A Family of (*N*-Salicylidene-α-amino acidato)vanadate Esters Incorporating Chelated Propane-1,3-diol and Glycerol: Synthesis, Structure, and Reaction

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The brown colored title complexes, $V^{V}O(Asal)(Hpd)$ and $V^{V}O(Asal)(H_2pt)$, have been synthesized in excellent yields by reacting $V^{IV}O(Asal)(H_2O)$ with propane-1,3-diol (H_2pd) and glycerol (H_3pt), respectively, in methanol. Here $Asal^{2-}$ is the deprotonated salicylaldimine of glycine (A = g), L-alanine (A = a), L-valine (A = v), or L-phenylalanine (A = p). The complexes have relatively low oxovanadium(V)−oxovanadium(IV) reduction potentials (−0.2 V vs SCE in dimethyl sulfoxide). The X-ray structures of VO(gsal)(Hpd) and VO(gsal)(H_2pt) have revealed distorted octahedral VO_5N coordination. Six-membered and five-membered O,O chelation occur for Hpd^- and H_2pt^-, respectively, an undissociated alcohol function lying trans to the oxo oxygen atom. The tridentate salicylaldimine ligand spans meridionally and has a folded structure consisting of two planar parts intersecting along a C−N bond. The V−O(alkoxide) bond in the complexes is ∼0.6 Å shorter than the V−O(alcohol) bond. The alkoxidic chelate ring partially hydrolyzes in moist solvents—the six-membered ring in VO(Asal)(Hpd) more easily than the five-membered ring in VO(Asal)(H_2pt). The hydrolysis is suppressed in the presence of the relevant free alcohol. The ^{51}V NMR chemical shifts differ by ∼20 ppm between VO(Asal)(Hpd) and VO(Asal)(H_2pt) and are diagnostic of the alkoxidic chelate ring size. Species with chiral $Asal^{2-}$ ligands display diastereoisomeric equilibria in solution, and the equilibrium constants K = [endo]/[exo] have been determined from the ^{51}V NMR signal intensity. The trend in K values is L-alanine < L-phenylalanine < L-valine (for given alkoxidic chelation) and $Hpd^- < H_2Pt^-$ (for given amino acid residue). These trends are consistent with size effects. Crystal data are as follows. VO(gsal)(Hpd): chemical formula, $C_{12}H_{14}NO_6V$; crystal system, monoclinic; space group, $P2_1/n$; a = 9.229(5), b = 12.655(6), c = 11.478(4) Å; β = 99.61(4)°; Z = 4. VO(gsal)(H_2pt): chemical formula, $C_{12}H_{13}NO_7V$; crystal system, monoclinic; space group, $P2_1/c$; a = 10.962(6), b = 9.544(4), c = 13.323(5) Å; β = 102.67(4)°; Z = 4.

Introduction

It has been known for a long time that vanadium, like phosphorus, forms esters in the pentavalent state.[1] The functional motif characterizing such species, also called oxovanadium alkoxides, is $V^{V}O(OR)$.[2] The richness of vanadate ester chemistry is however emerging only in recent years. A sizable number of compound types representing diverse forms of structure and reactivity are already available.[3−11] Oxovanadium alkoxides have been documented to act as selective redox reagents[12] and as mimics in studies of phosphorylation,[13] haloperoxidation[7,14] and insulin action.[15] The present work concerns the binding of simple polyols to oxovanadium(V)—specifically propane-1,3-diol and propane-1,2,3-triol (glycerol). The diol has received previous attention,[6d,10c,10d] but no instance is documented where it forms a six-membered V(O,O) chelate ring either in the solid state or in solution. Instead it is known to bridge two or more vanadium sites readily affording

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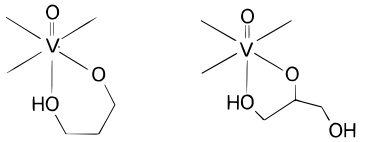
Table 1. Selected Spectral and Electrochemical Data

compds	IR data,[a] cm^{-1} VO	IR data,[a] cm^{-1} $-CO_2$	IR data,[a] cm^{-1} OH	UV−vis:[b] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$,[b-d] V (ΔE_p,[e] mV)
VO(gsal)(H_2pt)	975	1660, 1625, 1320	3180	485 (540), 350 (5760)	−0.24(140)
VO(L-asal)(H_2pt)	980	1675, 1620, 1310	3170	485 (520), 350 (5640)	−0.23(130)
VO(L-vsal)(H_2pt)	985	1680, 1620, 1300	3150	500 (660), 345 (4630)	−0.22(120)
VO(L-psal)(H_2pt)	978	1670, 1620, 1310	3200	490 (760), 345 (6180)	−0.23(140)
VO(gsal)(Hpd)	990	1660, 1630, 1330	3250	480[f] (510), 345 (6710)	−0.18(160)
VO(L-asal)(Hpd)	970	1670, 1610, 1310	3150	480[f] (480), 340 (6340)	−0.19(160)
VO(L-vsal)(Hpd)	980	1675, 1615, 1300	3220	485[f] (500), 340 (6560)	−0.16(150)
VO(L-psal)(Hpd)	970	1660, 1620, 1320	3200	475[f] (610), 340 (6330)	−0.17(150)

[a] In KBr disks. [b] In dry dimethyl sulfoxide containing 5−10% H_3pt or H_2pd. [c] At a platinum electrode; supporting electrolyte, tetraethylammonium perchlorate (TEAP; 0.1 M); scan rate, 50 mV s^{-1}; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M. [d] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [e] $\Delta E_p = E_{pa} - E_{pc}$. [f] Shoulder.

multinuclear species.[6d] As for glycerol, no report on the characterization of any authentic vanadate ester appears to exist.

The above state of development has prompted us to undertake the task of designing mononuclear oxovanadium alkoxides incorporating chelation by the above diol and triol. This objective has been acheived and the structural motifs with six-membered, **1**, and five-membered, **2**, chelate rings have been

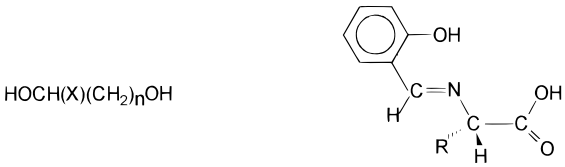


1 2

realized from propane-1,3-diol and glycerol, respectively. Salicylaldimines of α-amino acids are employed as coligands. The X-ray structures of two representative esters are reported. Chelate ring size and diastereoisomeric equilibria in solution are scrutinized with the help of ^{51}V NMR, and in this context complexes[8] of ethane-1,2-diol are revisited. Two reactions have been briefly scrutinized: hydrolysis of the alkoxidic chelate motif and one-electron electroredox of the metal site.

Results and Discussion

A. Ligands and Complexes. The alcohols concerning us in the present work and their abbreviations are set out in **3**. The potentially dissociable H atoms in H_2ed, H_2pd, and H_3pt belong to the alcohol groups. To ensure mononuclear configuration we used the strategy of blocking three oxovanadium coordination positions leaving just two (assuming hexacoordination) for possible chelation by alcohol/alkoxidic functions. Salicylaldimines of (α-amino acids (glycine, L-alanine, L-valine, and L-phenylalanine) have been used. These have also provided an opportunity for monitoring the effect of coligand chirality on diastereoisomeric population of the oxovanadium alkoxides formed. The salicylaldimine ligands will be generally abbreviated as H_2Asal, the two H atoms (phenolic and carboxylic) being potentially dissociable; abbreviations used for specific compounds are set out in **4**.



	X	n
H_2ed	H	1
H_2pd	H	2
H_3pt	CH_2OH	1

3

R	
H	H_2gsal
CH_3	L-H_2asal
$CHMe_2$	L-H_2vsal
CH_2Ph	L-H_2psal

4

The reaction of oxovanadium(IV) aquo complexes[4,16−19] of type $V^{IV}O(Asal)(OH_2)$ with excess propane-1,3-diol in methanol under ambient conditions afforded deep red solutions from which dark brown crystalline solids of composition $V^VO(Asal)$-(Hpd) deposited in high yields. Upon replacement of the diol by glycerol in the preparative procedure, complexes of type $V^VO(Asal)(H_2pt)$ deposited. In these synthetic reactions the vanadium oxidation state increases by one, oxygen of air being the oxidant. This is consistent with the low oxovanadium(V)−oxovanadium(IV) reduction potentials of the complexes (vide infra).

The new species incorporating Hpd^- and H_2pt^- chelation synthesized in the present work are listed in Table 1 along with selected spectral data. The V═O stretch occurs as a sharp intense peak in the frequency range 970−985 cm^{-1}, suggesting hexacoordination.[20] Carboxylate monocoordination is apparent from the presence of one symmetric ($\sim$1300 cm^{-1}) and two asymmetric ($\sim$1620 cm^{-1} and $\sim$1660 cm^{-1}) stretching

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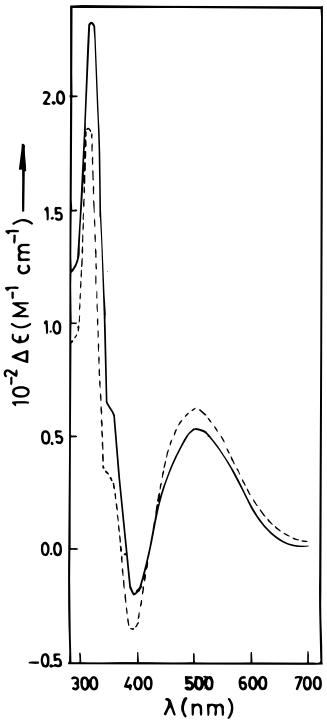

Figure 1. CD spectra of VO(L-asal)(H_2pt) (—) and VO(L-vsal)(H_2pt) (- - -) in dry dimethyl sulfoxide solution.

modes.[21] The alcoholic O−H stretch occurs as a broad band near 3200 cm^{-1} suggesting engagement in hydrogen bonding. These structural features are fully consistent with the X-ray work reported below.

In UV−vis spectra of the complexes an intense band occur in the region 340−350 nm associated with a relatively weak band/shoulder (480−500 nm). The latter is probably of O(alkoxide) → V LMCT origin.[7,14] Bond length data (*vide infra)* reveal that the complexes indeed involve strong O(alkoxide) → V π-donation. The complexes having chiral $Asal^{2-}$ ligands are optically active in solution and display characteristic CD spectra. Two representative spectra are displayed in Figure 1. In the LMCT region, there is a prominent positive peak near 500 nm associated with a weaker negative peak at ∼400 nm.

The retention of solution optical activity is significant in relation to diastereoisomeric equilibria considered in a later section.

B. Crystal and Molecular Structure. a. Coordination Sphere and the $Asal^{2-}$ Ligand. The structures of VO(gsal)(Hpd) and VO(gsal)(H_2pt) have been determined. Views of the two molecules are shown in Figures 2 and 3, and selected bond parameters are listed in Table 2. The vanadium coordination sphere VO_5N has a severely distorted octahedral geometry in either case—the metal atom being displaced ∼0.3 Å from the plane (mean deviation ∼0.05 Å) of the O4, O2, O6, and N atoms toward the oxo oxygen atom O1. The tridentate meridionally disposed $gsal^{2-}$ ligand is constituted of two excellently planar segments (OC_6H_4CHN and CCO_2; mean deviation <0.04 Å); the dihedral angles between them are 26.0 and 35.1° in VO(gsal)(Hpd) and VO(gsal)(H_2pt), respectively.

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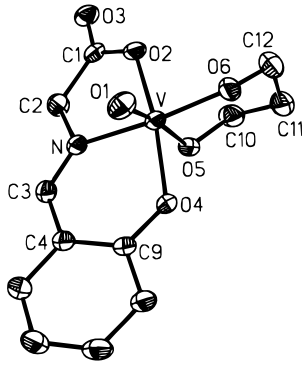


Figure 2. Perspective view and atom-labeling scheme of VO(gsal)(Hpd). All non-hydrogen atoms are represented by their 30% probability ellipsoids.

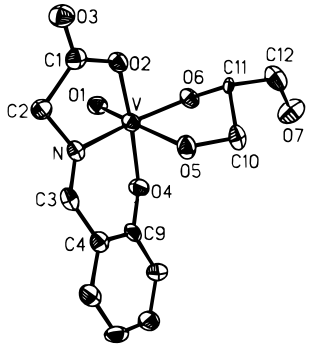


Figure 3. Perspective view and atom-labeling scheme of VO(gsal)(H_2pt). All non-hydrogen atoms are represented by their 30% probability ellipsoids.

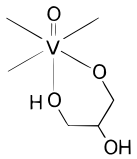
Table 2. Selected Bond Lengths (Å) and Angles (deg) for VO(gsal)(Hpd) and VO(gsal)(H_2Pt)

	VO(gsal)(Hpd)	VO(gsal)(H_2pt)
	Distances	
V−O1	1.591(3)	1.580(5)
V−O2	1.970(3)	1.965(5)
V−O4	1.863(3)	1.849(6)
V−O5	2.328(3)	2.312(5)
V−O6	1.771(3)	1.792(4)
V−N	2.098(3)	2.077(6)
O2−Cl	1.297(5)	1.299(8)
O3−Cl	1.218(5)	1.234(9)
	Angles	
O1−V−O2	101.8(1)	97.5(2)
O1−V−O4	98.2(1)	99.1(2)
O1−V−O5	172.7(1)	178.4(2)
O1−V−O6	101.7(2)	100.7(2)
O2−V−O4	153.4(1)	157.0(2)
O2−V−O5	80.0(1)	81.5(2)
O2−V−O6	89.2(1)	92.1(2)
O4−V−O5	78.0(1)	82.2(2)
O4−V−O6	103.7(1)	100.3(2)
O5−V−O6	85.3(1)	78.2(2)
O1−V−N	93.7(1)	101.9(2)
O2−V−N	76.9(1)	76.3(2)
O4−V−N	84.6(1)	84.9(2)
O5−V−N	79.8(1)	79.1(2)
O6−V−N	161.1(1)	155.7(2)

b. Alkoxidic Chelate Rings. The Hpd^- and H_2pt^- ligands bind respectively in the six-membered and five-membered chelate modes **1** and **2**. In VO(gsal)(Hpd) all the 14 H atoms in the complex were directly located in difference maps. The O5 and O6 atoms of the V(Hpd) fragment are respectively alcoholic and alkoxidic in nature. The V−O6 bond, 1.771(3) Å, is much shorter than the V−O5 bond, 2.328(3) Å. It is

logical that the alcoholic donor rather than the stronger alkoxidic donor lies trans to the oxo oxygen. This decreases competition between alkoxidic and oxo oxygen atoms for the same acceptor orbitals of the metal in O → V type donation. The six-membered chelate ring has a distorted chair conformation.

In the case of VO(gsal)(H_2pt) none of the H_2pt^- hydrogen atoms could be directly located. It is however clear from the bond length trends V−O6, 1.792(4) Å, and V−O5, 2.312(5) Å, that the oxygen atoms O6 and O5 are respectively alkoxidic and alcoholic in nature. Secondary alkoxides are better donors than primary alkoxides, and the present complex indeed involves secondary alkoxidic binding (V−O6). This factor as well as the inherently superior stability (vide infra) of the five-membered chelate ring as compared to the possible six-membered alternative, **5**, leads exclusively to the chelation mode **2**. In effect glycerol binds as a substituted ethane-1,2-diol rather than a substituted propane-1,3-diol.



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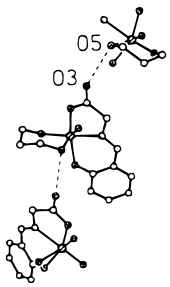
c. Hydrogen Bonding. Both the complexes are intermolecularly hydrogen bonded into infinite patterns. In VO(gsal)(Hpd) the bonding involves the alcoholic oxygen atom O5 of one molecule and the uncoordinated carboxylate oxygen atom O3 of a second molecule as in **6**, the internuclear O5···O3 distance being 2.745(10) Å. In the case of VO(gsal)(H_2pt) the pendent $-CH_2OH$ oxygen atom O7 of one molecule interlinks O5 and O3 atoms of two adjacent molecules as in **7**, the O7···O3 and O7···O5 lengths being 2.611(11) and 2.657(13) Å, respectively.



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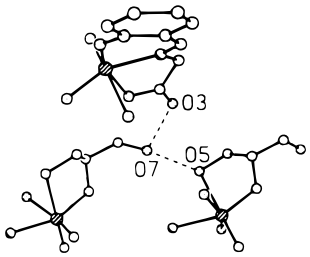

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C. Solution Structure. The ^{51}V NMR spectra of the complexes in dry dimethyl-d_6 sulfoxide solution have been found to be uniquely useful in revealing two aspects of solution structure: (i) size of the alkoxidic chelate rings; (ii) diastereoisomeric equilibria for species having optically active $Asal^{2-}$ ligands. Chemical shift data are listed in Table 3, and representative spectra are shown in Figure 4.

a. Ring Size. In the case of complexes of the achiral $gsal^{2-}$ ligand only a single ^{51}V NMR resonance is observed. In VO(gsal)(Hpd) having the six-membered chelate ring **1,** the ^{51}V chemical shift is −550 ppm, while, in the ethane-1,2-diol complex VO(gsal)(Hed), having the five-membered chelate ring **8**, it is −531 ppm. Interestingly in the glycerol complex VO(gsal)(H_2pt) the shift, −529 ppm, lies close to that of VO(gsal)(Hed) and there is no signal near −550 ppm. The rationale is that the glycerol complex has the five-membered chelate ring **2** in solution as well.

Table 3. ^{51}V NMR Spectral Data in Dimethyl-d_6 Sulfoxide at 300 K

compd	δ/ppm	K
VO(gsal)(Hed)	−531	
VO(L-asal)(Hed)	−524,[a] −534[b]	2.5
VO(L-vsal)(Hed)	−525,[a] −535[b]	31.4
VO(L-psal)(Hed)	−522,[a] −535[b]	3.8
VO(gsal)(H_2pt)	−529	
VO(L-asal)(H_2pt)	−523,[a] −534[b]	6.1
VO(L-vsal)(H_2pt)	−522,[a] −535[b]	40.5
VO(L-psal)(H_2pt)	−520,[a] −535[b]	8.3
VO(gsal)(Hpd)	−550	
VO(L-asal)(Hpd)	−549,[a] −556[b]	1.7
VO(L-vsal)(Hpd)	−547,[a] −556[b]	10.9
VO(L-psal)(Hpd)	−544,[a] −556[b]	2.3

[a] Exo configuration. [b] Endo configuration.

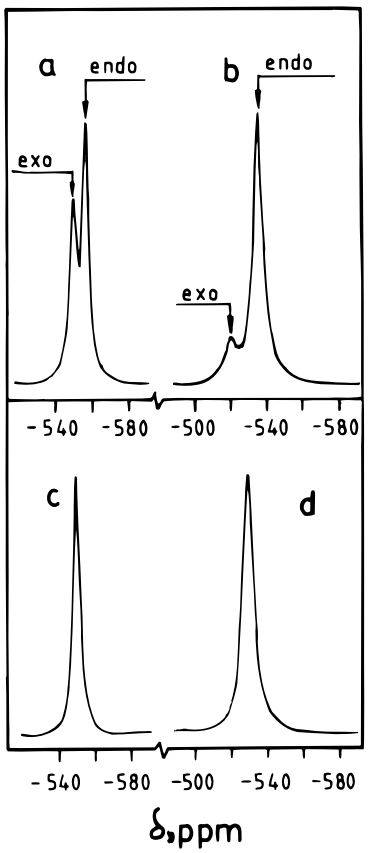
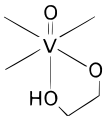


Figure 4. ^{51}V NMR spectra of (a) VO(L-asal)(Hpd), (b) VO(L-psal)(H_2-pt), (c) VO(gsal)(Hpd), and (d) VO(gsal)(H_2pt) in dry dimethyl-d_6 sulfoxide.



8

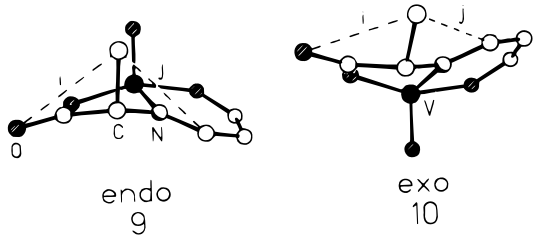
b. Diastereoisomerism. In the complexes with chiral $Asal^{2-}$ ligands two distinct ^{51}V resonances of unequal intensity are generally observed (Table 3). Again the chemical shifts in the six-membered Hpd^- complexes (near −547 ppm and −556 ppm) are more negative than those of the five-membered $Hed^-$and H_2pt^- species (near −522 ppm and −535 ppm). The metal site in the present complexes is inherently asymmetric. When $Asal^{2-}$ is chiral, two diastereoisomeric forms are thus

Table 4. Proton NMR Spectral Data[a,b] in Dimethyl-d_6 Sulfoxide [δ, ppm (J, Hz)]

compds	H2	H3	H10	H11	H12
VO(gsal)(H_2pt)	4.55 (d,[c] 19.2), 5.09 (d,[c] 19.2)	8.87s	3.64 m	4.91 m	3.32 m
VO(L-asal)(H_2pt)	4.56[d] (q, 7.2), 4.73[e] (q, 7.2)	8.80[d] s, 8.92[e] s	3.80 m	4.76 m	3.48 m
VO(L-vsal)(H_2pt)	4.15[d] (d, 7.3), 4.26[e] (d, 7.3)	8.81[d] s, 8.95[e] s	3.54 m	4.78 m	3.37 m
VO(L-psal)(H_2pt)	4.63[d] (dd, 10.0, 5.0), 4.98[e] (dd, 10.0, 5.0)	7.87[d] s, 7.64[e] s	3.78 m	4.80 m	3.56 m
VO(gsal)(Hpd)	4.54 (d,[c] 19.6), 4.91 (d,[c] 19.6)	8.74 s	3.61 m	1.99 m	5.54 m
VO(L-asal)(Hpd)	4.51[d] (q, 7.0), 4.69[e] (q, 7.0)	8.76[d] s, 8.87[e] s	3.60 m	1.98 m	5.54 m
VO(L-vsal)(Hpd)	4.12[d] (d, 7.2), 4.22[e] (d, 7.2)	8.78[d] s, 8.93[e] s	3.47 m	1.98 m	5.52 m
VO(L-psal)(Hpd)	4.58[d] (dd, 10.0, 5.0), 4.89[e] (dd, 10.0, 5.0)	7.82[d] s, 7.76[e] s	3.56 m	1.99 m	5.58 m

[a] The numbering system corresponds to that in Figures 2 and 3, e.g., H2 represents proton(s) attached to C2. [b] The chemical shift values of free alcohol [δ, ppm (J, Hz)] are follows. H_2pd: 1-CH_2 and 3-CH_2, 3.45 (q, 6.5); 2-CH_2, 1.57 (qn, 6.5); 1-OH and 3-OH, 4.41 (t, 5.0). H_3pt: 1-CH_2, 2-CH, and 3-CH_2, 3.33 m; 1-OH and 3-OH, 4.42 (t, 5.7); 2-OH, 4.49 (d, 4.7); s = singlet; d = doublet; t = triplet; q = quartet; qn = quintet; m = multiplet. [c] The two H_2 protons are inequivalent. [d] Endo configuration. [e] Exo configuration.

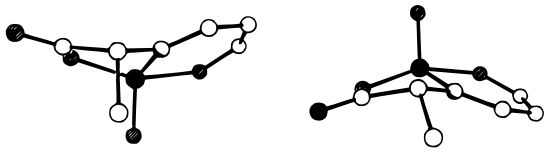
possible. These can be conveniently represented as endo **9** and



endo 9 exo 10

exo **10** forms corresponding to the two different relative positions of the R substituent in the amino acid residue and the oxovanadium oxygen atom (only the first carbon atom of R is shown in **9** and **10**). The interconversion between **9** and **10** implies inversion of the substitution-labile vanadium site.

Endo and exo forms can also arise due to $Asal^{2-}$ carbon inversion as represented in **11** and **12**. Here **9** and **12** are related



endo 11 exo 12

by carbon inversion and so are **10** and **11**. In effect **11** is the enantiomer of **9** and **12** that of **10**. However carbon inversion of the above type would be energetically very unfavorable and is unlikely to occur in the present situation. The lack of carbon racemization is proven by the retention of optical activity as revealed by circular dichroism of the chiral complexes, vide supra. The relevant endo and exo forms are thus **9** and **10** in which the chiral carbon retains the *S* configuration of the parent L-amino acid.

The two ^{51}V resonances are assigned to the endo, **9**, and exo, **10**, isomers existing in equilibrium in solution. The stronger signal lying at higher field corresponds to the endo form, see below. From the relative intensities of the two resonances the equilibrium constant K, eq 1, has been computed (Table 3,

$$K = [\text{endo}]/[\text{exo}] \quad (1)$$

estimated error in K is 10%). The K values are found to depend on the R group in the order Me < CH_2Ph < $CHMe_2$ and on the alkoxidic chelate ring in the order six-membered < five-membered.

These trends are consistent with steric control, the two crucial nonbonded interactions being those of the R group with the uncoordinated carboxyl oxygen atom and the azomethine carbon atom as depicted by the dotted vectors **i** and **j** in **9** and **10**. These interactions can vary significantly between the exo and endo configurations because the $Asal^{2-}$ ligand is not planar but has two separate planar regions (OC_6H_4CHN and CCO_2) intersecting along an N−C bond; vide supra.

An estimate of the above-noted steric effect can be made using the structure of the chiral complex VO(psal)(Hed) which is exclusively endo, **9**, in the crystalline state.[8a] The exo configuration **10** was generated from **9**. The values of the **i** and **j** vectors are respectively 3.14(1) and 3.22(1) Å in **9** and 2.88(1) and 2.71(1) Å in **10**. The interactions are thus strongly repulsive in the exo form, the van der Waals radii[22] of carbon and oxygen being 1.70 and 1.50 Å, respectively. The unfavorable exo form is not at all observed in the crystalline state, and it is only a minor equilibrium contributor in mobile solutions.

As the R group becomes bulkier, the repulsive interactions in the exo form evidently increase progressively diminishing its equilibrium concentration of this form. The dihedral angle between the planar parts of $Asal^{2-}$ ligand is ~10° lower in VO(gsal)(Hpd) compared to that in VO(gsal)(H_2pt); vide supra. The six-membered chelate ring (type **1**) is effectively bulkier than the five-membered counterpart (type **2**) tending to flatten the $Asal^{2-}$ ligand and thus decreasing the repulsive interactions in the exo configuration. The observed dependences of K on the R group and on the alkoxidic chelate ring size are thus internally consistent.

Diastereoisomers are also observable in the case of certain signals in ^{1}H NMR (Table 4). A representative example is shown in Figure 5a. Equilibrium constants (300 K) calculated from signal intensities are as follows: VO(L-asal)(H_2pt), 6.2; VO(L-vsal)(H_2pt), 40.0; VO(L-psal)(H_2pt), 8.3; VO(L-asal)(Hpd), 1.7; VO(L-vsal)(Hpd), 10.7; VO(L-psal)(Hpd), 2.1. The values agree satisfactorily with those (Table 3) derived from ^{51}V NMR data.[23]

D. Reactions. a. Alkoxide Hydrolysis. In dimethyl-d_6 sulfoxide solution, the methylene and methine ^{1}H NMR resonances of coordinated Hpd^- and H_2pt^- are systematically shifted to lower fields compared to those of the corresponding free alcohols, Table 4. In particular the shift of the bound alkoxidic signal can be as large as 2 ppm. This has provided a convenient tool for identifying the possible hydrolysis of the bound alkoxidic ligand. The VO(Asal)(Hpd) complexes indeed undergo partial hydrolysis even when the solvent is only slightly wet (~0.5% H_2O). A representative example is shown in Figure

(22) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(23) In an earlier report[8a] on VO(L-psal)(Hed), diastereoisomers were not detected in the ^{1}H NMR. However following the ^{51}V NMR results (Table 3) a more careful examination of the ^{1}H NMR spectra have been made revealing that the diastereoisomeric signals are actually present.

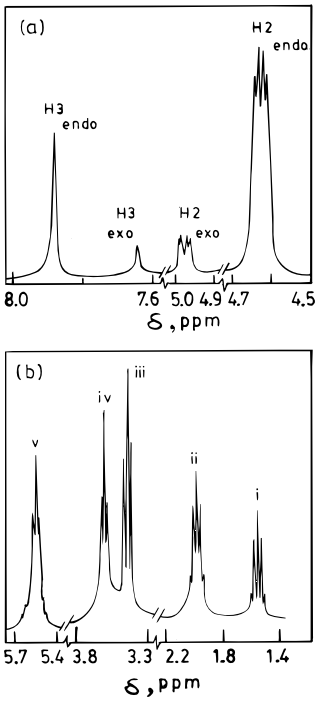


Figure 5. (a) ^{1}H NMR spectrum of VO(L-psal)(H_2pt) showing isomeric H2 and H3 signals in dimethyl-d_6 sulfoxide. (b) Methylene signals of VO(gsal)(Hpd) dissolved in dimethyl-d_6 sulfoxide solution containing ~0.5% water. Resonances i and iii correspond to the free diol while ii, iv, and v correspond to chelated diolate(1−)-O^1,O^2.

5b. The hydrolysis can be suppressed by adding H_2pd to the solution. The VO(Asal)(H_2pt) complexes are much less prone to hydrolysis, and in the same wet solvent as noted above there is no sign of formation of free H_3pt. Thus the five-membered chelate ring **2** has superior hydrolytic stability compared to the six-membered chelate ring **1**. The reported difficulty[6d,10c,d] in generation of vanadate esters incorporating propane-1,3-diol chelation in aqueous media is thus understandable. To ensure prevention of hydrolysis, solution studies of the present complexes were usually carried out in dry dimethyl sulfoxide containing 5−10% of the relevant free alcohol.

b. Metal Redox. All the complexes reported in this work are electroactive at platinum in dimethyl sulfoxide solution. A quasireversible one-electron response is observed near −0.2 V vs SCE. The $E_{1/2}$ values (Table 1) of the glycerol complexes are slightly more negative than those of the propane-1,3-diol complexes. The couple is assigned to $V^VO-V^{IV}O$ redox. In the synthesis of the present complexes from $V^{IV}O$(Asal)(H_2O) the metal oxidation state increases by one unit ($V^{IV}O \rightarrow V^VO$). Oxygen of air can spontaneously act as the oxidizing agent because the metal reduction potentials of the species formed are so low. Alkoxide formation greatly stabilizes the oxovanadium(V) state.

Concluding Remarks

The main findings of this work can now be summarized. The first oxovanadium alkoxides incorporating chelation by propane-1,3-diol and glycerol in the six-membered and five-membered modes **1** and **2**, respectively, have realized and characterized. Crucial to this synthetic success has been the utilization of salicylaldimines of α-amino acids as coligands.

^{51}V NMR data have been successfully utilized to reveal that the chelate rings **1** and **2** are conserved in solution and glycerol does not form the six-membered ring **5** at all. The more important finding is the endo−exo (**9**−**10**) isomerism in solution for the species incorporating chiral salicylaldimines. The steric factors controlling the equilibrium—bulk of the amino acid R group and the alkoxidic ring size—have been analyzed. The root of the phenomenon lies in the folded nature of the salicylaldime ligand.

The alkoxidic chelate ring is susceptible to hydrolysis in moist solvents, the six-membered ring **1** being more easily hydrolyzed. The low oxovanadium(V)−oxovanadium(IV) reduction potential reflects the strong stabilization of pentavalent state by alkoxide coordination.

Experimental Section

Materials. Electrochemical grade dry dimethyl sulfoxide, methanol, and tetraethylammonium perchlorate were obtained as before.[24] All other chemicals and solvents were of analytical grade and used as received.

Physical Measurements. ^{51}V NMR spectra were recorded on a Varian spectrometer of 78.8 MHz and 25 °C, referenced to $VOCl_3$ as the external reference. Proton NMR spectra were recorded on Bruker FT spectrometers, infrared spectra on a Perkin-Elmer 783 spectrophotometer, electronic spectra on a Hitachi 330 spectrophotometer, and CD spectra on a JASCO 500 spectropolarimeter. Electrochemical measurements were performed on a PAR model 370-4 system as previously.[25] All potentials reported in this work are uncorrected for junction contribution. Most solution experiments were performed in dry dimethyl sulfoxide incorporating 5−10% of the relevant free alcohol to supress the possible hydrolysis. The alcohol was not added only in ^{1}H NMR experiments in which the hydrolysis phenomenon itself was under scrutiny. A Perkin-Elmer elemental analyzer was used to collect microanalytical data (C, H, N).

Preparation of Complexes. The VO(Asal)(Hed) complexes were prepared by a reported[8] procedure. The VO(Asal)(H_2pt) and VO(Asal)(Hpd) complexes were prepared by using a general method with VO(Asal)(H_2O)[4,16−19] as the starting material. Details are given below for two representative cases. The synthesized complexes generally have good solubility in dimethyl sulfoxide but not in halocarbons and alcohols.

(Propane-1,2,3-triolato(l−)-*O*^{1},*O*^{2})oxo(*N*-salicylidene-L-valinato)-vanadium(V), VO(L-vsal)(H_2pt). To a methanolic solution (15 mL) of VO(L-vsal)(H_2O) (0.10 g, 0.33 mmol) was added propane-1,2,3-triol (1.23 g, 13.37 mmol; 1 mL). A dark red solution was formed. On slow evaporation in air at room temperature it afforded a deep brown crystalline compound. It was filtered off, washed thoroughly with water, and dried in *vacuo* over P_4O_{10}. Yield: 0.11 g (90%). Anal. Calcd for $C_{15}H_{20}NO_7V$: C, 47.74; H, 5.30; N, 3.71. Found: C, 47.64; H, 5.33; N, 3.73.

The compounds VO(gsal)(H_2pt), VO(L-asal)(H_2pt) and VO(L-psal)(H_2pt), were prepared similarly in 86%, 78%, and 84% yield, respectively. Anal. Calcd for VO(gsal)(H_2pt), $C_{12}H_{14}NO_7V$: C, 42.99; H, 4.18; N, 4.18. Found: C, 43.06; H, 4.22; N, 4.12. Calcd for VO(L-asal)(H_2pt), $C_{13}H_{16}NO_7V$: C, 44.70; H, 4.58; N, 4.01. Found: C, 44.83; H, 4.51; N, 4.06. Calcd for VO(L-psal)(H_2pt), $C_{19}H_{20}NO_7V$: C, 53.64; H, 4.70; N, 3.29. Found: C, 53.52; H, 4.77; N, 3.26.

(Propane-1,3-diolato(1−)-*O*^{1},*O*^{2})oxo(*N*-salicylidene-L-alaninato)-vanadium(V), VO(L-asal)(Hpd). A 0.10 g (0.36 mmol) sample of VO(L-asal)(OH_2) was dissolved in 15 mL of methanol. To the resulting light red solution was added 1 mL (1.05 g, 13.82 mmol) of propane-1,3-diol, and the mixture was warmed on water bath for a few minutes. The resulting dark red solution was slowly evaporated in air at room temperature affording a deep brown crystalline compound. It was filtered off, washed thoroughly with water, and dried in *vacuo* over P_4O_{10}. Yield: 0.10 g (85%). Anal. Calcd for $C_{13}H_{16}NO_6V$: C, 46.85; H, 4.80; N, 4.20. Found: C, 46.94; H, 4.75; N, 4.26.

(24) Dutta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673.
(25) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423.

The compounds VO(gsal)(Hpd), VO(L-vsal)(Hpd), and VO(L-psal)(Hpd) were prepared similarly in 82%, 85%, and 87% yield, respectively. Anal. Calcd for VO(gsal)(Hpd), $C_{12}H_{14}NO_6V$: C, 45.14; H, 4.39; N, 4.39. Found: C, 45.26; H, 4.55; N, 4.30. Calcd for VO(L-vsal)(Hpd), $C_{15}H_{20}NO_6V$: C, 49.86; H, 5.54; N, 3.88. Found: C, 49.73; H, 5.47; N, 3.92. Calcd for VO(L-psal)(Hpd), $C_{19}H_{20}NO_6V$: C, 55.74; H, 4.88; N, 3.42. Found: C, 55.86; H, 4.80; N, 3.47.

Determination of Equilibrium Constants. The equilibrium constant (K in eq 1) was determined from integration of the relevant ^{51}V and ^{1}H NMR signals at 300 K. The solute was dissolved in dry dimethyl-d_6 sulfoxide (Aldrich). The solute concentration was varied in the range $(0.02-0.06) \times 10^{-3}$ M. For a given system the maximum variation of the equilibrium constant from measurement to measurement was within 10%. Each value in Table 3 is the average of at least three measurements. Test measurements were also performed by adding excess free diol/triol ($\sim 10^{-3}$ M) to the solution in order to supress any possible hydrolysis. This did not affect the value of K to any significant extent. Representative data for one system are given in Table S12 (Supporting Information).

Computer Generation of Endo and Exo Configurations (9−12). The configuration **9** was taken from the experimentally determined endo structure of VO(L-psal)(Hed).[8a] Its enantiomer **11** was generated by inverting in an orthogonal coordinate system. The configuration **10** was generated from **11** by interchanging the positions of the H and the pendant-C groups on the chiral C atom followed by adjustment of C−H and C−C bond lengths to 0.95 and 1.55 Å, respectively. Finally, **12** was generated by inverting **10**. The programs of SHELXTL-PLUS[26] were used.

X-ray Structure Determination. Crystals of VO(gsal)(Hpd) (0.3 × 0.3 × 0.4 mm) and VO(gsal)(H_2pt) (0.4 × 0.3 × 0.2 mm) were grown by slow evaporation of a methanolic solution. For both complexes cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ, 15−30°). Data were collected by the ω-scan method in the 2θ range 3−50° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction. Data were corrected for Lorentz−polarization effects, and an empirical absorption correction was performed on both sets of data on the basis of azimuthal scans of six reflections.[27] Systematic absences led to the identification of the space group as $P2_1/n$ for VO(gsal)(Hpd) and a $P2_1/c$ for VO(gsal)(H_2pt). For VO(gsal)(Hpd), 2605 reflections were collected, 2291 were unique, and 1778 satisfying $I > 3.0\sigma(I)$ were used for structure solution. In the case of VO(gsal)(H_2pt) the corresponding numbers are 2038, 1789, and 1202 (satisfying $I > 3.0\sigma(I)$), respectively.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAXII computer with the programs of SHELXTL-PLUS.[26] Both the structures of VO(gsal)(Hpd) and VO(gsal)(H_2pt) were solved by direct methods and were refined by full-matrix least-squares procedures making all non-hydrogen atoms anisotropic. All the hydrogen atoms of VO(gsal)(Hpd) and a few $gsal^{2-}$ hydrogen atoms of VO(gsal)(H_2pt) were directly located in difference Fourier maps. The remaining hydrogen atoms of VO(gsal)(H_2pt) were included in calculated positions with fixed U (=0.08 Å^2). The highest difference Fourier peak for VO(gsal)(Hpd) is 0.37 e/Å^3, and for VO(gsal)(H_2pt)[28] it is 0.33 e/Å^3. Significant crystal data are listed in Table 5.

Table 5. Crystallographic Data for VO(gsal)(Hpd) and VO(gsal)(H_2Pt)

	VO(gsal)(Hpd)	VO(gsal)(H_2pt)
chem formula	$C_{12}H_{14}NO_6V$	$C_{12}H_{13}NO_7V$
fw	319.2	334.2
space group	$P2_1/n$	$P2_1/c$
a, Å	9.229(5)	10.962(6)
b, Å	12.655(6)	9.544(4)
c, Å	11.478(4)	13.323(5)
β, deg	99.61(4)	102.67(4)
V, Å^3	1321(1)	1360(1)
Z	4	4
T, °C	22	22
λ, Å	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	1.610	1.640
ρ_{calcd}, g cm^{-3}	1.606	1.637
μ, cm^{-1}	7.76	7.65
R,[a] %	4.14	4.96
R_w,[b] %	4.15	5.04

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; unit weights for VO(gsal)(Hpd) and $g = 0.0005$ for VO(gsal)(H_2pt).

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Supporting Information Available: For VO(gsal)(Hpd) and VO(gsal)(H_2pt), tables of crystal data (Table S1), complete atomic coordinates and thermal parameters (Tables S2 and S7), bond distances (Tables S3 and S8) and angles (Tables S4 and S9), anisotropic thermal parameters (Tables S5 and S10), and hydrogen atom positional and thermal parameters (Tables S6 and S11) and for VO(L-vsal)(H_2pt), a table of equilibrium constants (Table S12) (12 pages). Ordering information is given on any current masthead page.

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(26) Sheldrick, G. M. *SHELXTL-PLUS 88, Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.
(27) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(28) In VO(gsal)(H_2pt), two H_2pt^- carbons, C10 and C11, display 2-fold disorder which may have arise due to C11 becoming chiral upon chelation. The metal atom is a second chiral center making a diastereoisomeric situation feasible.