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Optically Active Vanadium(IV) and (V) Complexes Containing (*S*)-*N*-[1-(2-Pyridyl)ethyl]iminodiacetate Ion

Kenichi Okazaki and Kazuo Saito*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980

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New optically active vanadium(IV) and (V) and mixed valence(IV,V) complexes containing a quadridentate ligand (*S*)-*N*-[1-(2-pyridyl)ethyl]iminodiacetate (*S*-peida^{2-}) have been prepared: *i.e.* uninuclear distorted octahedral [$V^{IV}O$(*S*-peida)(H_2O)] and Li[$V^V(O)_2$(*S*-peida)], a mixed valence binuclear Na[$V_2{}^{IV,V}O_3$(*S*-peida)$_2$], and an oxo-peroxo complex Na[$V^VO(O_2{}^{(2-)})$(*S*-peida)]. The tertiary amino nitrogen of *S*-peida^{2-} occupies the trans position to the oxo ligand in the first three complexes, but *trans* to the peroxo ligand in the last complex. Three absorption bands of [$V^{IV}O$(*S*-peida)(H_2O)] in the region from 10000 to 30000 cm^{-1} have been assigned to the d-d transitions, $d_{xy}\rightarrow(d_{xz},d_{yz})$, $d_{xy}\rightarrow d_{z^2-y^2}$, and $d_{xy}\rightarrow d_{z^2}$, in the order of increasing frequency. The mixed valence complex gives an intervalence transfer band and two d-d bands in the region from 9000 to 25000 cm^{-1}. It gives a negative and a positive CD peak corresponding to the intervalence transition. The $V^V(O)_2$ and the $V^VO(O_2)$ complex give a characteristic absorption shoulder at 25000 and a peak at 23500 cm^{-1} with corresponding weak negative CD peaks, respectively. They are assigned to charge transfer bands from oxo and peroxo to V^V, respectively. The sign of CD peaks seems to be governed mostly by asymmetric arrangement of the ligating atoms and asymmetric deviation of ligating atoms from regular octahedron.

Oxo complexes of early transition metal ions are attracting increasing interest of coordination chemists. Asymmetric structure of some binuclear optically active $Mo^V(d^1)$ complexes was studied in solution and in solid by circular dichroism (CD) spectroscopy and X-ray diffraction.[1] However, much less is known for V^{IV} complexes with the same d^1 configuration. Jones and Larsen[2] first studied CD spectra of optically active oxovanadium(VI) complexes containing (*R*)-lactate, (*S*,*S*)-tartrate, and (*R*)-1,2-diiminopropanebis(acetylacetonate) ions with aims of assigning the absorption peaks. However, they succeeded in the isolation only of the complex with the third ligand. Optical activity was also studied with the complexes containing quadridentate Schiff bases derived from optically active diamines and salicylaldehyde derivatives.[3] Their absorption spectra involve not only d-d transitions (12000—20000 cm^{-1}) but also π-π^* transitions within the azomethine (*ca.* 28000) and the phenyl (*ca.* 36000) chromophore. The relationship between the sign of exciton CD bands of the azomethine chromophore and the configuration of the basal plane was mainly discussed. However, the CD spectra in the d-d region have not been much discussed.

Nishizawa and Saito synthesized new octahedral oxovanadium(IV) complexes with the quadridentate ligands *N*-(2-pyridylmethyl)iminodiacetate (pmida^{2-}) and nitrilotriacetate (nta^{3-}) in crystalline state. X-Ray crystallography of [$V^{IV}O$(pmida)(H_2O)][4] disclosed that only one of the geometrical isomers was exclusively formed with the tertiary amino nitrogen at the apical position. They also prepared a deep blue mixed valence binuclear complex bridged with oxide [$V_2{}^{IV,V}O_3$(nta)$_2$]$^{3-}$. X-Ray crystallography and ESR spectroscopy in the aqueous solution showed that the two vanadium atoms are equivalent to each other both in crystals and in aqueous solution.[5]

In order to clarify the electronic state and the relationship between the structure and the CD spectrum of the octahedral complexes with $V^{IV}O^{2+}$ and $V^V(O)_2{}^+$ core and of the mixed valence complex, we intended to introduce optical activity to those complexes by use of a similar quadridentate ligand (*S*)-*N*-[1-(2-pyridyl)ethyl]iminodiacetate ion (*S*-peida^{2-}).[6] Optically active complexes [$V^{IV}O$(*S*-peida)(H_2O)], [$V_2^{IV,V}O_3$(*S*-peida)$_2$]$^-$, [$V^V(O)_2$(*S*-peida)]$^-$, and [V^VO($O_2{}^{(2-)}$)(*S*-peida)]$^-$ have been prepared in crystalline state and their steric and electronic structures discussed.

Experimental

Preparation of Ligand. Sodium (*S*)-*N*-[1-(2-pyridyl)ethyl]iminodiacetate[6] was prepared in aqueous solution by treating (*S*)-1-(2-pyridyl)ethylamine[7] with sodium chloroacetate, and used without separating the crystals for preparing the complexes in aqueous phase.

Preparation of Complexes. *[$V^{IV}O$(S-peida)(H_2O)]·$2H_2O$:* [$V^{IV}O(acac)_2$][8] (Hacac, acetylacetone) (3.2 g, 0.012 mol) was stirred in an aqueous solution of the ligand (prepared from 0.02 mol of (*S*)-1-(2-pyridyl)ethylamine). The pH was maintained at 3 until [$VO(acac)_2$] dissolved completely. The dark blue solution was concentrated under a reduced pressure to about 5 cm^3 and poured onto a column (4 cm × 22 cm) of Dowex 50W-X8 (Na^+ form, 100—200 mesh). Elution with dilute $HClO_4$ (pH 4) gave three adsorption bands. The first eluate was dark green and seemed to contain negatively charged complexes. The third band was not eluted and may consist of aqua VO^{2+} complex. The purplish blue eluate (500 cm^3, pH *ca.* 4) of the second band was concentrated to give blue granules of the dihydrate. Yield: 4.0 g (93%). Found: C, 37.27; H, 5.27; N, 8.02%. Calcd for $C_{11}H_{18}N_2O_8V$: C, 36.98; H, 5.08; N, 7.84%.

Na[$V_2{}^{IV,V}O_3$(S-peida)$_2$]·$NaClO_4$·H_2O: This complex was prepared by oxidizing [VO(*S*-peida)(H_2O)] with half a mole of nitrite. The [VO(*S*-peida)(H_2O)]·$2H_2O$ (0.21 g, 0.59 mmol) was stirred in methanol (50 cm^3) containing $NaNO_2$ (0.021 g, 0.30 mmol) for 2 h at room temperature. Solid $NaClO_4$ (*ca.* 1 g) was added to the dark blue solution to precipitate dark blue granules, which were filtered off. Addition of diethyl ether to the filtrate gave further crops. Yield: 0.22 g (93%). Found: C, 33.44; H, 3.23; N, 7.00%. Calcd for $C_{22}H_{26}N_4O_{16}ClNa_2V_2$: C, 33.63; H, 3.33; N, 7.13%.

Li[$V^V(O)_2$(S-peida)]·$2CH_3OH$·$5H_2O$: The V^{IV} complex was oxidized with an excess of nitrite. The suspension of

$[V^{IV}O(S\text{-peida})(H_2O)]$ (1 g, 2.8 mmol) in methanol (20 cm^3) containing $LiNO_2$ (0.5 g, 9.4 mmol) was stirred for 3 h at room temperature until the solution turned yellow. The solution was mixed with diethyl ether (25 cm^3) and left in a refrigerator overnight to give yellow crystals. Yield: 1.0 g (89%). Found: C, 39.09; H, 5.14; N, 6.95%. Calcd for $C_{13}H_{21}N_2O_{8.5}LiV$: C, 39.11; H, 5.30; N, 7.02%.

$Na[V^VO(O_2)(S\text{-peida})]$: $[V^{IV}O(S\text{-peida})(H_2O)]$ (0.5 g, 1.4 mmol) was dissolved in 100 cm^3 of water and treated with an excess of hydrogen peroxide (30%, 5 cm^3) at room temperature to give orange solution immediately, which was made pH 6 with aqueous NaOH solution, concentrated to about 10 cm^3, mixed with ethanol (*ca.* 15 cm^3), and left in a refrigerator to give fine orange needles. Yield: 0.3 g (60%). Found: C, 36.85; H, 3.42; N, 7.52%. Calcd for $C_{11}H_{12}N_2O_7NaV$: C, 36.89; H, 3.38; N, 7.82%.

Measurement. The pK_a value of $[VO(S\text{-peida})(H_2O)]$ (Eq. 1) was obtained by titrating the aqueous solution of the complex (30 cm^3, 0.005 mol dm^{-3}) with *ca.* 0.1 mol dm^{-3} NaOH solution at $I=0.1$ mol dm^{-3} ($NaClO_4$) and 25±0.3 °C in a current of nitrogen. The complex $[V_2^{IV,V}O_3(S\text{-peida})_2]^-$ is in equilibrium with the V^{IV} and V^V complexes in an aqueous solution.[5] The equilibrium constant (see Eq. 2) was determined spectrophotometrically[9] at 740 nm by use of the complex solutions of 2.5—10 mmol dm^{-3} at $I=0.1$ mol dm^{-3} ($NaClO_4$), pH 4.5, and at 6.3±0.8, 15.0±0.4, and 25.0±0.1 °C.

The absorption and CD spectra were recorded in aqueous solutions and KBr disks with a Hitachi 323 Spectrophotometer, and JASCO Model J-40 A (200—700 nm), J-20 A (700—1000 nm), and J-200 (1000—2000 nm) CD Spectropolarimeters. A Varian A 60 D NMR Spectrometer was used for recording ^1H-NMR spectra of the two vanadium(V) complexes in D_2O.

Results and Discussion

Structure. X-Ray crystallography disclosed the structure of $[V^{IV}O(S\text{-peida})(H_2O)]$, $[V_2^{IV,V}O_3(S\text{-peida})_2]^-$, and $[V^V(O)_2(S\text{-peida})]^-$ (Fig. 1); the details are reported elsewhere.[10] The tertiary amine is at the trans position to the oxo ligand in all these complexes, and the methyl group on the asymmetric carbon has an equatorial orientation in the puckered five membered chelate ring.

The $[V^{IV}O(S\text{-peida})(H_2O)]$ and the mixed valence complex have similar CD patterns both in solution and in solid (see CD spectra). ^1H-NMR spectrum of the $V^V(O)_2$ complex supports the existence of only one isomer in solution. Its structure estimated by ^1H-NMR spectroscopy (*vide infra*) is not in conflict with the X-ray analysis. Hence all these three complexes seem to have the same geometrical isomerism in solution as in crystals.

The ^1H-NMR spectrum of the $[V^V(O)_2(S\text{-peida})]^-$ ion in D_2O (Table 1 and Fig. 2) exhibits one doublet, three quartets, and three multiplets from the high field. The doublet and one of the quartets with average chemical shifts 1.73 and 5.23 ppm, respectively, and with a common coupling constant 7 Hz, are assigned to the protons of the methyl group and that on the asymmetric carbon, respectively. The AB patterns centered at 3.46 and 4.18 ppm must arise from methylene protons of the acetates of which the ligating oxygens are at trans and cis to the pyridine nitrogen, respectively. The reasons are follows. The two protons of the cis acetate are subject to a more marked influence of the methyl group on the asymmetric carbon, and have therefore lower chemical shifts than those of the trans acetate; the difference between the anisotropic effects upon the two protons of the cis acetate can also cause a rather large difference of the chemical shifts between them ($\delta_A-\delta_B$ in Table 1). A free pyridine gives three multiplets over 7 ppm which correspond to the 3- and 5-, 4-, and 2- and 6-protons from the high field. Therefore, the multiplets over 7.5 ppm are assigned to the 3- and 5-, 4-, and 6-protons on the pyridine ring from the high field.

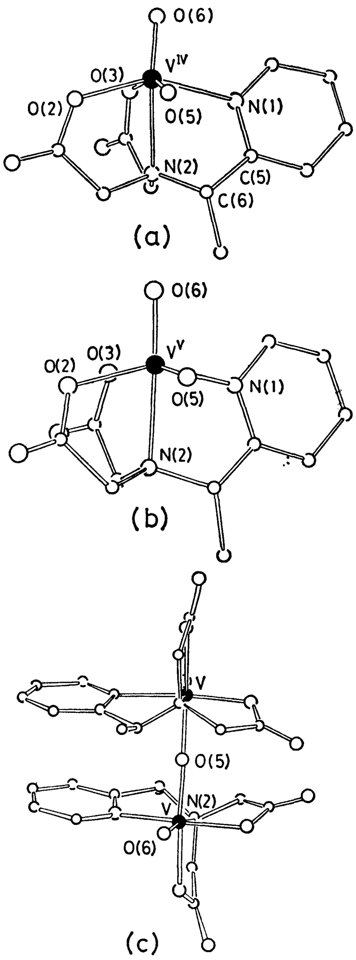

Fig. 1. Structures of the complexes determined by X-ray crystallography.
(a); $[V^{IV}O(S\text{-peida})(H_2O)]$. O(5) is oxygen atom of H_2O. The torsion angle between N(1)–N(2) and C(5)–C(6) is 17.0° (δ). (b); $[V^V(O)_2(S\text{-peida})]^-$. (c); $[V_2^{IV,V}O_3(S\text{-peida})_2]^-$.

The structure of $[V^VO(O)_2(S\text{-peida})]^-$ has not been determined by the X-ray method. Its NMR spectrum shows a similar pattern to $[V^V(O)_2(S\text{-peida})]^-$ in D_2O except that the signal of the 6-proton on pyridine shifts to lower field by *ca.* 0.8 ppm. The similarity suggests that there are two different acetate chelates. The O_2^{2-} ligand may be at the trans site to the tertiary amine, because the signal of the 6-proton has the largest shift and therefore should be nearest to the trans site of the tertiary amine. The

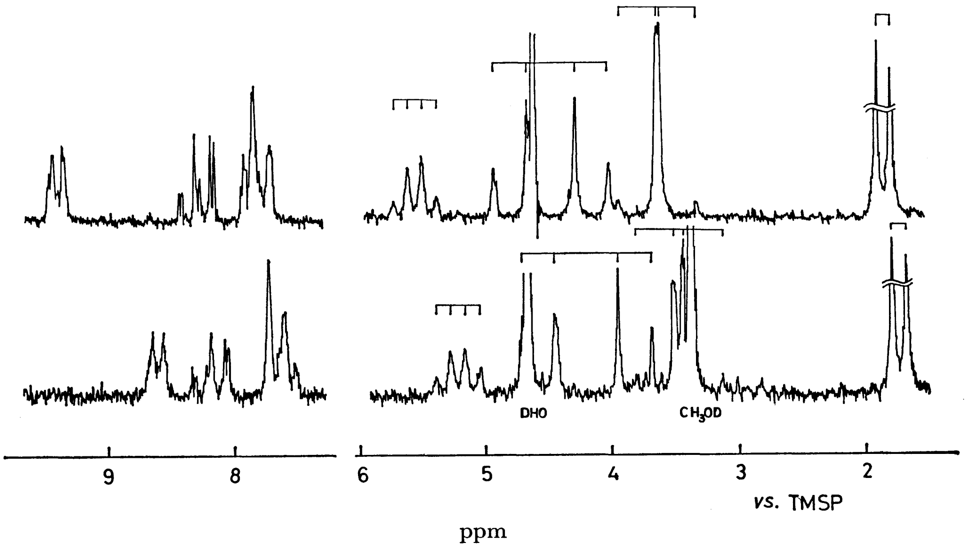

Fig. 2. ^{1}H-NMR spectra of $[\mathrm{V^VO(O)_2}(S\text{-peida})]^-$ (upper) and $[\mathrm{V^V(O)_2}(S\text{-peida})]^-$ (lower) in $\mathrm{D_2O}$ at *ca.* 30 °C.

TABLE 1. ^{1}H-NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF $[\mathrm{V^V(O)_2}(S\text{-peida})]^-$ AND $[\mathrm{V^VO(O_2)}(S\text{-peida})]^-$

A. The methylene protons of the two acetate groups.

Complex	$\{(\delta_A+\delta_B)/2\}$	$\delta_A-\delta_B$	J_{AB}/Hz
$\mathrm{V(O)_2^+}$	3.46	0.21	18.0
	4.18	0.71	16.0
$\mathrm{VO(O_2)^+}$	3.63	0.18	17.5
	4.48	0.59	16.0

B. The methyl and methylidyne protons.

Complex	Proton	δ	J/Hz
$\mathrm{V(O)_2^+}$	$-\mathrm{CH_3}$	1.73	7.0
	$>$CH	5.23	
$\mathrm{VO(O_2)^+}$	$-\mathrm{CH_3}$	1.86	7.0
	$>$CH	5.57	

C. The pyridyl protons.

Complex	Proton	δ
$\mathrm{V(O)_2^+}$	3-, 5-	7.6
	4-	8.1
	6-	8.6
$\mathrm{VO(O_2)^+}$	3-, 5-	7.8
	4-	8.3
	6-	9.4

NMR spectrum, however, cannot clarify the bonding mode of the peroxo ligand and the geometrical relationship between this ligand and the others. Nevertheless, X-ray structure of the oxo-peroxo complexes[11–13] of early transition metal ions suggests that the present peroxo complex is the isomer in which the peroxide ion is of side-on type and the V=O and the O–O ($\mathrm{O_2^{2-}}$) bonds are across each other (Fig. 3).

Equilibrium. The pK_a of the $\mathrm{V^{IV}O}$ complex to give the hydroxo complex is 6.5 at 25 °C and I=1.0 mol dm^{-3} in aqueous solution.

$$[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})] \rightleftharpoons [\mathrm{V^{IV}O(OH)}(S\text{-peida})]^- + \mathrm{H^+} \tag{1}$$

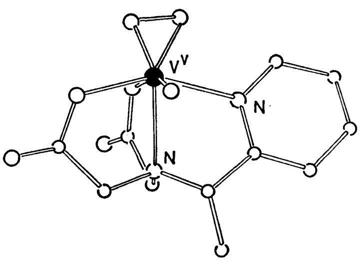

Fig. 3. Estimated structure of $[\mathrm{V^VO(O)_2}(S\text{-peida})]^-$.

The mixed valence complex of $[\mathrm{V_2^{IV,V}O_3}(S\text{-peida})_2]^-$ is in equilibrium with $[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})]$ and $[\mathrm{V^V(O)_2}(S\text{-peida})]^-$ in water as shown in Eq. 2.

$$[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})] + [\mathrm{V^V(O)_2}(S\text{-peida})]^- \rightleftharpoons [\mathrm{V_2^{IV,V}O_3}(S\text{-peida})_2]^-(+\mathrm{H_2O}) \tag{2}$$

The equilibrium constant, K, is 44±1 mol^{-1} dm^3 at 15 °C, I=0.1 mol dm^{-3} and pH 4.5. The $\Delta H°$ and $\Delta S°$ are -6 ± 3 kJ mol^{-1} and 11±8 J mol^{-1} K^{-1}, respectively, in the temperature region from 5 to 25 °C. The small negative $\Delta H°$ and the small positive $\Delta S°$ suggest that the mixed valence complex is slightly more stable than the mixture of the $\mathrm{V^{IV}O}$ and $\mathrm{V^V(O)_2}$ complexes. Since the number of particles does not change on the reaction, the positive $\Delta S°$ suggests that the formation of mixed valence complex brings about less hydration of the system. The charge distribution in the more bulky $[\mathrm{V_2^{IV,V}O_3}(S\text{-peida})_2]^-$ ion should be less concentrated than in the $\mathrm{V^{IV}O}$ and $\mathrm{V^V(O)_2}$ complexes.

Absorption Spectra. *V^{IV} Complex*: Oxo-vanadium(IV) complexes generally give three absorption bands with low intensity (ε=10—200), in the region from 10000 to 30000 cm^{-1} at room temperature. The two lower frequency bands sometimes overlap each other, and the highest frequency band in 21000—30000 cm^{-1} region is not always observed because of the overlap with a band of higher intensity at a higher frequency. Ballhausen and Gray[14] first assigned the three d-d absorption bands of some oxovanadium(IV) complexes to $d_{xy}\rightarrow(d_{xz},d_{yz})$, $d_{xy}\rightarrow d_{x^2-y^2}$, and $d_{xy}\rightarrow d_{z^2}$ transitions in the order of increasing frequency (z axis on the V=O bond, C_{4v} symmetry) with the aid of a molecular orbital energy level scheme. However, Selbin and co-workers[15] found a fine structure with three peaks in the first absorption band (at *ca.* 13000 cm^{-1}) of [VO(acac)$_2$] (C_{2v} symmetry) at 77 K and assigned the three peaks to those from d_{xy} to d_{xz}, d_{yz}, and $d_{x^2-y^2}$, respectively. They assigned the second band at *ca.* 18000 cm^{-1} to $d_{xy}\rightarrow d_{z^2}$ transitions. Jones and Larsen studied the CD spectra of (*R*)-lactato-, (*S,S*)-tartrato-, and (*R*)-1,2-diiminopropanebis(acetylacetonato)oxovanadium(IV) complexes and discussed the usefulness of CD spectrum for assigning the d-d transitions. However, only the third Schiff base complex was isolated and others were known only in solution. They also failed to observe the important peaks in the low frequency region.

The spectral pattern of the [V^{IV}O(*S*-peida)(H$_2$O)] complex gives four peaks at 13200 (ε=27.4), 17700 (16.4), 28200 (357), and 38800 cm^{-1} (4970) and a shoulder at *ca.* 34000 cm^{-1} (642) in aqueous solution of pH *ca.* 4 (Fig. 4). The first three bands are assigned to d-d transitions in the V^{IV}O complex of pseudo C_{4v} symmetry, $d_{xy}\rightarrow(d_{xz},d_{yz})$, $d_{xy}\rightarrow d_{x^2-y^2}$, and $d_{xy}\rightarrow d_{z^2}$. The band in the 13200 cm^{-1} region gives two CD peaks, whilst those at 17700 and 28200 cm^{-1} do one each. Hence the first peak should involve the transition to the degenerated levels, $d_{xy}\rightarrow(d_{xz},d_{yz})$. The other two bands at 17700 and 28200 cm^{-1} are assigned to the $d_{xy}\rightarrow d_{x^2-y^2}$ and $d_{xy}\rightarrow d_{z^2}$, respectively. The band at 28200 cm^{-1} has a larger intensity (ε=357) than the first two bands do. The absorption bands of oxovanadium(IV) complexes of other amino carboxylates without pyridine ring give small ε values (*ca.* 20) at similar wave numbers.[16] Hence the large peak may involve some charge transfer transition related to the pyridine ring. The shoulder at 34000 cm^{-1} gives a CD shoulder (Fig. 4). However, V^{IV}O complexes with amino carboxylates without pyridine ring do not give this absorption shoulder.[16] Hence the transition should be of charge transfer nature involving the pyridine ring. Not only the V^{IV}O complex but also [V^V(O)$_2$(*S*-peida)]$^-$ and[V^{V}O(O$_2$)(*S*-peida)]$^-$ give strong bands near 38800 cm^{-1} (Fig. 4). They are assinged to π-π^* transitions within the pyridine ring, since the π-π^* transitions of pyridine itself exist around 39000 cm^{-1}.

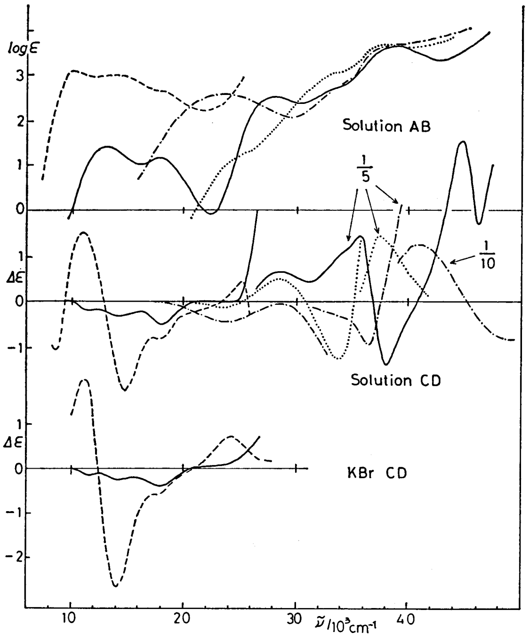

Fig. 4. Absorption and CD spectra of [V^{IV}O(*S*-peida)(H$_2$O)] (——), [V$_2$^{IV,V}O$_3$(*S*-peida)$_2$]$^-$ (— —), [V^V(O)$_2$(*S*-peida)]$^-$ (······), and [V^{V}O(O)$_2$(*S*-peida)]$^-$ (—·—). Upper, absorption in solution; middle, CD in solution; lower, CD spectra in KBr disks.

Mixed Valence Complex: The absorption spectrum was estimated by use of the equilibrium constant, 44 mol^{-1} dm^3. The ε values are calculated per unit molarity of $V_2O_3^{3+}$. To increase the concentration of mixed valence complex in the equilibrium state, a concentrated solution (0.013 mol dm^{-3}) was used in a 0.1 cm cell. Because of the strong absorption in the ultraviolet region under this condition, the discussion is limited in the visible and near infrared region. Three bands are seen in the measurable region: *i.e.* 10200 (ε=1200), 13600 (940), and 17700 cm^{-1} (shoulder, 470), and each overlaps the neighboring band. The frequencies of the second and third bands are similar to those of the first and second bands of [V^{IV}O(*S*-peida)(H$_2$O)] and assigned to the d-d transitions, $d_{xy}\rightarrow(d_{xz},d_{yz})$ and $d_{xy}\rightarrow d_{x^2-y^2}$, respectively. The first band should be due to the intervalence transition. The high intensity of the second and third bands may result from partial mixing of the metal d orbitals with the p orbitals of the bridging O atom.

V^V(O)$_2$ Complex: The spectrum of [V^V(O)$_2$(*S*-peida)]$^-$ has two strong bands at *ca.* 33300 (shoulder, ε=1070) and 37700 cm^{-1} (peak, 4640) in aqueous solution of pH 4.5. The former may be the charge transfer band from the pyridine ring to V^V and the latter is assigned to the π-π^* transition within the pyridine moiety by the same reason as for the V^{IV} complex. A weak shoulder is seen at *ca.* 25000 cm^{-1} (ε=17.8). The spectrum of [V^V(O)$_2$(OH$_2$)$_4$]$^+$ solution prepared by dissolving NH$_4$VO$_3$ in *ca.* 4.5 mol dm^{-3} HClO$_4$ has a weak shoulder at 24000 cm^{-1} (ε=7.15).[17] Na$_3$[V^V(O)$_2$(edta)][18] also gives an absorption shoulder at 25000 cm^{-1} (ε=25.8). Since V^V has no d electron, the origin of these shoulders must be a transition involving the oxo or the aqua ligands, most probably a spin-forbidden (singlet to triplet) charge transfer band from oxo to V^V. The reasons are as follows: (i) Its low intensity denies the participation of spin allowed charge transfer. (ii) The oxo ligand has π-bonding p orbitals with higher energy than the σ-bonding orbital of oxo and aqua ligands.[14] Hence the charge transfer from the π orbital to the d orbital may possess the lowest energy among the charge transfers from ligand to V^V.

V^{V}O(O)$_2$ Complex: The [V^{V}O(O)$_2$(*S*-peida)]$^-$ gives two peaks and a shoulder in aqueous solution at 23500 (ε=372), 33300 (shoulder, 500), and 38500 cm^{-1} (3720). Lever and Gray[19] discussed the origin of electronic spectra of side-on peroxo complexes of some early transition metals and assigned their lowest energy bands to the transition from the highest occupied π antibonding orbital of O_2^{2-} to the metal d orbital. We tend to assign the band at 23500 cm^{-1} to the charge transfer from O_2^{2-} to V^V and those at 33300 and 38500 cm^{-1} to the charge transfer from the pyridine ring to V^V and the π-π^* transition within the pyridine ring, respectively. The possible spin forbidden transition from the oxo ligand to V^V around 25000 cm^{-1} may be hidden by the strong band at 23500 cm^{-1}.

Pattern of CD Spectra. *V^{IV} Complex*: The CD spectra of $[V^{IV}O(S\text{-peida})(H_2O)]$ and $[V_2^{IV,V}O_3(S\text{-peida})_2]^-$ in KBr disks (Fig. 4) have similar pattern in the region from 10000 to 25000 cm^{-1} to those in aqueous solution. The $V^{IV}O$ complex gives four peaks in the d-d region. The two at 11900 ($\Delta\varepsilon = -0.23$) and 14300 cm^{-1} (−0.33) must correspond to the absorption band at 13200 cm^{-1} $[d_{xy} \rightarrow (d_{xz}, d_{yz})]$. This complex has a lower symmetry than C_{4v} and the degenerate levels of d_{xz} and d_{yz} split to give two CD peaks. The peaks at 18100 (−0.53) and 28200 cm^{-1} (+3.4) are naturally assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ (17700 cm^{-1}) and the $d_{xy} \rightarrow d_{z^2}$ band (28200 cm^{-1}), respectively. A positive and a negative peak are seen from lower wave number around 38000 cm^{-1}, corresponding to the π-π^* transition. A large positive peak is also seen at 44800 cm^{-1} (Table 2).

Mixed Valence Complex: The discussion is limited in the infrared and visible region (*vide supra*). This complex gives two CD peaks at 8620 ($\Delta\varepsilon = -1.1$) and 11100 cm^{-1} (+1.6) in the intervalence transfer region. The intensities are much larger than those of $V^{IV}O$ complex. It has two peaks at 14700 (−2.0) and 17500 cm^{-1} (−0.84) in the d-d region (13000—20000 cm^{-1}). The patterns in these regions are more or less similar to those of the $V^{IV}O$ complex.

$V^V(O)_2$ and $V^VO(O)_2$ Complexes: The two V^V complexes naturally fail to give CD in the lower wave number region than 19000 cm^{-1}. The $V^V(O)_2$ complex has two negative peaks and one positive peak in the region from 20000 to 34000 cm^{-1} (Table 2). They must correspond to the absorption shoulders at the respective wave numbers. Its large positive peak at 37500 cm^{-1} should correspond to the π-π^* transition of the pyridine moiety. The peroxo complex gives one broad negative peak and one negative shoulder in the 20000 to 34000 cm^{-1} region, corresponding to the broad absorption band at 23500 and a shoulder at 33300 cm^{-1}, respectively. In the π-π^* transition region there are two peaks at 36400 ($\Delta\varepsilon = -4.7$) and 41000 cm^{-1} (+12.8).

Source of CD Spectra. It is generally understood that the magnitude of contribution of various sources of asymmetry to the CD of a coordination compound with regular polyhedral structure decreases in the sequence; asymmetric configuration of chelate rings designated by Δ or $\Lambda >$ asymmetric arrangement of ligating atoms $\geq$ vicinal effect including asymmetry on ligating atoms, asymmetry on remote atoms and asymmetric conformation of chelates. The importance of asymmetric deviation of ligating atoms from regular polyhedra has been lately discussed and the magnitude of contribution is sometimes comparable to that of asymmetric configuration of chelate rings.[1,20)]

Since both the V^{IV} and the mixed valence complex give similar CD patterns in aqueous solution and in KBr disk, the asymmetric field influencing the CD spectra should not be very different in solution and in the solid state, at least for the transitions in the d-d and intervalence charge transfer region. Hence the relation between structure and CD can be discussed on the basis of X-ray crystal structure.

TABLE 2. ABSORPTION AND CD SPECTRA

	Absorption[a)]	CD in solution[b)]	CD in KBr[b)]
$[V^{IV}O(S\text{-peida})(H_2O)]$	13.2 (27.4)	11.9 (−0.23, −2.4)	11.6 (−0.17, −6.2)
		14.3 (−0.33, −12)	14.2 (−0.27, −9.9)
	17.7 (16.4)	18.1 (−0.53, −30)	17.7 (−0.42, −26)
	28.2 (357)	28.2 (+3.4, +9.5)	
	sh. 34.0 (642)	sh. 34.3 (+5.6, +8.7)	
	38.8 (4970)	35.8 (+7.5, +1.5)	
		38.0 (−7.0, −1.4)	
		44.8 (+14, +4.4[c)])	
$Na[V_2^{IV,V}O_3(S\text{-peida})_2]$	10.2 (1200)	8.6 (−1.1, −0.92)	
		11.1 (+1.6, +1.3)	11.0 (+2.0, +1.7)
	13.6 (940)	14.7 (−2.0, −2.1)	14.0 (−2.7, −2.9)
	17.7 (470)	17.5 (−0.84, −1.8)	17.5 (−0.55, −1.2)
$Li[V^V(O)_2(S\text{-peida})]$	sh. 25.0 (17.8)	23.7 (−0.081, −4.6)	
	sh. 33.3 (1070)	28.6 (+0.53, +0.50)	
		33.9 (−1.25, −1.2)	
	37.7 (4640)	37.5 (+7.52, +1.6)	
$Na[V^VO(O_2)(S\text{-peida})]$	23.5 (37.2)	24.1 (−0.44, −1.2)	
	sh. 33.3 (500)	sh. 33.3 (−1.39, −2.8)	
	sh. 38.5 (4720)	36.4 (−4.7, −1.0)	
		41.0 (+12.8, +2.7)	

a) $\nu/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}). b) $\nu/10^3$ cm^{-1} ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}, $\Delta\varepsilon$ at peak/ε at absorption peak or shoulder ($\times 10^3$)). c) $\Delta\varepsilon/\varepsilon$ at 44800 cm^{-1}.

The present *S*-peida complexes have no chilarity coming from the configuration of chelate rings, but the non-equivalent ligating atoms have asymmetric arrangement as shown in Fig. 5. The present $\mathrm{V^{IV}}$ complex has configuration (a) of Fig. 5.

There is no established way for expressing the asymmetric deviation, although proposals have been made by some authors.[1,20] The vanadium atom is slightly over the mean basal plane consisting of N(1), O(2), O(3), and O(5) in Fig. 1 (a) by 0.4 Å and the location of ligating atoms deviates largely from a regular octahedron. When one considers an imaginary basal plane which passes the V atom and is perpendicular to the V=O bond, the asymmetric deviation can be expressed by the torsion angles of the basal edges connecting the ligating atoms in cis positions toward the edges of the imaginary plane. These angles are listed in Table 3.

The vicinal effect, the asymmetric arrangement of ligating atoms, and the asymmetric deviation of ligating atoms from regular octahedron can be responsible for the CD. The vicinal effect can come from the asymmetric carbon and the δ-conformation of the five-membered chelate ring containing the asymmetric carbon. Such a vicinal contribution cannot be denied but does not seem predominating because of the following reasons: (i) The 5-membered chelate ring involving asymmetric carbon gives an envelope-like conformation with δ-chilarity and the torsion angle between N(1)–N(2) and C(5)–C(6) (Fig. 1 a) is rather small as compared with other puckered rings of various metal complexes in which significant vicinal contribution is seen in the d-d transition region (*e.g.* (*R*)- or (*S*)-1,2-propanediamine rings in $\mathrm{Co^{III}}$ complexes). (ii) The $\mathrm{V^{IV}}$ complex of (*S*)-alanine-*N*,*N*-diacetate has a similar skeletal structure to $[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})]$, and has a common asymmetrically distorted δ-conformation of the 5-membered chelate ring containing *S*-carbon atom. However, its CD strength is nearly one tenth of that of $[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})]$ in the d-d transition region, and the sign is reversed.[16] Hence we tend to consider that the vicinal contribution is not significant. The contribution of asymmetric arrangement and asymmetric deviation can be separated with difficulty, because the ligating atoms are connected by chelate rings. The main origin of CD strength may come from the asymmetric arrangement of the ligating atoms and asymmetric deviation from regular octahedron.

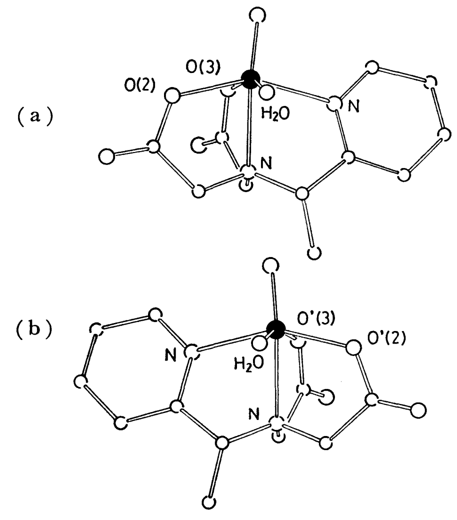

Fig. 5. Optical isomers of $[\mathrm{V^{IV}O}(S\text{-peida})(\mathrm{H_2O})]$ due to asymmetric arrangement of ligating atoms.

TABLE 3. DISTORSIONS AROUND THE VANADIUM[a)]

Edge	$\mathrm{V^{IV}O}$	$\mathrm{V_2^{IV,V}O_3}$		$\mathrm{V^V(O)_2}$
1) Angles against the perpendicular plane to $\mathrm{V{-}O_6}$ bond in Fig. 1.				
$\mathrm{N_1{-}O_5}$	1.92 λ	0.11 δ	0.31 λ	2.77 λ
$\mathrm{N_1{-}O_3}$	3.97 λ	4.91 δ	6.74 λ	7.10 λ
$\mathrm{O_2{-}O_5}$	3.51 λ	2.92 λ	2.90 λ	2.93 λ
$\mathrm{O_2{-}O_3}$	9.87 δ	7.76 δ	10.36 δ	12.92 δ
2) Torsion angles between basal edges.				
$(\mathrm{N_1{-}O_3})$ *vs.* $(\mathrm{O_2{-}O_5})$	10.62 λ	7.88 λ	9.64 λ	10.01 λ
$(\mathrm{N_1{-}O_5})$ *vs.* $(\mathrm{O_2{-}O_3})$	7.84 δ	9.19 δ	10.82 δ	10.59 δ

a) See Ref. 10.

The CD strength of the mixed valence complex is much larger than that of the $\mathrm{V^{IV}}$ complex, particularly in the intervalence charge transfer region. This must be related to the large absorption intensity of the former. In the region from 15000 to 23000 $\mathrm{cm^{-1}}$, both patterns are more or less similar, suggesting the function of a common origin. If very small angles less than 1° are ignored (Table 3), both the $\mathrm{V^{IV}}$ and the mixed valence complexes are reckoned to have qualitatively similar distorsion. This fact provides support to the above mentioned discussion in the d-d transition region.

The peaks and shoulders of the $\mathrm{V^{IV}O}$, $\mathrm{V^V(O)_2}$, and $\mathrm{V^VO(O_2)}$ complexes over 30000 $\mathrm{cm^{-1}}$ give corresponding CD peaks or shoulders. All the absorption peaks and shoulders are considered to be related to the transitions from the pyridine ring (*i.e.* π-π* transition or N(pyridine)-$\mathrm{V^{IV}}$ charge transfer). However, there does not seem to be simple relationship between the CD sign and the structure of the complexes including the asymmetric distorsion (Table 3). The asymmetry linked to such transitions may be related to the distortion of the N(py)-site from the regular octahedron, or to the orientation of the pyridine ring, both depending on the delicate skeletal structure of the complex. It is difficult to discuss the CD pattern in the UV region more precisely at the present stage.

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