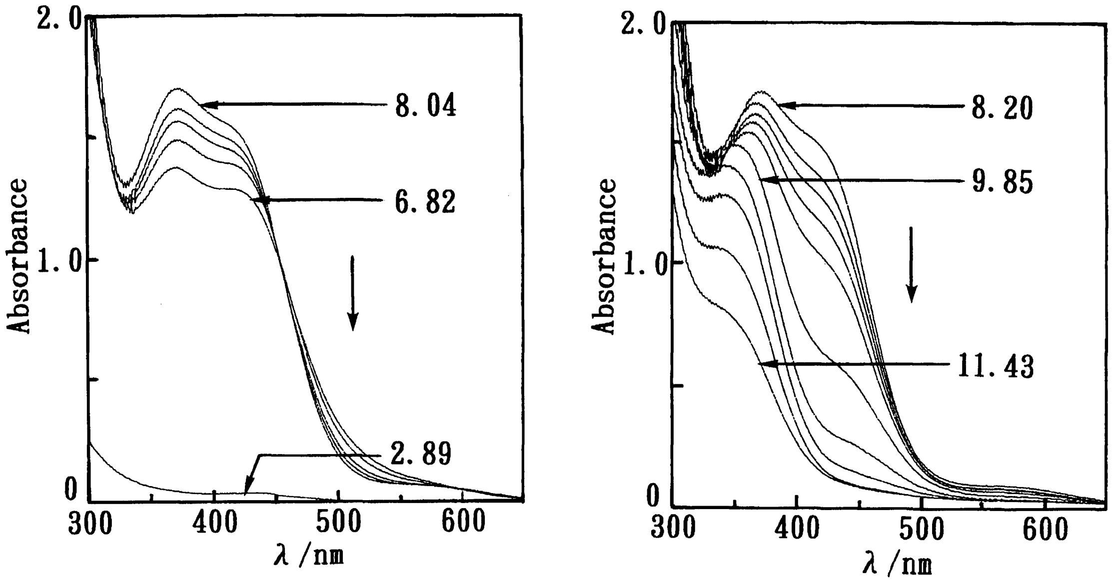
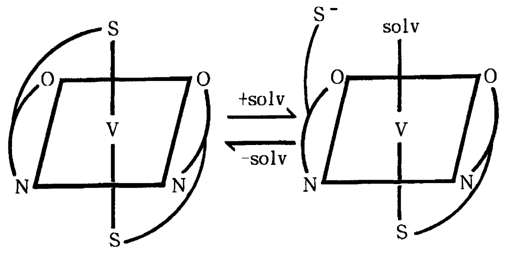


Fig. 4. pH dependence of the electronic absorption spectra of bis(L-cysteinato)vanadate (III): concentration, [complex]$=9.0\times10^{-4}$ mol dm^{-3}, [cys]$=5.0\times10^{-2}$ mol dm^{-3}: left figure, from top to down, pH=8.04, 7.83, 7.44, 7.23, 6.82, 2.89, and right figure, from top to down, pH=8.20, 8.59, 8.81, 9.00, 9.22, 9.85, 10.42, 10.82, 11.25, 11.43.



Scheme 1.

be determined crystallographically, since the complex gave very fine needles which were not appropriate for a single-crystal X-ray analysis. The coordination geometry was thus determined on the basis of its UV-vis spectrum. Figures 2 and 3 show the diffuse reflectance spectra of Na[V^{III}(L-cys)$_2$] and K[V^{III}(D-pen)$_2$], respectively. The band at 580 nm (17200 cm^{-1}) of Na[V^{III}(L-cys)$_2$] and the band at 556 nm (18000 cm^{-1}) of K-[V^{III}(D-pen)$_2$] can be assigned to d–d transitions. The intense bands at 420 nm (23800 cm^{-1}) of Na[V^{III}(L-cys)$_2$] and at 423 nm (23600 cm^{-1}) of K[V^{III}(D-pen)$_2$] are assignable to the ligand-to-metal charge-transfer (LMCT) transitions of the V(III)–S bonds based on their intensities. The spectral characteristics of K-[V^{III}(D-pen)$_2$] correspond well to those of Na[V^{III}(L-cys)$_2$] over the entire UV-vis region, indicating that K-[V^{III}(D-pen)$_2$] also has a *trans(S)* configuration.

Structure in Solution. The structure of the vanadium(III) complex in solution might differ from that in the solid state, due to the substitution lability of vanadium(III) complexes. We examined the coordination chemistry of the present complexes in solution based on their UV-vis spectra.

Figure 2 shows the absorption spectrum of Na[V^{III}(L-cys)$_2$] in an aqueous solution. The absorption spectrum was obtained in the presence of excess free L-cysteinate. When free cysteinate is absent and the concentration of the complex solution is less than 6×10^{-2} mol dm^{-3}, the solution gives a precipitate probably due to hydrolysis. The LMCT-band contour observed for the aqueous complex solution consists of the two LMCT bands at ca. 24000 and 26700 cm^{-1}. The lower energy component of these two bands corresponds in position to the maximum observed for the solid sample. In DMF, on the other hand, the cysteinato complex exhibits only one CT band at 27500 cm^{-1} (see Fig. 2). This absorption maximum shows a good correlation to the higher energy component observed for the aqueous solultion. These facts indicate that two species are equilibrated in aqueous solution. The cleavage of one of the two V(III)–S bonds, as shown in Scheme 1, would most likely occur in solution, since the V(III)–S bonds are weakened by a strong trans influence of the coordinated thiolato groups, as detected in the crystal structure of Na[V^{III}(L-cys)$_2$]. The higher energy CT band is thus assignable to that for a complex in which one cysteinato ligand is coordinated in a tridentate, and the other in a didentate. The absorption spectrum of the DMF solution suggests that [V^{III}(L-cys-*N,O,S*) (L-sys-*N,O*) (dmf)] is a dominant species in this media. This assignment is consistent with the above discussion. Since DMF has a larger donor number than does water, it is reasonably expected that one of the coordinated thiolato groups is substituted almost completely by a solvent molecule in DMF.

Bis(D-penicillaminato)vanadate(III) in an aqueous solution is more stable than the cysteinato complex, since the penicillaminato complex does not give any pre-

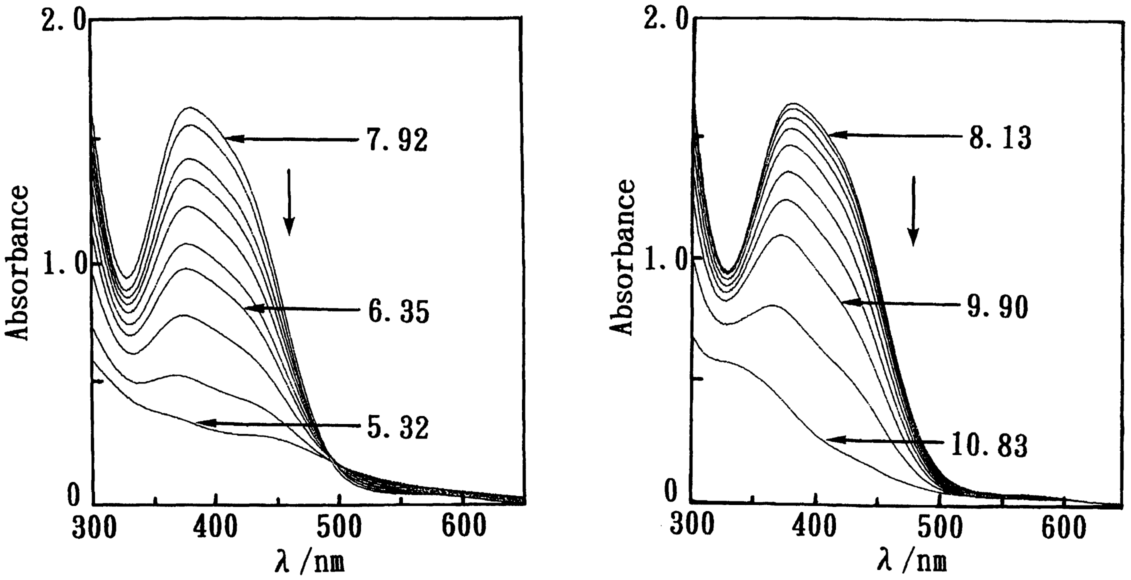
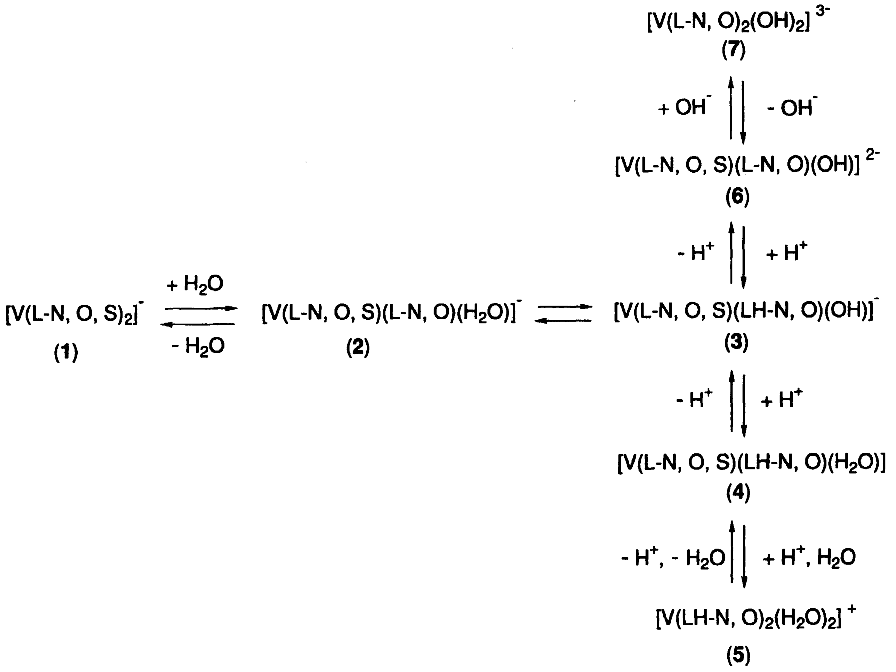


Fig. 5. pH dependence of the electronic absorption spectra of bis(D-penicillaminato)vanadate(III): concentration, [complex]=1.0×10^{-3} mol dm^{-3}: left figure, from top to down: pH=7.92, 7.52, 7.21, 6.95, 6.76, 6.61, 6.35, 6.08, 5.72, 5.32, and right figure, from top to down; pH=8.13, 8.45, 8.73, 8.92. 9.14, 9.50, 9.68, 9.90, 10.00, 10.83.



Scheme 2.

cipitate, even when a free ligand is absent. The absorption spectra of the penicillaminato complex are shown in Fig. 3. This complex also shows two CT bands at ca. 24000 and 26800 cm^{-1} in aqueous solution and one CT band at 27500 cm^{-1} in DMF. Again, the lower energy component of the solution spectrum correlates well to the band observed for the solid sample, and the higher energy band to the band observed for the DMF solution. Equilibrium simlar to that for the cysteinato complex is also expected for the penicillaminato complex in aqueous solution.

In general, vanadium(III) complexes with amino acids are easily hydrolyzed in acidic and alkaline aqueous solutions. The absorption spectra of the cysteinato and penicillaminato complexes as a function of the pH were measured in order to investigate the stability of the complexes in acidic and basic media. Figures 4 and 5 show the UV-vis spectra of the cysteinato and penicillaminato complexes, respectively, as a function of pH. The observed pH dependence of the absorption spectra of the L-cys and D-pen complexes can be interpreted in terms of the equilibria shown in Scheme 2. In this

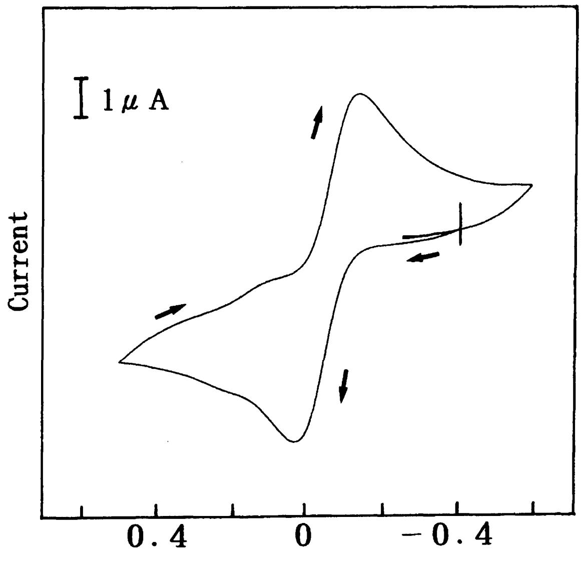


Fig. 6. Cyclic voltammogram of Na[V^{III}(L-cys)$_2$] in DMF; scan rate=50 mV s^{-1}.

Scheme, L stands for L-cys^{2-} or D-pen^{2-} and LH for the ligand of which the thiolate group is protonated. Neither system showed any rigorous isosbestic points, though below pH 8 some aggregation of the absorption spectra was noticed at around 450 nm for the V^{III}–L-cys system and at around 490 nm for the V^{III}–D-pen system. Considering the pK_a for the thiol group (10.36 for L-cysH$_2$ and 10.46 for D-penH$_2$[9]) and the pK_a of a water molecule coordinated to the V(III) center (6.2 for V(III)–nta complex[10]) it is expected that **1**, **3**, and **4** are the major species in the neutral pH region. The decrease in absorbance in the CT region observed for both systems along with increasing the proton or hydroxide ion concentration can be ascribed to the formation of the diaqua (**5**) or dihydroxo (**7**) species, which has no thiolato coordination. The shoulder at ca. 350 nm observed for both systems in a solution of pH 11 may be due to the dihydroxo species, since a similar shoulder was observed for the V(III)–nta complex in a high pH region.[11] Konstantatos et al.[5] examined the number of protons released by complex formation between V(III) and cysteine. They found that the number of the released protons increased from 1 (pH 2.3) to 4.4 (pH 8) monotonously without any flat regions. A similar behavior can be reasonably expected for the V(III)–D-pen system. The continuous decrease of the absorbance in the CT region with decreasing pH of the solution observed here is consistent with the result obtained by Konstantatos et al.

In the pH region of 3—6 for the V (III)–L-cys system, a green-brown precipitate appeared. Below pH 3, although the precipitate dissolved again, the color of the solution turned green. The LMCT band was not observed in this pH region, indicating that the thiolato group of the cysteinato ligand is not coordinated at all to the vanadium (III) center. On the other hand, the penicillaminato complex does not give any precipitate in acidic solutions. These facts indicate the higher stability of the penicillaminato complex in solution compared with that of the cysteinato complex. The stability of the penicillaminato complex may be attributed to an increase in the electron density on the S atoms resulted from the electron-donating ability of CH_3 substituents.

Electrochemical experiments were performed in 0.1 mol dm^{-3} [$(C_2H_5)_4N$]ClO_4/DMF at a platinum-disk electrode. As shown in Fig. 6, the cyclic voltammogram of the D-pen complex initiated at −0.4 V (vs. Ag/AgCl) with a positive potential scan yields an oxidation wave at +0.03 V and a coupled reduction wave at −0.14 V. Taking into account the spectroscopic results, the quasi-reversible wave at $E_{1/2}=-0.05$ V ($i_{pa}/i_{pc}=0.92$) can be assigned as the redox couple corresponding to [V^{IV}(D-pen-*N,O,S*) (D-pen-*N,O*) (dmf)]/[V^{III} (D-pen-*N,O,S*) (D-pen-*N,O*) (dmf)]$^-$. The oxidation of V(III) to V(IV) is usually irreversible, since the oxidation of V(III) typically produces an oxovanadium, vanadyl, species.[12] In this respect it is of interest whether the present D-pen complex was reversibly oxidized to produce a species with no gross structural change, i. e., a non-oxo or bare V(IV) species, on the cyclic voltammetric time scale. A very weak redox couple at approximately +0.16 V is probably due to a decomposition product of the V(IV) species. On the other hand, the cyclic voltammogram of the L-cys complex gave an irreversible oxidation wave at +0.14 V under the same condition. This indicates that the L-cysteinatovanadium (IV) species is unstable compared with the corresponding D-penicillaminatovanadium (IV), which is consistent with the stability of the V(III) species in solution.

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