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Redox reactions of $[VO(salen)]^{+/0}$ couple in acetonitrile: Volume analyses in relation to large chiral recognitions observed for electron self-exchange reactions of $[VO(Schiff\text{-}Base)]^{+/0}$

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Abstract

Kinetic measurements were carried out for the outer-sphere electron transfer reactions involving $[VO(Schiff\text{-}Base)]^{+/0}$ couples. Electron self-exchange rate constant for $[VO(3\text{-}MeOsal\text{-}(RR)\text{-}chxn)]^{+/0}$ couple was determined as $k_{ex} = (5.2 \pm 0.8) \times 10^6\ kg\ mol^{-1} s^{-1}$ at 25 °C. It was found that added water in acetonitrile solvent retarded the electron transfer reactions between $[VO(salen)]^+$ and $[Co(o\text{-}phen)_3]^{2+}$: the six-coordinate V(V) species, $[VO(salen)(OH_2)]^+$ was found to be ca. 3.5 times less reactive compared with the five-coordinate species, $[VO(salen)]^+$. This small difference between the reactivity of five- and six-coordinate species indicates that the reaction through the direct O=V(V)–O=V(IV) interaction is outer-sphere in nature, contrary to the previously proposed inner-sphere mechanism. Activation volumes corresponding to the electron self-exchange reactions for $[VO(salen)]^+/[VO(salen)]^0$ and $[VO(salen)OH_2]^+/[VO(salen)]^0$ couples were estimated from the volume profiles of the reduction reactions of $[VO(salen)]^+$ by $[Co(o\text{-}phen)_3]^{2+}$, with and without added water in acetonitrile: $\Delta V^* = -3.4 \pm 3.7$ and $-8.0 \pm 4.0\ cm^3\ mol^{-1}$ for $[VO(salen)]^+/[VO(salen)]^0$ and $[VO(salen)OH_2]^+/[VO(salen)]^0$ couples, respectively. It was suggested that previously reported chiral recognitions in the redox reactions involving $[VO(Schiff\text{-}Base)]^{+/0}$ redox couples take place within the encounter complex through the outer-sphere mechanism by maximizing the direct coupling between the dπ orbitals of V(IV) and V(V) species (Scheme 2).

Keywords: Redox reaction; Volume analyses; Oxovanadium(V)/(IV); Schiff-Base complexes; Chiral recognition

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1. Introduction

Investigation of chiral recognitions in electron transfer (ET) reactions is important both for the understanding of biological processes and for the development of stereoselective catalytic systems. In the inner-sphere reaction systems, chiral recognition may take place at the step of the bond formation between reducing and oxidizing reagents, and the succeeding electron transfer process is very rapid. In contrast to the inner-sphere electron transfer processes, time allowed for the reacting complexes to recognize suitable molecular orientations before the electron transfer process is limited for the outer-sphere reactions.

Most of the reported results concerning the molecular recognition in the outer-sphere electron transfer reactions involve either chiral Co(III) complexes [1–3] or chiral Ru(III) complexes [4], since the racemization reactions of these complexes are rather slow compared with the ET processes. However, the enantiomeric excess (ee) observed for

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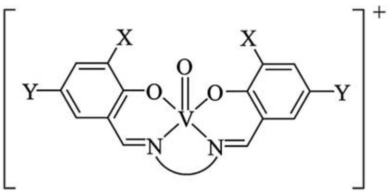
these reactions are usually below 20%, that corresponds to the difference in the rate constants of only 20% at its maximum for different molecular orientations. Therefore, it is generally understood that the detection of such a small difference in the rate constants is very difficult to confirm. Moreover, little structural information has been given to date for the probable molecular orientations for such chiral recognitions.

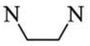
In 1995, Nakajima et al. [5] reported a large difference in the rate constants for the electron transfer reactions between the optically active, substituted oxovanadium(V)/(IV)-Schiff-Base complexes in acetonitrile: up to 50% difference between $k_{RR\text{–}SS}$ and $k_{RR\text{–}RR}$ was observed for the following reaction.

$$\begin{aligned}&[\mathrm{VO}(3\text{-MeOsal-}(RR)\text{or -}(SS)\text{-chxn})]\\&\quad+[\mathrm{VO}(\text{sal-}(RR)\text{-chxn})]^+\\&\qquad\rightarrow[\mathrm{VO}(3\text{-MeOsal-}(RR)\text{ or -}(SS)\text{-chxn})]^+\\&\qquad\quad+[\mathrm{VO}(\text{sal-}(RR)\text{-chxn})]\end{aligned}\tag{1}$$

where structures of salchxn and 3-MeOsal-chxn complexes are shown in Scheme 1. Although the reactions do not involve any change in the coordination geometry around V(IV) and V(V) complexes, they attributed this large stereochemical selection to the inner-sphere O═V(V)–O═V(IV) interaction. Such a speculation seems to have emerged, as the interaction between the vacant dπ-orbitals with the filled pπ-orbitals of the oxygen atom may be possible. On the other hand, a direct dπ–dπ interaction between the two vanadium ions is equally plausible along the same reaction coordinate since the energy levels between dπ orbitals on V(IV) and V(V) ions are closer to each other.

Therefore, it is interesting to examine the nature of the electron transfer process in this reaction system: the self-exchange rate constant estimated from the reaction of the V(V)/(IV) couple with typical outer-sphere reagents should be much smaller than that directly measured by the NMR method, when the reaction through the O═V(V)–O═V(IV) interaction is truly inner-sphere in nature, since the inner-sphere interaction should induce strong electronic coupling that leads either to the rapid superexchange or the sequential transfer [6].



complex	X,Y	
$[\mathrm{VO(salen)}]^+$	H,H	
$[\mathrm{VO\{3\text{-}MeOsal\text{-}(RR)\text{-}chxn\}}]^+$	MeO,H	
$[\mathrm{VO\{3\text{-}Phsal\text{-}(RR)\text{-}chxn\}}]^+$	Ph,H	

Scheme 1. Oxovanadium complexes used in this study.

Chiral selection in the outer-sphere electron transfer reaction originates from the recognition of molecular shapes within a very short lifetime of the encounter complex, although the lifetime of the encounter complex depends largely on the charge-type of the two colliding species [7]. However, chiral recognition through the molecular re-orientation within the encounter complex is still possible to occur for some of the outer-sphere reactions since the average correlation time for molecular rotation is somewhat shorter ($\sim 10^{-10\sim-12}$ s) than the lifetime of the encounter complex unless the reactants carries large like charges [8].

In this study, we carried out the reduction reactions of various chiral Schiff-Base complexes of oxovanadium(V) at ambient and elevated pressures to investigate the origin of the relatively large ee (enatiomeric excess) reported for the pseudo self-exchange process in the previous study [5].

2. Experimental

2.1. Materials

Acetonitrile was obtained from Wako Pure Chemicals Inc., and purified by distillation from phosphorus pentoxide. As acetonitrile treated with phosphorus pentoxide contains species that induce strong acid-base interaction with ligands, the solvent was re-distilled twice from molecular sieves before use. The content of the residual water in thus purified acetonitrile was examined by a Mitsubishi Kasei CA07 Karl-Fisher apparatus, by which the amount of residual water was determined to be less than 1 mmol kg^{-1}. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized twice from the mixture of ethyl acetate/pentane solution, and dried under reduced pressure. All other chemicals used for the syntheses of metal complexes were purchased from Wako, Aldrich, and Nakarai, and were used without further purification.

The Schiff-Base ligands and corresponding vanadium(V) complexes were synthesized according to the literature methods [9,10], by using appropriate chiral diamines as starting materials. Vanadium complexes thus obtained were sufficiently pure for the electrochemical and kinetic analyses, although it was shown by the NMR analyses that purified V(V) complexes contained up to 5% of corresponding V(IV) species while no significant deviations from the calculated values were observed for the results of microanalyses (Appendix 1). The microanalyses, UV–Vis absorption spectra, and NMR spectra of these complexes are summarized in Table 1. The structures and abbreviations of oxovanadium complexes used in this study are summarized in Scheme 1.

Table 1
Results of microanalyses, UV–Vis absorption spectra, NMR spectra, and the observed electron self-exchange rate constants for the vanadium(V) complexes by using NMR

Vanadium(V) complex	Microanalysis[a]			UV–Vis		^{1}H NMR (CD_3CN)	Self-exchange rate[b]constant
	C (%)	H (%)	N (%)	λ (nm)	ε (M^{-1} cm^{-1})	δ (ppm) (TMS)	k_{ex} (kg mol^{-1} s^{-1})
$[VO(salen)(H_2O)]ClO_4$				568.8	1.28×10^3		$(1.6 \pm 0.1) \times 10^6$
	43.25	3.28	6.33	291.8	1.89×10^4	9.07 (s, PhC*H*=N)	
	(42.64)	(3.85)	(6.22)	249.4	2.96×10^4	7.92–7.09 (Ph)	
				224.8	3.40×10^4	4.48, 4.24 (s, CH_2CH_2–N)	
$[VO(3\text{-MeOsal-}(RR)\text{-chxn})(H_2O)]ClO_4$						9.08, 8.81 (s, PhC*H*=N)	$(5.2 \pm 0.8) \times 10^6$
	46.65	4.51	4.91	255.6	2.77×10^4	7.65–7.22 (Ph)	
	(46.78)	(4.64)	(4.96)	221.4	3.93×10^4	3.99 (s, OMe)	
						3.62–1.49 (chxn)	
$[VO(3\text{-Phsal-}(RR)\text{-chxn})(H_2O)]ClO_4$				599.8	1.04×10^3	8.82, 8.04 (s, PhC*H*=N)	
	57.70	4.56	5.76	318.6	1.28×10^4	7.61–6.73 (Ph)	
	(58.50)	(4.60)	(4.26)	241.4	4.30×10^4	3.67–0.92 (chxn)	

[a] Calculated values are in the bracket.
[b] Determined from the NMR line-broadening method at 297.9 K.

[VO(salen)] was synthesized by mixing $VOSO_4$ with salen in methanol with the existence of triethylamine. The green product was recrystallized from acetonitrile. *Anal.* Calc. for $VOC_{16}H_{14}N_2O_2$: C, 57.67; N, 8.40; H, 4.23. Found: C, 57.22; N, 8.12; H, 4.22%.

$[Co(o\text{-phen})_3](ClO_4)_2$ (*o*-phen = 1,10-phenanthroline) and $[Co(4,7\text{-Me}_2phen)_3](ClO_4)_2 \cdot H_2O$ (4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline) complexes were synthesized by the literature method [11] *Anal.* Calc. for $CoC_{36}H_{24}N_6Cl_2O_8$: C, 54.15; N, 10.53; H, 3.03. Found: C, 53.55; N, 10.47; H, 3.13%. *Anal.* Calc. for $CoC_{42}H_{38}N_6Cl_2O_9$: C, 56.01; N, 4.25; H, 9.33. Found: C, 55.86; N, 4.18; H, 9.46%. $[Co(o\text{-phen})_3](ClO_4)_3$ and $[Co(4,7\text{-Me}_2phen)_3](PF_6)_3 \cdot 2.5H_2O$ complexes were also synthesized by the reported method [11]. *Anal.* Calc. for $CoC_{36}H_{24}N_6Cl_3O_{12}$: C, 48.16; N, 9.36; H, 2.69. Found: C, 46.49; N, 9.69; H, 2.77%. *Anal.* Calc. for $CoC_{42}H_{41}N_6P_3F_{18}O_{2.5}$: C, 43.35; N, 7.22; H, 3.55. Found: C, 43.76; N, 7.22; H, 3.64%.

2.2. Kinetic and electrochemical measurements

Kinetic measurements at ambient pressure were carried out by a Unisoku RA401 stopped-flow apparatus, while the measurements at elevated pressures were performed by using a Hi-Tech HPSF-50 apparatus. Deaerated paraffin oil was used as the pressurizing fluid. The reactions were monitored by observation of the absorbance change at 370 nm (an absorption maximum in the case of [VO(salen)] species).

Electrochemical measurements at ambient pressure were carried out by using a BAS 100B/W Electrochemical Analyzer with a standard three-electrode configuration: a 3 mm∅ glassy carbon (GC) was used as the working electrode, a platinum wire as the counter electrode, and a $Ag/AgNO_3$ electrode in 0.1 M solution of TBAP in acetonitrile was used as the reference electrode. The redox potentials of complexes are reported in Table 2 with reference to the redox potential observed for the ferricinium/ferrocene couple in the same solvent. The reaction volumes were determined from the pressure dependence of the redox potentials at 25 °C by using a BAS 100B/W Electrochemical Analyzer. The pressure vessel used for the measurements is similar to that reported elsewhere [12]. We used an all-glass electrochemical cell equipped with a 3 mm∅ GC disk and a 1.0 mm∅ Pt wire as the working and counter electrodes, respectively.

A Hitachi U-3000 UV–Visible spectrophotometer and a JASCO DIP-360 polarimeter were used for the measurements of the absorption spectra and the angles of rotation of sample solutions, respectively. A JEOL JMN-400 and a Bruker AMX-400WB were used for the measurements of the ^{1}H NMR spectra.

3. Results and discussion

3.1. Self-exchange rate constants for $[VO(salen)OH_2]^{+/0}$ and $[VO(3\text{-MeOsal-}(RR)\text{-chxn})OH_2]^{+/0}$ couples

The crystal structure of $[VO(salen)OH_2]NO_3$ has been reported: V–OH_2 distance is 2.225 Å [13]. On the other hand, most of the corresponding V(IV) complexes are five-coordinate with a square pyramidal geometry [14,15] (see Appendix 2). It has also been known that the water exchange rate constant for pentaaquaoxovanadium(IV) is ca. 10^8 s^{-1} at its axial position which is *trans* to the oxo anion, while the water exchange at the equatorial position is significantly slower (ca. 0.1–1 s^{-1}) [16]. The crystal structure of $[VO(salen)OH_2]NO_3$ indicates that the water molecule *trans* to the oxo anion is the more tightly bound to the metal ion in V(V) compared with the corresponding V(IV) species: no coordinated ligand at the trans position to the oxo anion in the crystal structure of V(IV) complex [15].

The electron self-exchange rate constants for $[VO(salen)OH_2]^{+/0}$ and $[VO(3\text{-MeOsal-}(RR)\text{-chxn})OH_2]^{+/0}$ couples were estimated by the NMR line broadening method [17] in dry acetonitrile at 297.9 ± 0.3 K. All but the ring proton

Table 2
Redox potentials of complexes used in this study[a]

Redox couple	$E_{1/2}$ (mV)[b]
$[VO(salen)]^{+/0}$	85
$[VO(3\text{-MeOsal-}(RR)\text{-chxn})]^{+/0}$	49
$[VO(3\text{-Phsal-}(RR)\text{-chxn})]^{+/0}$	21
$[Co(o\text{-phen})_3]^{3+/2+}$	−17
$[Co(4,7\text{-Me}_2\text{phen})_3]^{3+/2+}$	−186

[a] $I = 0.1$ mol kg^{-1} (TBAP), $T = 298.2$ K.

[b] vs. $E_{\text{ferricinium/ferrocene}}$.

signals of V(V) complexes broadened by adding small amounts of V(IV), ([V(IV)]/[V(V)] < 10%), to the solution of V(V). The –N=CH– proton signal was used for the estimation of the electron self-exchange rate constant. As these proton signals were observed at the identical positions for solutions containing different amounts of V(IV), the slow exchange limit was assumed [17] for the kinetic analyses.

Fig. 1 shows the dependence of $\pi\Delta\nu$ for the –N=CH– proton of the V(V)-salen complex on [V(IV)], when extra amounts of V(IV)-salen complex was added to the solution ($\Delta\nu$ stands for the difference between the observed line width for the sample solution that contains extra amounts of V(IV) and the natural line width, see Appendix 1): filled circles represent the experiments for the sample solutions with no appreciable amount of water in the solvent, while open circles represent the results for the sample solutions with more than 30 mmol dm^{-3} of water (30–80 mmol dm^{-3}). As shown in Fig. 1 (Tables S0), no significant effect by added water was observed for the rate of electron self-exchange reaction (Appendix 1). Estimated electron self-exchange rate constants for salen and 3-MeOsal complexes are summarized in Table 1.

Nakajima et al. reported pseudo-electron self-exchange reactions between chiral $[VO(3\text{-MeOsal-}(RR\text{ or }SS)\text{-chxn})]^+$ and $[VO(sal\text{-}(RR)\text{-chxn})]$ in acetonitrile [5]: $k_{RR-RR} = (2.8 \pm 0.1) \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_{SS-RR} = (5.6 \pm 0.7) \times 10^6$ dm^3 mol^{-1} s^{-1}. These values may be compared with the directly obtained $k_{\text{ex}} = (5.2 \pm 0.8) \times 10^6$ kg mol^{-1} s^{-1} for $[VO(3\text{-MeOsal-}(RR)\text{-chxn})]^{+/0}$ couple in this study. The close coincidence between these independently obtained self-exchange rate constants indicates that the electron self-exchange and pseudo-exchange reactions proceed through the identical activation process for each reactant.

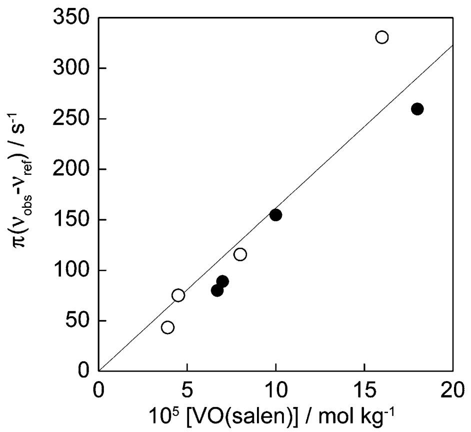


Fig. 1. Dependence of the first-order rate constant estimated from the broadening of the line width of the imine proton signal on the concentration of paramagnetic [VO(salen)] in acetonitrile at 298.2 K. (○): $[VO(salen)^+] = (1.19\text{–}1.33) \times 10^{-3}$ mol kg^{-1}. $[H_2O] = 3\text{–}7 \times 10^{-2}$ mol kg^{-1}. (●): $[VO(salen)^+] = (1.25\text{–}1.35) \times 10^{-3}$ mol kg^{-1}. $[H_2O] < 10^{-2}$ mol kg^{-1}.

Retardation of the electron transfer reaction by added water was observed for the cross reaction of $[VO(salen)]^+$ with $[Co(o\text{-phen})_3]^{2+}$ in acetonitrile, as described in the later section: the estimated formation constant of $[VO(salen)\text{-}OH_2]^+$ from $[VO(salen)]^+$, 8 ± 3 kg mol^{-1}, indicates that dissociation of coordinated water takes place upon dissolution of $[VO(salen)OH_2]^+$ in dry acetonitrile (see Appendixes 1 and 2). In the following sections, we will describe V(V) complexes dissolved in dry acetonitrile without including coordinated water, such as $[VO(salen)]^+$: acetonitrile molecule, that probably replaces the coordinated water molecule, was also omitted from the formula because of the inferior basicity of this solvent molecule. The linewidth of the ^{1}H signal for impure acetonitrile in the bulk was very narrow (<1 Hz) and was unaffected by the existence of V(V), indicating either a very rapid exchange with the coordinated acetonitrile or no coordination of acetonitrile to V(V) complex (see Appendixes 1 and 2).

3.2. Self-exchange rate constant for the $[Co(o\text{-phen})_3]^{3+/2+}$ couple in acetonitrile

The electron self-exchange rate constant for $[Co(o\text{-phen})_3]^{3+/2+}$ couple was measured in acetonitrile, from the reaction of optically active $(+)\text{-}[Co(o\text{-phen})_3]^{3+}$ and racemic $[Co(o\text{-phen})_3]^{2+}$. As the racemization reaction of Co(II) complex is rapid, the loss of the optical activity of the reaction mixture is attributed to the slow electron self-exchange reaction between $[Co(o\text{-phen})_3]^{3+}$ and $[Co(o\text{-phen})_3]^{2+}$. A typical change of the optical rotation with time is shown in Fig. 2. We used a home-made rapid mixer to achieve equivolume mixing of $(+)\text{-}[Co(o\text{-phen})_3]^{3+}$ and racemic $[Co(o\text{-phen})_3]^{2+}$: the optical rotation measurements required 10 cm^3 of sample solutions for each measurement. The temperature of the sample solutions were, therefore, guaranteed to only ±1 K, since the temperature equilibration of samples with such large amount of solvent takes relatively long time (up to several minutes). The observed rate constant was $k_{\text{ex}} = 2.16 \pm 0.12$ kg mol^{-1} s^{-1} at 298.2 ±1.0 K.

$$\begin{aligned} &(+)\text{-}[Co(o\text{-phen})_3]^{3+} + rac\text{-}[Co(o\text{-phen})_3]^{2+} \\ &\quad \xrightarrow{k_{\text{obs}}} (+)\text{-}[Co(o\text{-phen})_3]^{2+} + rac\text{-}[Co(o\text{-phen})_3]^{3+} \\ &(+)\text{-}[Co(o\text{-phen})_3]^{2+} \xrightarrow{\text{rapid}} rac\text{-}[Co(o\text{-phen})_3]^{2+} \\ &-\frac{d[(+)\text{-Co(III)}]}{dt} = k_{\text{obs}}[k(+)\text{-Co(III)}] \quad k_{\text{ex}} = 2k_{\text{obs}} \end{aligned} \tag{2}$$

This value may be compared with that estimated for the same reaction in water, 12 dm^3 mol^{-1} s^{-1} [6].

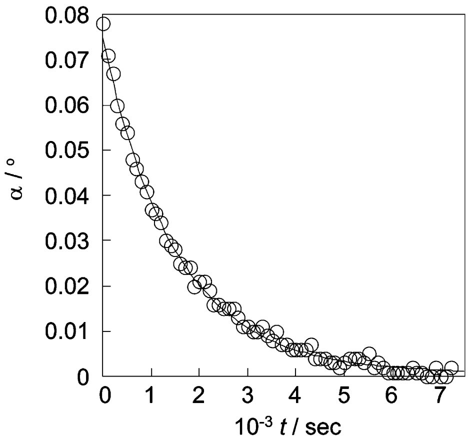


Fig. 2. Typical change of optical rotation for the reaction between (+)-$[Co(o\text{-}phen)_3]^{3+}$ and racemic $[Co(o\text{-}phen)_3]^{2+}$ with time. $[Co(o\text{-}phen)_3^{2+}] = 7.35 \times 10^{-4}$ mol kg^{-1}. $[(+)\text{-}Co(o\text{-}phen)_3^{3+}] = 1.57 \times 10^{-4}$ mol kg^{-1}. $I = 1.1$ mol kg^{-1} (TBAP). $[o\text{-phen}] = 1.0 \times 10^{-3}$ mol kg^{-1}. $T = 298 \pm 1$ K. Free o-phen was added to the solution to suppress decomposition of $[Co(o\text{-}phen)_3]^{2+}$.

3.3. Cross reactions of V(V) with $[Co(o\text{-}phen)_3]^{2+}$ and $[Co(4,7\text{-}Me_2\ phen)_3]^{2+}$

Redox potentials of the complexes synthesized in this study were examined in acetonitrile, and are summarized in Table 2. Cross reactions of these V(V) complexes with $[Co(o\text{-}phen)_3]^{2+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ were examined in acetonitrile, to confirm the activation mode of these species for the redox reactions: it has been known that the Marcus/Ratner cross relation holds only when the activation process of each reactant for the self-exchange reaction is identical to that for cross reactions [18]. Fig. 3 (Table S1) shows the typical dependence of the reduction rate constant for $[VO(3\text{-}MeOsal(RR)\text{-}chxn)]^+$ by $[Co(o\text{-}phen)_3]^{2+}$ on the concentration of excess [Co(II)] at various temperatures. Plots for other cross reactions together with the corresponding tables are included in the supporting materials (Figs. S1–S4 and Tables S2–S5).

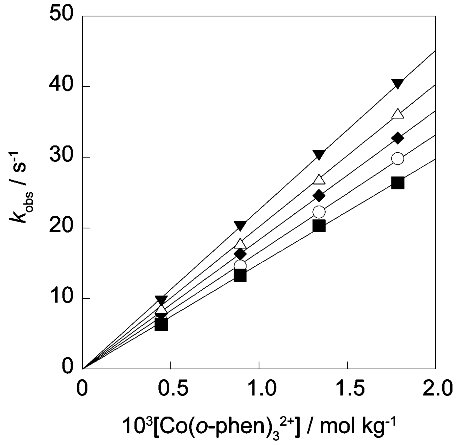


Fig. 3. Dependence of the rate constant for the reduction reaction of $[VO(3\text{-}MeOsal\text{-}(RR)\text{-}chxn)]^+$ by $[Co(o\text{-}phen)_3]^{2+}$ in acetonitrile at various temperatures. $[VO(3\text{-}MeOsal\text{-}(RR)\text{-}chxn)^+] = 3.35 \times 10^{-5}$ mol kg^{-1}. $[o\text{-phen}] = 1.05 \times 10^{-3}$ mol kg^{-1}. $I = 0.1$ mol kg^{-1} (TBAP). $T = 288$ (■), 293 (○), 298 (◆), 303 (△), and 308 (▼) K. Free o-phen was added to the solution to suppress decomposition of $[Co(o\text{-}phen)_3]^{2+}$.

The self-exchange rate constants for V(V)/V(IV) couples were estimated by using the Marcus/Ratner cross relation [19]: the self-exchange rate constant for $[Co(o\text{-}phen)_3]^{3+/2+}$, 2.16 ± 0.12 kg mol^{-1} s^{-1}, determined in this study was used for this purpose. Then, the self-exchange rate constant for $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ couple was estimated from the cross reaction rate constants for the reactions with V(V) complexes, by using the cross relation. The electron self-exchange rate constants for the redox couples thus estimated are summarized in Table 3, in which we assumed two different distances for the closest approach between the reactants: the shorter distance corresponds to the contact of two reactants at the coordination site trans to the oxo anion of V(V) complex (axial approach) while the longer distance corresponds to that through the salen-type ligand of V(V) complex (equatorial approach). It is seen that the electron self-exchange rate constant for $[VO(salen)]^{+/0}$ couple obtained directly by the NMR method is consistent with that estimated by using the cross relation, especially when the axial approach was assumed.[1] It should be noted that Marcus/Ratner type cross relation holds for both inner- and outer-sphere type reactions, as far as the activation processes for each reactant are identical for the cross and self-exchange reactions. From the results summarized in Table 3, however, we can safely conclude that the self-exchange reactions between V(V) and V(IV) complexes proceed though the outer-sphere mechanism, since the estimated self-exchange rate constants for the V(V)/(IV) redox couples from the rate constants for cross reactions with typical outer-sphere reagents are identical to those estimated either by the NMR method or from the pseudo-exchange reaction [5].

3.4. Dependence of the rate constant for the reduction reaction of $[VO(salen)]^+$ by $[Co(o\text{-}phen)_3]^{2+}$ on the concentration of water in acetonitrile

Dependence of the second-order rate constant for reaction (3) on the water concentration was examined in acetonitrile.

$$[VO(salen)]^+ + [Co(o\text{-}phen)_3]^{2+} \rightarrow [VO(salen)] + [Co(o\text{-}phen)_3]^{3+} \qquad (3)$$

The reaction was retarded by added water, as shown in Fig. 4 (Table S6). Such retardation of the electron transfer rate by water may be explained by the following mechanism in which a less reactive water adduct is formed by the addition of water.

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[1] Since the solvent used for this experiment contains less than 4 mmol kg^{-1} of water, it is probable that the axial position opposite to the oxo anion in V(V) complex is available for the redox reactions (see later section for the equilibrium constant for the aquation of this site, 8 ± 3).

Table 3
The electron self-exchange rate constants calculated for the V(V)/(IV) redox couples in two different types of interactions[a]

Redox couple	Counter reagent	Axial approach (400 pm)	Equatorial approach (890 pm)
$[VO(salen)]^{+/0}$	$[Co(o\text{-phen})_3]^{3+/2+}$	1.60×10^6	9.68×10^5
$[VO(3\text{-MeOsal-}(RR)\text{-chxn})]^{+/0}$	$[Co(o\text{-phen})_3]^{3+/2+}$	7.54×10^6	4.59×10^6
$[VO(3\text{-Phsal-}(RR)\text{-chxn})]^{+/0}$	$[Co(o\text{-phen})_3]^{3+/2+}$	2.07×10^6	1.27×10^6
$[Co(4,7\text{-Me}_2\text{phen})_3]^{3+/2+}$	$[VO(3\text{-MeOsal-}(RR)\text{-chxn})]^{+/0}$	1.05×10^{-1}	9.86×10^{-2}
$[Co(4,7\text{-Me}_2\text{phen})_3]^{3+/2+}$	$[VO(3\text{-Phsal-}(RR)\text{-chxn})]^{+/0}$	6.61×10^{-2}	6.32×10^{-2}

$I = 0.1$ mol kg^{-1} (TBAP), $T = 298.2$ K.

[a] kg mol^{-1} s^{-1}.

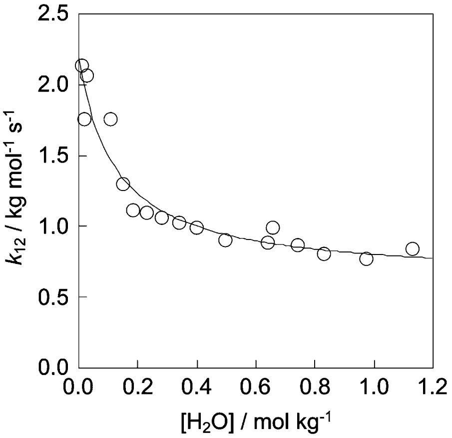


Fig. 4. Dependence of the rate constants for the reduction reaction of $[VO(salen)]^+$ by $[Co(o\text{-phen})_3]^{2+}$ on the concentration of water in acetonitrile. $[Co(o\text{-phen})_3^{2+}] = 4.4 \times 10^{-4}$ mol kg^{-1}, $[VO(salen)^+] = 4.3 \times 10^{-5}$ or 2.2×10^{-5} mol kg^{-1}, $I = 0.1$ mol kg^{-1} (TBAP), $[o\text{-phen}] = 1.0 \times 10^{-3}$ mol kg^{-1}, $T = 298.2$ K. Free *o*-phen was added to the solution to suppress decomposition of $[Co(o\text{-phen})_3]^{2+}$.

$$[VO(salen)]^+ + H_2O \overset{K}{\rightleftharpoons} [VO(salen)OH_2]^+ \quad (4)$$

$$[VO(salen)]^+ + [Co(o\text{-phen})_3]^{2+} \xrightarrow{k_1} [VO(salen)] + [Co(o\text{-phen})_3]^{3+} \quad (5)$$

$$[VO(salen)OH_2]^+ + [Co(o\text{-phen})_3]^{2+} \xrightarrow{k_2} [VO(salen)OH_2] + [Co(o\text{-phen})_3]^{3+} \quad (6)$$

The apparent first-order rate constant k is expressed by the following equation:

$$k = \frac{k_1 + k_2K[H_2O]}{1 + K[H_2O]}[Co(o\text{-phen})_3^{2+}] \quad (7)$$

The best-fit curve according to Eq. (7) is also shown in Fig. 4, and the values of k_1, k_2, and K are $(2.2 \pm 0.1) \times 10^4$ kg mol^{-1} s^{-1}, $(6.3 \pm 1.0) \times 10^3$ kg mol^{-1} s^{-1}, and 8 ± 3 kg mol^{-1}, respectively. The value of k_1 is 3.5 times larger than k_2: $[VO(salen)OH_2]^+$ is *less reactive* compared with $[VO(salen)]^+$ only by a factor of only 3.5.

The water molecule in $[VO(salen)OH_2]^+$ complex may be positioned at the position trans to the oxo anion of $[VO(salen)]^+$, by considering that the electron transfer rate generally decreases with increasing the distance between reactants in the encounter complex [19]. Therefore, it is highly probable that the rate of the electron transfer reaction is fast for the O=V–O=V conformation while it is somewhat slower when a water molecule exists between the reactants. However, such a O=V–O=V interaction does not necessarily induce the inner-sphere type electron transfer: the very small degree of acceleration by this configuration strongly indicates that the reaction is outer-sphere in nature, and that the electron transfer takes place through the dπ–dπ interaction. As the water content of acetonitrile solvent was small in the previous study [5], the relatively large stereochemical selection reported for the pseudo-exchange reactions between [VO(3-MeOsal-(*RR* or *SS*)-chxn)] and $[VO(sal\text{-}(RR)\text{-chxn})]^+$ should have taken place with the direct O=V(V)–O=V(IV) interaction.

3.5. Reaction volumes of $[VO(salen)]^{+/0}$ and $[Co(o\text{-phen})_3]^{3+/2+}$ couples in acetonitrile

It is necessary to know the reaction volumes of $[VO(salen)]^{+/0}$ and $[Co(o\text{-phen})_3]^{3+/2+}$ couples for the purpose of the volume analysis of cross reactions (5) and (6). The reaction volumes were obtained by measuring the pressure dependence of the redox potential of an acetonitrile solution containing $[VO(salen)]^+$ or $[Co(o\text{-phen})_3]^{3+}$ with 0.1 mol kg^{-1} of tetra-*n*-butylammonium perchlorate (Table S7). The observed reaction volume of a redox couple includes the reaction volume of the reference electrode.

$$\overbrace{M^{n+} + \underbrace{Ag \rightleftharpoons Ag^{+}}_{\Delta V^0_{\mathrm{reference}}} + M^{(n-1)+}}^{\Delta V^0_{M^{n+/(n-1)+}}} \quad (8)$$

We do not have to know the reaction volume for the Ag/Ag$^+$ reference couple ($\Delta V^0_{\mathrm{reference}}$), since it cancels when the specific reaction volume is calculated for reaction (5).

The overall reaction volumes for reaction (8), $\Delta V^0_{M^{n+/(n-1)+}} + \Delta V^0_{\mathrm{reference}}$, were -12.4 ± 2.7 and 15.2 ± 0.5 cm^3 mol^{-1} for $[VO(salen)]^{+/0}$ and $[Co(o\text{-phen})_3]^{3+/2+}$ couples, respectively. The reaction volumes for the sample solutions containing less than 5 mmol kg^{-1} of water and more than 100 mmol kg^{-1} of water were identical to each other for both redox couples, within the experimental uncertainty, indicating that the existence of water molecule at the trans position of the oxo anion in V(V) complex does not significantly alter the reaction volume: the volume difference of these V(V)/(IV) couples is identical and the water molecule at the trans position of the oxo anion is withheld during the electrode reaction (6). The specific reaction volume, ΔV^0_{12}, was estimated as $-27.6 \pm 2.7\ \mathrm{cm^3\ mol^{-1}}$ for both reactions (5) and (6).

3.6. Reduction reaction of $[VO(salen)]^+$ by $[Co(o\text{-}phen)_3]^{2+}$ at elevated pressures

The dependence of the rate constant for cross reaction (5) on pressure at 25 °C in dry acetonitrile is shown in Fig. 5. The activation volume was estimated from the slope of the plot as $-17.6 \pm 1.3\ \mathrm{cm^3\ mol^{-1}}$. In the acetonitrile solution that contains ca. 100 mmol $\mathrm{kg^{-1}}$ of water, the activation volume was estimated as $-19.9 \pm 1.5\ \mathrm{cm^3\ mol^{-1}}$ (Fig. 5). By using the following volume cross relation (Eq. (9)) [20,21], we obtained activation volumes for the self-exchange reactions of $[\mathrm{VO(salen)}]^+/[\mathrm{VO(salen)}]^0$ and $[\mathrm{VO(salen)OH_2}]^+/[\mathrm{VO(salen)}]^0$ couples: $\Delta V^*_{\mathrm{ex}} = -3.4 \pm 3.7\ \mathrm{cm^3\ mol^{-1}}$ and $-8.0 \pm 4.0\ \mathrm{cm^3\ mol^{-1}}$, for the reactions in dry acetonitrile and in acetonitrile containing 100 mmol $\mathrm{kg^{-1}}$ of water, respectively. Under the latter condition, ca. 50% of V(V) species are expected to exist as $[\mathrm{VO(salen)(OH_2)}]^+$. The relatively large mathematical errors of the estimated activation volumes for the self-exchange processes represent the accumulation of the maximum errors for measured activation and reaction volumes. However, it has been shown that the comparison with the theoretically calculated value can be made when the difference from the experimentally estimated activation volume is within the $\pm 1\ \mathrm{cm^3\ mol^{-1}}$ range of the theoretical value, as the error of $\pm 1\ \mathrm{cm^3\ mol^{-1}}$ is the allowed maximum that originates from the ignorance of the inner-sphere contribution to the total activation volume [22,23].

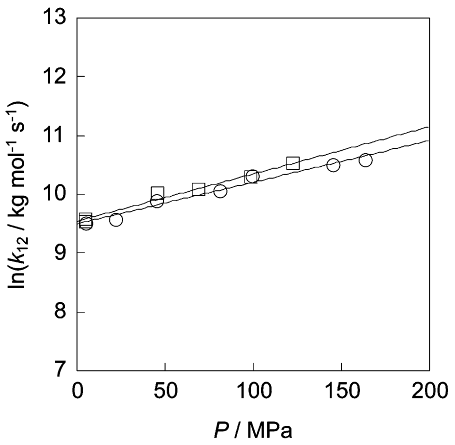


Fig. 5. Pressure dependence of the rate constants for the reduction reaction of $[\mathrm{VO(salen)}]^+$ by $[\mathrm{Co}(o\text{-phen})_3]^{2+}$ in acetonitrile. (○): $[\mathrm{VO(salen)}^+] = 4.04 \times 10^{-5}\ \mathrm{mol\ kg^{-1}}$. $[\mathrm{Co}(o\text{-phen})_3^{2+}] = 4.47 \times 10^{-4}\ \mathrm{mol\ kg^{-1}}$. $[\mathrm{H_2O}] < 10\ \mathrm{mmol\ kg^{-1}}$. $I = 0.1\ \mathrm{mol\ kg^{-1}}$ (TBAP). $[o\text{-phen}] = 1.0 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$, $T = 298$ K. (□): $[\mathrm{VO(salen)}^+] = 4.08 \times 10^{-5}\ \mathrm{mol\ kg^{-1}}$. $[\mathrm{Co}(o\text{-phen})_3^{2+}] = 8.20 \times 10^{-4}\ \mathrm{mol\ kg^{-1}}$. $[\mathrm{H_2O}] > 100\ \mathrm{mmol\ kg^{-1}}$. $I = 0.1\ \mathrm{mol\ kg^{-1}}$ (TBAP). $[o\text{-phen}] = 9.5 \times 10^{-4}\ \mathrm{mol\ kg^{-1}}$, $T = 298$ K. Free o-phen was added to the solution to suppress decomposition of $[\mathrm{Co}(o\text{-phen})_3]^{2+}$.

$$\Delta V^*_{12} = \frac{\Delta V^*_{11} + \Delta V^*_{22} + \Delta V^0_{12}}{2} + C$$
$$C = \frac{X \Delta V^0_{12} \ln K_{12} - 2(\ln K_{12})^2 (\Delta V^*_{11} + \Delta V^*_{22} - \Delta V^W_{11} - \Delta V^W_{22})}{X^2}$$
$$X = 4\left[\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{RT}\right] \tag{9}$$

where ΔV^*_{12} is the activation volume of the cross reaction, ΔV^*_{11}, ΔV^*_{22}, k_{11}, and k_{22} are the activation volumes and corresponding rate constants for each electron self-exchange reaction, ΔV^0_{12} is the reaction volume of the cross reaction, and Z is the collision frequency which is usually taken to be $10^{11}\ \mathrm{M^{-1}\ s^{-1}}$, respectively. When the redox potential of the cross reaction is close to zero, C is negligibly small.

For this calculation, a theoretically calculated value of $-4.2\ \mathrm{cm^3\ mol^{-1}}$ was used for the activation volume of $[\mathrm{Co}(o\text{-phen})_3]^{3+/2+}$ couple [24,25]. The parameters used for this calculation are summarized in Table 4. Theoretical values of the activation volumes corresponding to the two different configurations of activated complexes were estimated by the following Stranks-Hush-Marcus equation [26,28]:

$$\Delta V^*_{11} = \Delta V^*_{\mathrm{is}} + (\Delta V^*_{\mathrm{os}} + \Delta V^*_{\mathrm{coul}} + \Delta V^*_{\mathrm{DH}}) + \beta RT \tag{10}$$

in which the β is the isothermal compressibility of the solvent, and the inner-sphere contribution to the activation volume, ΔV^*_{is}, is usually very small and ignored [22,23,26]. Other terms in the above equation is given by the following expression:

$$\Delta V^*_{\mathrm{os}} = \frac{Ne^2}{16\pi\varepsilon_0}\left[\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{a}\right)\left\{\frac{\partial}{\partial P}\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right)\right\}_T - \frac{\beta}{3a}\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right)\right]$$
$$\Delta V^*_{\mathrm{coul}} = \frac{Nz_1z_2e^2}{16\pi\varepsilon_0 a}\left[\left(\frac{\partial}{\partial P}\frac{1}{D_{\mathrm{s}}}\right)_T - \frac{\beta}{3D_{\mathrm{s}}}\right]$$
$$\Delta V^*_{\mathrm{DH}} = \frac{RTz_1z_2C\sqrt{\mu}}{(1 + Ba\sqrt{\mu})^2}\left[\left(\frac{\partial \ln D_{\mathrm{s}}}{\partial P}\right)_T (3 + 2Ba\sqrt{\mu} - \beta)\right] \tag{11}$$

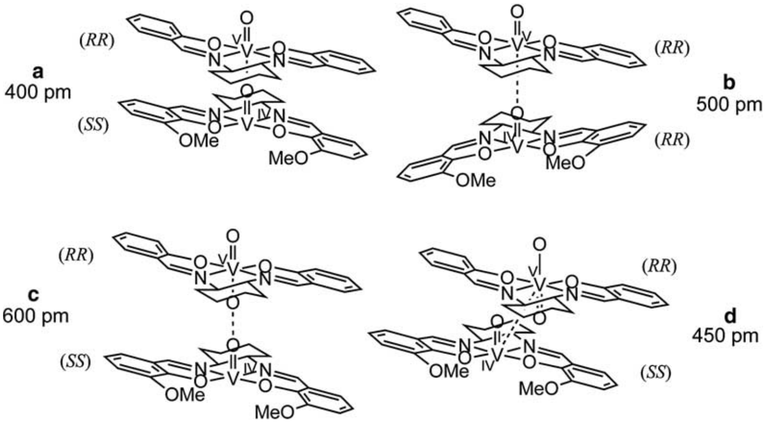
where a_1 and a_2 are the radii of oxidized and reduced species ($a = a_1 + a_2$), respectively. D_{op} and D_{s} are the high- and low-frequency dielectric constants of the solvent,

Table 4
Activation volumes for the self-exchange reaction of $[\mathrm{VO(salen)}]^{+/0}$

ΔV^*_{12} ($\mathrm{cm^3\ mol^{-1}}$)	ΔV^0 ($\mathrm{cm^3\ mol^{-1}}$)	ΔV^*_{22} ($\mathrm{cm^3\ mol^{-1}}$)	ΔV^*_{11} ($\mathrm{cm^3\ mol^{-1}}$)
-17.6 ± 1.3[a]	-27.6 ± 2.7	-4.2	-3.4 ± 3.7
-19.9 ± 1.5[b]			-8.0 ± 4.0
Axial approach			-3.8 (890 pm)
Equatorial approach			-8.4 (400 pm)

[a] $[\mathrm{H_2O}] < 10\ \mathrm{mmol\ kg^{-1}}$.

[b] $[\mathrm{H_2O}] > 100\ \mathrm{mmol\ kg^{-1}}$.



Scheme 2. Configurations of the encounter complexes: (a) closest approach for the *RR*-*SS* combination in the axial approach, (b) the closest approach for the *RR*–*RR* combination in the axial approach, (c) and (d) possible close approach for the six coordinate V(V) and five coordinate V(IV) [the distance between two vanadium centers is ca. 480–500 pm in this configuration where no specific interaction that induces the stereo selectivity]. The V(V)–V(IV) distance in (a) is shorter by more than 100 pm than that for (b). When no water is added to the solvent, the self-exchange reaction proceeds through a-, b-, and d-type interactions. The reported stereochemical selection can be explained by the largest rate constant for the ET process through (a): the largest electronic coupling between V(V) and V(IV) is achieved in this configuration. On the other hand, the reaction takes place via (c) and (d) with the existence of sufficient amounts of water in the solvent: the rate constant for the reaction involving this type of interaction is smaller because of the longer distance between V(V) and V(IV).

respectively, and μ is the ionic strength of the solution. Each volume term in Eq. (10) was estimated for different configurations of the encounter complex (Scheme 2) and also listed in Table 4. As seen in Table 4, the activation volume calculated by assuming the axial approach of $[VO(salen)]^+$ and [VO(salen)] is consistent with the experimentally obtained activation volume for the self-exchange reaction, when $[H_2O]_{free} < 10$ mmol kg^{-1}. It is, therefore, suggested that the electron self-exchange reaction of $[VO(salen)]^{+/0}$ couple proceeds with the short O=V(V)–O=V(IV) interaction distance as described in Scheme 2(a) when the water content in the solvent is small. It seems that the oxo anion on V(IV) complex approaches from the opposite side of the oxo anion of V(V) complex, since V(IV) is stabilized in a C_{4v} form without a ligand at the trans position to the oxo anion (Appendixes 1 and 2).

On the other hand, the self-exchange reaction involving $[VO(salen)(OH_2)]^+$ species should also take place with the optimized geometry through which the electronic coupling between two vanadium ions is maximized. In this case, the maximum overlap between two dπ orbitals on V(IV) and V(V) complexes is achieved in the manner described in Scheme 2(c) and (d): the distance between V(IV) and V(V) centers are some 50–200 pm longer than the case in Scheme 2(a). Since the rate of the electron transfer decreases exponentially with increasing the distance between metal centers, a somewhat smaller rate constant for the k_2 process (Eq. (6)) than the k_1 process may be explained by this small difference in the interaction distances between two metal ions. The preference of the *RR*–*SS* combination for V(V) and V(IV) complexes to the *RR*–*RR* combination may be explained by the difference of the steric repulsion between the salicylaldoimine moieties on two vanadium complexes in these two combinations (Scheme 2(a) and (b)).

The relatively large enantiomeric excess reported for the reaction of [VO(3-MeOsal-(*RR* or *SS*)-chxn)]^0 with [VO(sal-(*RR*)-chxn)]$^+$ in acetonitrile with no added water in the acetonitrile solvent, therefore, may be explained by the preferred configuration described in Scheme 2: the distance between vanadium ions is some 100 pm shorter for the *RR*–*SS* interaction (Scheme 2(a)) than that for the *RR*–*RR* combination (Scheme 2(b)). In both cases, however, the electron transfer reactions proceed through the outer-sphere mechanism.

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Appendix 1

It was not possible to obtain pure V(V) complexes: samples with small but noticeable amounts of V(IV) were used in this study. Although such a contamination by V(IV) did not create a serious problem for the measurements of cross reactions, the results of direct measurements of the self-exchange rate were somewhat obscured: the natural line widths for the V(V) solutions were significantly broadened as shown by ν_{ref} in Table S0. Addition of an extra amount of V(IV) further broadened the signal, and the self-exchange rate constant was determined by the slope of the plot in Fig. 1: the rate constant was obtained by multiplying π after subtraction of ν_{ref} from the observed line widths, ν_{obs}, of the sample solution that contains extra amounts of V(IV). A rather inferior V(V) complex in terms of the purity (contaminated with ca 8% of V(IV)) was also used (a plot shown by open circles in Fig. 1), showing no significant deviation from the expected slope. Therefore, it was concluded that no impurity other than V(IV) complex was contained in the synthesized V(V) complexes provided by the method described in Section 2.

Appendix 2. Ground state structures of $[VO(salen)X]^{+/0}$ complexes

Six-coordinate vanadium(IV) complexes with d^1 electronic configuration suffers from distortion primarily by the first-order Jahn–Teller effect (FOJT) [27], that causes the ordinary tetragonal distortion to a structure with the C_{4v} symmetry. On the other hand, corresponding V(V) species seems to suffer from the second-order Jahn–Teller effect (SOJT) [28]: the strong color of the complex indicates existence of low-energy CT bands that originate from the filled high-energy ligand π orbitals to the metal t_{2g} and/or e_g^* orbital. The ligand π level consists of t_{2u}, t_{1u}, and t_{1g} orbitals, and the possible low-energy ligand-to metal charge transfer (LMCT) transitions induce vibrations of the T_{1u} and T_{2u} modes as a result of the direct product. The T_{1u} normal mode (ν_4) vibration not only causes deformation to the C_{4v} symmetry, but also to place the central vanadium atom off the equatorial plane. Therefore, the ground state structure of $[VO(salen)OH_2]^+$ not only exhibits a relatively long V(V)–OH_2 distance (ca. 2.23 Å) but also the central vanadium(V) is located slightly above the ONNO pseudo-plane of the salen ligand, as seen in the crystal structure [14]. A very rapid water exchange at the axial site of $[VO(OH_2)_5]^{2+}$ and 5-coordination of [VO-(salen)] can be explained by the FOJT effect, while a moderately fast water exchange (40–100 s^{-1}) for $[VO\text{-}(salen)OH_2]^+$ is explained by the SOJT effect.

Appendix 3. Supplementary data

Eight tables (Tables S0–S7) of all experimental data are available from the author or from the editor. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.10.028.

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