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Kinetic Studies of Stereoselective Vanadyl(IV) Tartrate Reactions

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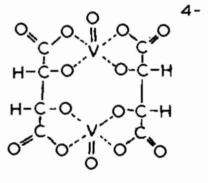
The stereoselective ligand substitution reaction, $(VO)_2(\text{l-}C_4H_2O_6)_2^{4-} + \text{d-}C_4H_4O_6^{2-} \rightleftarrows (VO)_2(\text{d-}C_4H_2O_6)(\text{l-}C_4H_2O_6)^{4-} + \text{l-}C_4H_4O_6^{2-}$*, and ligand exchange reaction,* $\frac{1}{2}(VO)_2(\text{l-}C_4H_2O_6)_2^{4-} + \frac{1}{2}(VO)_2(\text{d-}C_4H_2O_6)_2^{4-} \rightleftarrows (VO)_2(\text{d-}C_4H_2O_6)(\text{l-}C_4H_2O_6)^{4-}$*, both occur by parallel path processes. The major paths for the two reactions have reaction rate laws of the forms* $d[(VO)_2(\text{d-}C_4H_2O_6)(\text{l-}C_4H_2O_6)^{4-}]/dt = k_1[(VO)_2(\text{l-}C_4H_2O_6)_2^{4-}]$ *for ligand substitution and* $d[(VO)_2(\text{d-}C_4H_2O_6)(\text{l-}C_4H_2O_6)^{4-}]/dt = k_3\{[(VO)_2(\text{l-}C_4H_2O_6)_2^{4-}] + [(VO)_2(\text{d-}C_4H_2O_6)_2^{4-}]\}$ *(for equimolar reactants) for ligand exchange. The respective kinetic parameters at 25.0 °C and* $\mu = 3.00$ *mol* l^{-1} *(*$LiClO_4$*) are* $k_1 = 0.0112 \pm 0.0013$ sec^{-1}, $\Delta H^{\neq} = 25 \pm 2$ *kcal* mol^{-1}, $\Delta S^{\neq} = 17 \pm 7$ *eu and* $k_3 = 0.00693 \pm 0.00027$ sec^{-1}, $\Delta H^{\neq} = 23.5 \pm 1.0$ *kcal* mol^{-1}, $\Delta S^{\neq} = 10 \pm 3$ *eu. That corresponding activation parameters are equal indicates that the first-order pathways of the two reactions may have identical dissociative rate determining steps. The secondary, autocatalytic paths, which are also present in these reactions, apparently involve product-assisted ligand dissociations.*

Introduction

In aqueous solution, the optically active binuclear vanadyl(IV) tartrate(4–) complex $(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}$ (*1*) reacts with *d*-tartrate(2–), $d\text{-}C_4H_4O_6^{2-}$, in a ligand substitution reaction to give the more stable *dl* isomer, $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$. In a related reaction, mutual ligand exchange between *dd* and *ll* isomers occurs to give the *dl* form [1]. Thermodynamic studies have shown an equilibrium constant of 16 (25 °C, $\mu = 0.10$ mol l^{-1}, KNO_3) [2] and a reaction enthalpy of -1.64 ± 0.10 kcal mol^{-1} (after correcting the reported value [3] of -1.46 kcal mol^{-1} for incompleteness of reaction using this equilibrium constant) for the reaction



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$$\tfrac{1}{2}(VO)_2(l\text{-}C_4H_2O_6)_2^{4-} + \tfrac{1}{2}(VO)_2(d\text{-}C_4H_2O_6)_2^{4-} \rightleftarrows (VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-} \quad (1)$$

In this paper, we report the results of kinetic studies on these ligand substitution and ligand exchange reactions.

Experimental

Materials

Tetrasodium di-μ-*d*-tartrato(4–)bis(oxovanadate(IV)) 6-hydrate, $Na_4[(VO)_2(d\text{-}C_4H_2O_6)_2]\cdot 6H_2O$, and the enantiomeric salt, $Na_4[(VO)_2(l\text{-}C_4H_2O_6)_2]\cdot 6H_2O$ were prepared by a previously described method [1]. Baker AR sodium *d*-tartrate(2–) 2-hydrate, $Na_2(d\text{-}C_4H_4O_6)\cdot 2H_2O$, was used as obtained. G. F. Smith lithium perchlorate was recrystallized to give the 3-hydrate solid. All materials gave satisfactory elemental and water analyses.

Kinetic Measurements

The reactants and lithium perchlorate 3-hydrate were weighed out and aqueous solutions were prepared under strict anaerobic conditions (to prevent vanadium oxidation [4]). Reactions were initiated by injecting one reactant solution into another in a stirred absorption cell using a calibrated gas-tight syringe. Both the syringe and absorption cell were water-jacketed and thermostatted to ±0.1 °C. The absorbance change (±0.004 absorbance units), as a function of time, was followed at the wavelength of maximum change (940 nm [1]) using a Cary model 14RI recording spectrometer. No attempts were made to vary or to buffer the solution pH in these studies since (*i*) reactions involving polydentate ligand complexation are notorious for their susceptibility to catalysis by potential complexing agents [5] (which would be introduced by a buffer), (*ii*) the vanadyl-

TABLE I. Rate Constants Assuming Strict First-Order Behavior.[a]

Initial Concentrations[b] × 10^3, (mol l^{-1})				10^3 k[c] (sec^{-1})
M_2ll	M_2dl	d	l	
		$M_2ll + d \rightarrow M_2dl + l$		
10.0	–	10.0	–	10.3(1.1)
10.0	10.0	10.0	–	11.8(0.6)
10.0	20.0	10.0	–	13.7(1.8)
10.0	10.0	10.0	10.0	14.6(0.4)
10.0	10.0	20.0	10.0	13.6(2.2)

[a] T = 25.0 °C, μ = 3.00 mol l^{-1} ($LiClO_4$). [b] Concentrations after mixing assuming no reaction. 'M_2ll' = $(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}$, '$M_2dl$' = $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$, '$d$' = $d\text{-}C_4H_4O_6^{2-}$, 'l' = $l\text{-}C_4H_4O_6^{2-}$. [c] Average deviations for three determinations are given in parentheses.

(IV) tartrate(4–) binuclear complexes of the structure shown in *1* exist only over a narrow pH range, and (*iii*) most buffers interfere with vanadyl(IV) tartrate complexation as evidenced by spectral changes [6].

Computerized simplex minimizations were employed to determine values of the rate constants in the two-term rate laws found and of the baseline absorbance which minimized the sum of the squared deviations between observed and calculated absorbances. For convenience in carrying out experiments, baseline spectral absorbances were not determined for most runs. Where they were determined, the values of the rate constants found in fits employing only the rate constants as variables agreed with those found in fits where the baseline absorbance was also treated as a variable. The absorbance data (to 50% completion of reaction) were fit to within 0.004 absorbance units in all cases where a two-term rate law was employed.

Avarage absolute deviations are given for reported rate constants, and standard deviations, determined in the least-squares fits of ln(k/T) *vs.* 1/T, are given for activation parameters.

Results

Ligand Substitution Reaction

$$(VO)_2(l\text{-}C_4H_2O_6)_2^{4-} + d\text{-}C_4H_4O_6^{2-} \rightleftarrows$$

$$(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-} + l\text{-}C_4H_4O_6^{2-} \quad (2)$$

Though 1:2 complexes occur in these systems in the presence of excess ligand, equilibrium constants and extinction coefficients indicate that little or no interference by such species takes place under the conditions used for these experiments [6].

Rate measurements for varying reactant concentrations show that the initial reaction rates are first-order in reacting binuclear complex and zero-order in reacting ligand in the concentration range 0.005 to 0.020 mol l^{-1} for the two reactants. However, the appropriate logarithmic plots are found to have a slight curvature with the observed rate constant increasing during the reaction. Unsuccessful attempted fits of the data and results for varying experimental conditions allow us to rule out reversibility, formation of an intermediate, and experimental problems such as incomplete mixing as causes for the small nonlinearities observed. It is found, however, that the measured values of the rate constant determined assuming a strict first-order reaction increase with the addition of $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$ product (Table I). A rate equation assuming a reaction with two pathways – one autocatalytic – is therefore indicated (eqn. (3)).

$$d[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}]/dt =$$

$$= k_1[(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}] +$$

$$+ k_2[(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}]$$

$$[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}] \quad (3)$$

Integration of eqn. (3) gives the concentration of product, $[M_2dl]$, as a function of time, t, and initial reactant concentration, $[M_2ll]_o$:

$$[M_2dl] = \frac{k_1[M_2ll]_o\{e^{(k_2[M_2ll]_o + k_1)t} - 1\}}{k_2[M_2ll]_o + k_1e^{(k_2[M_2ll]_o + k_1)t}} \quad (4)$$

The spectral absorbance, A, for unit cell-path length is then given by

$$A = [M_2dl]\epsilon_{dl} + ([M_2ll]_o - [M_2dl])\epsilon_{ll} \quad (5)$$

At 940 nm, values of ϵ_{ll} = 39.70 l mol^{-1} cm^{-1} and ϵ_{dl} = 7.79 l mol^{-1} cm^{-1} have been determined for the extinction coefficients. The latter value has been corrected for incomplete formation of the *dl* isomer using the equilibrium constant of K = 16 for reaction (1) [2].

The two-term rate law given in eqn. (3) allows an excellent fit of the absorbances collected. The kinetic parameters determined are given in Table II. The values found for the first-order rate constant, k_1, are constant over a wide range of ligand and reactant complex concentrations for constant ionic strength and temperature. At μ = 3.00 mol l^{-1} and T = 25.0 °C, an average value of k_1 = 0.0112 ± 0.0013 sec^{-1} is found for all determinations excluding those carried out in the presence of added product. Utiliza-

TABLE II. Kinetic Parameters for Ligand Substitution.

T (°C)	μ (mol l^{-1})	Initial Concentrations[a] × 10^3, (mol l^{-1})				10^3 k_1[b] (sec^{-1})	k_2[b] (l mol^{-1} sec^{-1})
		M_2ll	M_2dl	d	l		
		$M_2ll + d \rightleftarrows M_2dl + l$					
25.0	3.00	5.0	–	5.0	–	12.6(0.9)	0.3(0.4)
25.0	3.00	5.0	–	10.0	–	11.1(2.3)	2.2(0.9)
25.0	3.00	5.0	–	20.0	–	11.6(0.9)	2.6(0.3)
25.0	3.00	10.0	–	10.0	–	8.6(2.1)	0.8(0.5)
25.0	3.00	10.0	–	20.0	–	10.1(0)	2.2(0.0)
25.0	3.00	20.0	–	20.0	–	13.3(1.5)	0.4(0.1)
25.0	1.00	10.0	–	10.0	–	12.6(1.3)	0.6(0.4)
25.0	2.00	10.0	–	10.0	–	9.7(1.2)	0.8(0.2)
25.0	4.00	10.0	–	10.0	–	9.1(0.8)	1.1(0.1)
20.0	3.00	10.0	–	10.0	–	5.0(1.0)	0.5(0.7)
15.0	3.00	10.0	–	10.0	–	2.5(0.2)	0.2(0.1)
25.0	3.00	10.0	–	10.0	40.0	11.6(0.5)	0.0(0.0)
25.0	3.00	10.0	10.0	10.0	–	14.1(0.6)	0.0(0.0)
25.0	3.00	10.0	10.0	20.0	–	13.2(2.1)	0.0(0.0)
25.0	3.00	10.0	10.0	10.0	10.0	14.9(3.0)	0.0(0.0)

[a] Concentrations after mixing assuming no reaction. 'M_2ll' = $(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}$, '$M_2dl$' = $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$, '$d$' = $d\text{-}C_4H_4O_6^{2-}$, 'l' = $l\text{-}C_4H_4O_6^{2-}$. [b] Average deviations for three determinations are given in parentheses.

tion of all data for $\mu = 3.00$ mol l^{-1} (again excluding data collected for systems with added product) permits the calculation of $\Delta H^{\neq} = 25 \pm 2$ kcal mol^{-1} and $\Delta S^{\neq} = 17 \pm 7$ eu. We recognize, of course, that nonideality in these electrolyte solutions may affect these parameters.

The values determined for the autocatalytic path rate constant, k_2, show a large variation, which is not unexpected. The k_2 values measure small deviations from strict first-order behavior and are subject to influence by any factors which cause such deviations. In the present case, reversibility of the overall reaction causes a deviation from strict first-order in a direction opposite to that caused by the second-order, autocatalytic path. Thus observed k_2 values are larger for those experiments where there is an excess of reactant ligand driving the reaction towards completion and are smaller for those experiments where there is added product. Use of fewer data points to determine values of k_2 near the start of the reaction (far from equilibrium) is not practical since there are then insufficient data to determine two constants (one of which, k_2, influences the data to only a small degree). Likewise, the number of data does not warrant the addition of yet another parameter to take reversibility into account – particularly when that parameter and k_2 are expected to show a correlation. At best, we can say that the larger values determined for k_2 are probably closer to the actual value, *i.e.*, $k_2 \gtrsim 3$ l mol^{-1} sec^{-1}.

Ligand Exchange Reaction

Studies of reaction (1) were carried out only with equimolar reactants since otherwise treatment of data and interpretation of results where there are two strongly coupled reactions becomes exceedingly difficult. The data under these conditions are fit well assuming the two-term rate equation

$$\begin{aligned} & d[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}]/dt = \\ & = k_3\{[(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}] + \\ & + [(VO)_2(d\text{-}C_4H_2O_6)_2^{4-}]\} + \\ & + k_4\{[(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}] + \\ & + [(VO)_2(d\text{-}C_4H_2O_6)_2^{4-}]\} \\ & [(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}]. \qquad (6) \end{aligned}$$

Integration of this rate equation gives a relationship of the same form as eqn. (4) except that $[M_2ll]$ is replaced by $[M_2dd] + [M_2ll]$. The kinetic parameters determined in the minimization of the squared deviations between calculated and observed absorbances are given in Table III.

An average value of $k_3 = 0.00693 \pm 0.00027$ sec^{-1} at $\mu = 3.00$ mol l^{-1} and T = 25.0 °C is found for the first-order rate constant. The variations of k_3 with temperature permit the calculation of the activation parameters $\Delta H^{\neq} = 23.5 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\neq} = 10 \pm 3$ eu.

TABLE III. Kinetic Parameters for Ligand Exchange.[a]

T (°C)	Initial Concentrations[b] × 10^3, (mol l^{-1})		10^3 k_3[c] (sec^{-1})	k_4[c] (l mol^{-1} sec^{-1})
	M_2ll	M_2dd		
		$\frac{1}{2}M_2ll + \frac{1}{2}M_2dd \rightleftarrows M_2dl$		
25.0	2.5	2.5	7.30(0.14)	0.20(0.07)
25.0	5.0	5.0	6.97(0.55)	0.07(0.02)
25.0	10.0	10.0	6.52(0.16)	0.07(0.01)
20.0	10.0	10.0	3.18(0.06)	−0.13(0.01)
15.0	10.0	10.0	1.61(0.02)	0.02(0.02)

[a] μ = 3.00 mol l^{-1}. [b] Concentrations after mixing assuming no reaction. 'M_2ll' = $(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}$, '$M_2dd$' = $(VO)_2(d\text{-}C_4H_2O_6)_2^{4-}$. [c] Average deviations for three determinations are given in parentheses.

The measured values of the rate constant, k_4, for the secondary path of the ligand exchange reaction are subject to the same vagaries as those of the rate constant, k_2, of the secondary path of the ligand substitution reaction. Moreover, since the values determined for k_4 are very small, the uncertainties are even larger. The ligand exchange reaction exhibits only very small deviations from strict first-order behavior.

Discussion

The rate determining step for the first-order path of the ligand substitution reaction must occur prior to ligand addition. That this step is dissociative is consistent with the positive activation entropy and with the magnitude of the activation enthalpy; however, the absence of a significant ionic strength effect on k_1 (Table II) indicates that the dissociation is only partial at this point. On the other hand, the results of the ligand exchange reaction study indicate that in that reaction, and probably therefore in the ligand substitution reaction, ligand loss occurs prior to ligand addition. These observations indicate the following primary steps for ligand substitution where M_2ll^* represents a partially dissociated species and M_2l represents the 2:1 complex remaining after ligand loss. Since protonation by solvent may occur during these steps, the charges on the intermediate species are not defined.

$$(VO)_2(l\text{-}C_4H_2O_6)_2^{4-} \underset{k_b}{\overset{k_a}{\rightleftarrows}} M_2ll^* \qquad (7)$$

$$M_2ll^* \underset{k_d}{\overset{k_c}{\rightleftarrows}} M_2l + l\text{-}C_4H_4O_6^{2-} \qquad (8)$$

$$M_2l + d\text{-}C_4H_4O_6^{2-} \underset{k_f}{\overset{k_e}{\rightleftarrows}} (VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-} \qquad (9)$$

Applying the steady state approximation to the intermediates and neglecting the reversibility of the last reaction we obtain the rate law

$$d[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)_2^{4-}]/dt = \frac{k_ak_ck_e[(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}][d\text{-}C_4H_4O_6^{2-}]}{(k_ck_e + k_bk_e)[d\text{-}C_4H_4O_6^{2-}] + k_bk_d[l\text{-}C_4H_4O_6^{2-}]} \qquad (10)$$

This rate equation gives the first term of eqn. (3) with $k_1 = k_ak_ck_e/(k_ck_e + k_bk_e)$ if $k_bk_d[l\text{-}C_4H_4O_6^{2-}] \ll (k_ck_e + k_bk_e)[d\text{-}C_4H_4O_6^{2-}]$. It is of interest that even in the presence of added $l\text{-}C_4H_4O_6^{2-}$, the observed rate constant k_1 is not changed (Table II).

In the ligand exchange reaction, ligand loss must occur prior to ligand addition in order to account for the form of the rate equation found and for the coupling of two enantiomeric reactions. For equimolar reactants, $[d\text{-}C_4H_4O_6^{2-}] = [l\text{-}C_4H_4O_6^{2-}]$ at all times and, if the same mechanism holds for the principle path in this reaction as proposed for the ligand substitution first-order path (eqns. (7)–(9)), a rate law identical to the first term of eqn. (6) is found with $k_3 = k_ak_bk_c/(k_ck_e + k_bk_e + k_bk_d)$. Since the work on the ligand substitution reaction indicates that $k_bk_d \ll (k_ck_e + k_bk_e)$, one would predict that $k_3 \sim k_1$ if the two types of reaction proceed by this same mechanism. Though the rate constants are similar (0.0112 and 0.00693 sec^{-1}), their difference exceeds that which can be accounted for by experimental error. On the other hand, the activation parameters for the ligand substitution and ligand exchange reactions are equal within experimental error. It is likely that, in fact, both reactions proceed by identical mechanisms, as evidenced by the similarity in their kinetic parameters, and that k_1 and k_3 differ marginally owing to media effects (absence or presence of added ligand).

A mechanism involving dissociation or partial dissociation of ligand assisted by the product com-

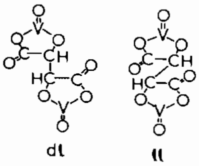

Fig. 1. 'Stair-step' and colinear arrangement of vanadium atoms in *dl* and *ll* isomers, respectively (side view, only one tartrate group shown).

plex is consistent with the autocatalytic path rate equation found for the ligand substitution reaction. One such mechanism would involve the following steps:

$$(\mathrm{VO})_2(l\text{-}\mathrm{C_4H_2O_6})_2^{4-} + (\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} \xrightleftharpoons[k_v]{k_u} (\mathrm{VO})_2(l\text{-}\mathrm{C_4H_2O_6})_2^{4-}\cdot(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} \qquad (11)$$

$$(\mathrm{VO})_2(l\text{-}\mathrm{C_4H_2O_6})_2^{4-}\cdot(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} \xrightleftharpoons[k_x]{k_w} \mathrm{M_2}ll^*\cdot(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} \qquad (12)$$

$$\mathrm{M_2}ll^*\cdot(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} + d\text{-}\mathrm{C_4H_4O_6^{2-}} \xrightleftharpoons[k_z]{k_y} 2(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-} + l\text{-}\mathrm{C_4H_4O_6^{2-}} \qquad (13)$$

Application of the steady state approximation (ignoring reversibility of the last step) gives

$$d[(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-}]/dt = \frac{k_u k_w k_y [(\mathrm{VO})_2(l\text{-}\mathrm{C_4H_2O_6})_2^{4-}]}{(k_w k_y + k_v k_y)[d\text{-}\mathrm{C_4H_4O_6^{2-}}] + k_v k_x} \times [(\mathrm{VO})_2(d\text{-}\mathrm{C_4H_2O_6})(l\text{-}\mathrm{C_4H_2O_6})^{4-}]\,[d\text{-}\mathrm{C_4H_4O_6^{2-}}] \qquad (14)$$

This gives the rate equation observed for the secondary, autocatalytic path (see eqn. (3)) with

$$k_2 = \frac{k_u k_w k_y [d\text{-}\mathrm{C_4H_4O_6^{2-}}]}{(k_w k_y + k_v k_y)[d\text{-}\mathrm{C_4H_4O_6^{2-}}] + k_v k_x} \qquad (15)$$

A similar mechanism could hold for the autocatalytic path found for the ligand exchange reaction. In this case, however, $[d\text{-}\mathrm{C_4H_4O_6^{2-}}]$ is expected to be very small and, when this is true, k_2 (now designated k_4) decreases (eqn. 15).

The presence of an autocatalytic path in these reactions (though nearly negligible in the ligand exchange reaction) is not surprising. The *dl* isomeric form of the vanadyl(IV) tartrate binuclear complex has a 'stair-step' geometry [7] in which a sixth, axial site on vanadium may be available for coordination (Fig. 1). This site is blocked by the second vanadium atom in the *dd* and *ll* isomers [8]. Metal ions often catalyze reactions involving complexation of multidentate ligands [5]; moreover, we have observed catalysis of ligand exchange reactions of vanadyl(IV) tartrates by copper ion in our laboratory.

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