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Stereospecific Formation of Dinuclear Vanadium(V) Tartrato Complexes

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The first dinuclear nonperoxido tartrato complexes of vanadium(V), $(NMe_4)_2[V_2O_4((2R,3R)\text{-}H_2tart)_2]\cdot 6H_2O$ (**1**), $(NMe_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (**2**), $(NEt_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (**3**) (tart = tartrato(4−) = $C_4H_2O_6^{4-}$) have been prepared from water−ethanol medium and characterized by X-ray structure analysis and spectral methods. The formation of the complexes has been found to be stereospecific; the composition and structure of anions containing one or both enantiomers of the ligand are profoundly different. The structure of anions in **1**−**3** also differs significantly from the structure of other dinuclear vanadium(V) α-hydroxycarboxylato complexes, but, interestingly, the geometry of the $[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]^{2-}$ ion resembles the structure of the $[(VO)_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]^{4-}$ ion which has a vanadium(IV) center. Using Raman and ^{51}V NMR spectroscopy the solvent dependent mutual transformations of $[V_4O_8((2R,3R)\text{-}tart)_2]^{4-}$ (V_4L_2-RR), $[V_4O_8((2S,3S)\text{-}tart)_2]^{4-}$ (V_4L_2-SS), $[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{2-}$ (V_2L_2-RR), $[V_2O_4((2S,3S)\text{-}H_2tart)_2]^{2-}$ (V_2L_2-SS), and $[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]^{2-}$ (V_2L_2-rac) have been established. In aqueous solution the following reactions take place; 2 V_2L_2-rac → V_2L_2-RR + V_2L_2-SS followed by partial decomposition, V_2L_2-RR → V_4L_2-RR + 2 L (V_2L_2-SS → V_4L_2-SS + 2 L). On the other hand V_2L_2-rac is stable in CH_3CN solution while V_2L_2-RR (V_2L_2-SS) decomposes into several species.

Introduction

Since the historical discovery of spontaneous resolution by Louis Pasteur, tartaric acid and metal-tartrato complexes have provided an important tool for the resolution of racemic compounds.[1] Metal-tartrato complexes are also often used as enantioselective catalysts for asymmetric oxidation of sulfides,[2] Henry reactions,[3] and other reactions. Also, vanadium-tartrato complexes have been studied as insulinomimetic complexes[4] and as catalysts for asymmetric coupling in polymerization reactions.[5]

An interesting property of vanadium(IV) tartrato complexes is the stereospecificity of their formation. Alkaline solutions of 1:1 vanadium(IV) tartrates differ profoundly in color and other properties according to whether (2*R*,3*R*)-, *rac*-, or *meso*-tartrate is the reactant.[6] X-ray structure analysis revealed that both $(NH_4)_4[(VO)_2((2S,3S)\text{-}tart)_2]\cdot 2H_2O$[7] and $Na_4[(VO)_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]\cdot 12H_2O$[8] contain dinuclear anions with two tartrato(4−) bridging groups of the same or opposite enantiomeric form of the ligand. Recently, the complexation of VO^{2+} ion with 2*R*,3*R* (2*S*,3*S*) and racemic tartrate at high ligand to metal ratios was studied in aqueous solution.[9]

X-ray structural characterization of solid complexes may be helpful for the elucidation of the structure of solution species. While speciation by NMR and potentiometry can provide M:L ratios, nuclearity, and charge of the solution species, it does not normally provide detailed structural information. However, comparison of the spectral properties of solid complexes with the spectral properties of their solutions often enables quite reliable conclusions about structure of solution species to be drawn. UV−vis, infrared, and especially Raman spectroscopy are useful spectral techniques for this purpose.

As can be seen from Table 1, the $V_2O_4(\mu\text{-}O)_2$ core is a typical feature for almost all molecular structures of nonperoxido

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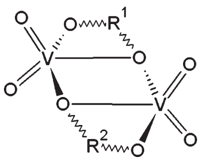
Table 1. Selected Stereochemical Features of Nonperoxido Vanadium(V) Complexes with α-Hydroxycarboxylato Ligands (According to CSD)

type of anion; coordination geometry of vanadium atoms[a]	ligand	planarity of $V_2(\mu\text{-}O)_2$ group (torsion angle), τ for $\{VO_5\}$[b]	compounds with references[c]
dinuclear achiral anion, SPY-5 (TBPY-5)	achiral	planar, 0.18−0.54	$(NH_4)_6[V_2O_4(cit)_2]\cdot 6H_2O$,[13] $K_2(NH_4)_4[V_2O_4(cit)_2]\cdot 6H_2O$,[14] $Na_2[V_2O_4(H_2cit)_2]\cdot 2H_2O$,[15] $(NMe_4)_2[V_2O_4(H_2cit)_2]\cdot 4H_2O$,[15] $(NH_4)_2[V_2O_4(H_2cit)_2]\cdot 2H_2O$,[16] $K_2[V_2O_4(H_2cit)_2]\cdot 4H_2O$,[16,17] $(NH_4)_2[V_2O_4(glyc)_2]$,[18] $Rb_2[V_2O_4(glyc)_2]$,[19] $Na_2[V_2O_4(mlact)_2]\cdot 7H_2O$,[20] $(NBu_4)_2[V_2O_4(mlact)_2]\cdot 2H_2O$,[21] $(NH_4)_2[V_2O_4(deglyc)_2]\cdot H_2O$[22]
dinuclear achiral anion, SPY-5	chiral	planar, 0.26−0.45	$(NH_4)_4[V_2O_4(Hcit)_2]\cdot 4H_2O$,[13] $K_4[V_2O_4(Hcit)_2]\cdot H_2O$,[23] $Cs_2[V_2O_4((R)\text{-}Hmal)((S)\text{-}Hmal)]\cdot 2H_2O$,[19] $K_2[V_2O_4((R)\text{-}H_2hcit)((S)\text{-}H_2hcit)]\cdot 6H_2O$[24]
dinuclear chiral anion, SPY-5	chiral	non planar (1.64°−24.28°), 0.25−0.47	*rac*-$[Ni(phen)_3][V_2O_4(Hcit)(EtO)]\cdot 2H_2O$,[25] *rac*-$(ncpH)_2[V_2O_4(Hcit)(OH)]\cdot 2H_2O$,[25] $[(Ph_3P)_2N^+]_2[V_2O_4((S)\text{-}lact)_2]\cdot CH_3CN$,[26] $Cs_2[V_2O_4\text{-}((S)\text{-}lact)_2]\cdot 2H_2O$[19]
dinuclear chiral anion, SPY-5	achiral	non planar (1.83°) 0.30 and 0.31	$K_2Na_2[V_2O_4(cit)(H_2cit)]\cdot 9H_2O$[27] [d]
mononuclear chiral anion, OC-6, $\{VO_5N\}$ core	achiral		*rac*-$pyH[VO(benz)_2(py)]\cdot py$[28]
tetranuclear chiral anion, SPY-5, $\{V_4O_{12}(\mu\text{-}O_4)\}$ core	chiral	0.023−0.32	*rac*-$Na_8[V_4O_8((2R,3R)\text{-}tart)_2][V_4O_8((2S,3S)\text{-}tart)_2]\cdot 24H_2O$,[29] $(NEt_4)_4[V_4O_8((2R,3R)\text{-}tart)_2]\cdot 6H_2O$[29]

[a] The core is $\{V_2O_4(\mu\text{-}O)_2\}$ except the last two rows. [b] Estimation of index of trigonality degree (τ)[30] is hindered in regard of the two possible pyramidal apex (two terminal oxygen atoms). Hence only the lower value of τ for the vanadium atom was involved. [c] Abbreviations: ncp = neocuproine, py = pyridine, phen = 1,10-phenanthroline, NEt_4 = tetraethylammonium(1+) cation, NMe_4 = tetramethylammonium(1+) cation, NBu_4 is tetra(n-butyl)ammonium(1+) cation, *rac* = racemic compound. The ligand abbreviation, see Chart 2. [d] $K_3Na[V_2O_4(Hcit)_2]\cdot 7H_2O$[31] contains a similar anion. This anion possesses non planar $V_2(\mu\text{-}O)_2$ group, torsion angle 3.14°, τ were found to be 0.21 and 0.37. Full stereochemical description is impossible because hydrogen atoms were not localized.

Chart 1

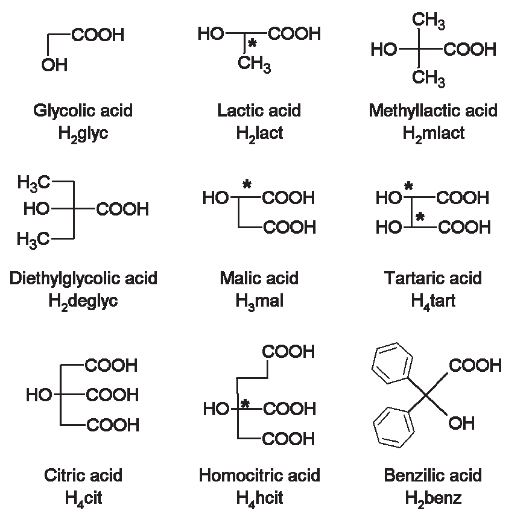


α-hydroxycarboxylato complexes of vanadium(V) (Chart 1). Similar structures are also found for complexes with 1,2-diols,[10,11] and with β-mercaptoethanol.[12] Each vanadium atom is pentacoordinated: the geometry of the coordination polyhedron $\{VO_5\}$ can be described in terms of square pyramid distorted toward trigonal bipyramidal geometry.

The molecular structures of benzilato (mononuclear, OC-6) and tartrato complexes (tetranuclear) are excluded from the set of structures in Table 1. With a view toward expanding our understanding of α-hydroxylcarboxylato systems we decided to study the structure and properties of dinuclear vanadium(V) tartrato complexes and to compare them with the structure and properties of other dinuclear α-hydroxycarboxylato vanadium(V) complexes.

We have recently reported partial speciation of the vanadium(V)-tartrate aqueous system and structural characterization of the two complexes, *rac*-$Na_8[V_4O_8((2R,3R)\text{-}tart)_2][V_4O_8((2S,3S)\text{-}tart)_2]\cdot 24H_2O$ (**4**) and $(NEt_4)_4[V_4O_8\text{-}((2R,3R)\text{-}tart)_2]\cdot 6H_2O$ (**5**).[29] In acidic solutions (pH ≈ 2.5) in addition to tetranuclear species a dinuclear species, designated as V_2L_2, is present. In this article we discuss the structures and solution properties of V_2L_2 complexes using, as a basis, X-ray structure and spectroscopic (UV−vis, IR, Raman, and NMR) analytical methods.

Chart 2



While a tetranuclear anion $[V_4O_8(tart)_2]^{4-}$ always contains tartrato groups of the same enantiomeric form, irrespective of whether it is formed from racemic or optically active ligand,[29] the formation of dinuclear complexes has been found to be stereospecific.

Experimental Section

Materials and Syntheses. NH_4VO_3 was purified by recrystallization from water; all other chemicals were reagent grade and

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were used as commercially obtained (Sigma-Aldrich, Lachema, Merck) without further purification.

$(NMe_4)_2[V_2O_4((2R,3R)\text{-}H_2tart)_2]\cdot 6H_2O$ (1). NH_4VO_3 (0.117 g, 1.00 mmol) was dissolved in a NMe_4OH aqueous solution (0.90 mL of a 1.1 mol/L solution, 1.0 mmol) and 2.0 mL of water. An aqueous solution of (2*R*,3*R*)-tartaric acid (2.0 mL of a 1.0 mol/L solution, 2.0 mmol) was added, and the red solution obtained (pH ≈ 2.4) was layered with ethanol (10.0 mL). Yellow crystals were isolated after 24 h of standing at −20 °C. The compound is well soluble in water and slightly soluble in ethanol and acetonitrile. Anal. Calcd for $C_{16}H_{44}N_2O_{22}V_2$ (found): C 26.7 (26.7); H 6.2 (6.1); N 3.9 (3.9); V 14.2 (15.1).

$(NMe_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (2). NH_4VO_3 (0.117 g, 1.00 mmol) was dissolved in a $N\mathit{Me}_4OH$ aqueous solution (0.90 mL of a 1.1 mol/L solution, 1.0 mmol) together with 2.0 mL of water. To this solution, a solution of *rac*-tartaric acid (2.0 mL of a 1.0 mol/L solution, 2.0 mmol) and ethanol (10.0 mL) were added. Red crystals were isolated after 24 h of standing at 3 °C. The compound is soluble in water and slightly soluble in acetonitrile. Anal. Calcd for $C_{16}H_{28}N_2O_{14}V_2$ (found): C 33.5 (32.6); H 4.9 (5.0); N 4.9 (4.6); V 17.7 (16.7).

$(NEt_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (3). NH_4VO_3 (0.117 g, 1.00 mmol) was dissolved in a $N\mathit{Et}_4OH$ aqueous solution (0.41 mL of a 2.43 mol/L solution, 1.0 mmol) together with 2.0 mL of water. To this solution, a solution of *rac*-tartaric acid (2.0 mL of a 1.0 mol/L solution, 2.0 mmol) and ethanol (10.0 mL) were added. Red crystals were isolated after 24 h standing at 3 °C. The compound is well soluble in both water and acetonitrile. Anal. Calcd for $C_{24}H_{44}N_2O_{14}V_2$ (found): C 42.0 (42.6); H 6.5 (6.0); N 4.1 (4.1); V 14.8 (15.0).

Table 2. Crystallographic Data and Refinement Results for $(NMe_4)_2[V_2O_4((2R,3R)\text{-}H_2tart)_2]\cdot 6H_2O$ (**1**), $(NMe_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (**2**), and $(NEt_4)_2[V_2O_2((2R,3R)\text{-}tart)((2S,3S)\text{-}tart)]$ (**3**)

	1	**2**	**3**
formula	$C_{16}H_{44}N_2O_{22}V_2$	$C_{16}H_{28}N_2O_{14}V_2$	$C_{24}H_{44}N_2O_{14}V_2$
CSD no.	733437	733438	733439
M (g/mol)	718.41	574.29	686.50
space group	$I222$ (no. 23)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	8.0275(16)	7.5271(6)	12.7340(2)
b (Å)	8.3123(17)	9.2238(8)	17.8983(3)
c (Å)	22.674(5)	9.9377(8)	13.5159(3)
α (deg)	90.00	68.550(10)	90.00
β (deg)	90.00	86.610(10)	98.03(2)
γ (deg)	90.00	66.380(10)	90.00
V (Å^3)	1513.0(5)	585.30(10)	3050.30(18)
Z	2	1	4
ρ_{calcd} (g/mL)	1.577	1.636	1.495
μ (mm^{-1})	0.709	0.874	0.682
R_1 ($I > 2\sigma_I$)^a	0.0261	0.0265	0.0278
wR_2 ($I > 2\sigma_I$)^b	0.0709	0.0702	0.0817

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum w(F_o^2 - F_c^2)/\sum wF_o^2\}^{1/2}$.

For details about synthesis of $Na_8[V_4O_8((2R,3R)\text{-}tart)_2][V_4O_8((2S,3S)\text{-}tart)_2]\cdot 24H_2O$ (**4**), $(NEt_4)_4[V_4O_8((2R,3R)\text{-}tart)_2]\cdot 6H_2O$ (**5**), and $Na_4[V_4O_8((2R,3R)\text{-}tart)_2]\cdot 12H_2O$ (**6**) see ref 29.

Physical Measurements. The IR spectra were recorded on a Nicolet Magna 750 FT IR spectrometer with either Nujol mulls or KBr discs. The Raman spectra were obtained at room temperature on a FTRA model FRA 106/S connected to a FT IR spectrometer FS 55 Equinox (Bruker); a Nd:YAG laser (1064 nm) was used. Elemental analysis (C, H, N) was performed on a 1106 CHN analyzer (Carlo Erba, Italy). Vanadium(V) was determined gravimetrically as V_2O_5 in a Pt crucible at 773 K or volumetrically by titration with $FeSO_4$ ($c = 0.1$ mol/L) using diphenylamine as indicator. UV−vis spectra were recorded on a Jasco V-530 UV/vis spectrophotometer at room temperature using 2 mm cuvettes. ^{51}V NMR spectra were recorded at 278 or 295 K on either a Varian Mercury Plus 300 MHz spectrometer operating at 78.94 MHz (^{51}V) or a Varian Unity Inova 600 MHz spectrometer operating at 157.68 MHz (^{51}V) in 5 mm tubes without locking on D_2O. Chemical shifts are in parts per million relative to a $VOCl_3$ external reference, also determined at 278 or 295 K. The pH was measured with a Precision Digital pH Meter OP-208/1 (Radelkis, Budapest) by using of combined semimicro pH electrode SEOJ 252 (DHJ).

Crystal Structure Determination. The intensity data were collected on a KUMA KM-4 *κ*-axis diffractometer at 120(2) K using a graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) equipped with an Oxford Cryosystem LT-device, and corrected for absorption effects using *ψ*-scan. The *ω* scan technique with different *κ* and *φ* offsets for covering an independent part of reflections in the 2°−25° *θ* range was used. The cell parameters were refined from all strong reflections. The data reductions were carried out using the CrysAlis RED (Oxford Diffraction, U.K.) program. The structures were determined with SHELXS-97[32] and refined with SHELXL-97,[33] the data for publication were prepared with SHELXL,[34] and the figures with Diamond.[35] Crystal data and structure determination summaries for **1**−**3** are listed in Table 2. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 733437 (**1**), 733438 (**2**), and 733439 (**3**). Copies of the data can be obtained, free of charge,

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Table 3. Stretching Vibrations of Terminal Vanadium−Oxygen Groups in Tartrato Complexes of Vanadium(V)

	IR		Raman		
compound/system	(s)	(CH_3CN)	(s)	(CH_3CN)	(H_2O)
$(NMe_4)_2[V_2O_4((2R,3R)\text{-}H_2tart)_2]\cdot 6H_2O$ (**1**)	930 vs, 909 vs	a	938 s,909 s	a	a
$(NMe_4)_2[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]$ (**2**)	992 vs	996 vs	993 vs	996 vs	b
$(NEt_4)_2[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]$ (**3**)	993 vs	996 vs	995 vs	1003 vs	994 vs, 936 m, 901 w[b]
$(NEt_4)_4[V_4O_8((2R,3R)\text{-tart})_2]\cdot 6H_2O$ (**5**)	957 vs	956 vs	977 vs	978 vs	a
$Na_4[V_4O_8((2R,3R)\text{-tart})_2]\cdot 12H_2O$ (**6**)	973 vs	a	989 vs	a	993 vs
Solution I[c]					982 s, 933 s, 896 s
Solution II[c]					985 s, 937 s, 898 s

[a] Not measured, mostly because of low solubility or decomposition. [b] Formed a mixture of V_4L_2 and V_2L_2 in aqueous solution. [c] Prepared by mixing of aqueous solutions. Solution I: 4.0 mL (2*R*,3*R*)-H_4tart (c = 1.0 mol/L) + 2.0 mL $NaVO_3$ (c = 0.50 mol/L), pH = 1.71; Solution II: 4.0 mL *rac*-H_4tart (c = 1.0 mol/L) + 2.0 mL $NaVO_3$ (c = 0.50 mol/L), pH = 1.71. See Figure 10 for the spectra.

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Results and Discussion

Synthesis and Characterization of Solid Complexes. The complexes $(NMe_4)_2[V_2O_4((2R,3R)\text{-}H_2tart)_2]\cdot 6H_2O$ (**1**), $(NMe_4)_2[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]$ (**2**), and $(NEt_4)_2[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]$ (**3**) were prepared by crystallization from the NH_4VO_3—MOH (M = NMe_4, NEt_4)—((2*R*,3*R*) or *rac*)-tartaric acid—H_2O—ethanol systems. The synthesis was not straightforward; the necessary conditions for successful synthesis (as given in the Experimental Section) were found only after many attempts. The complexes with optically active and racemic ligands differ in composition and color; **1** is yellow, **2** and **3** are red. The compounds are generally slightly photosensitive: exposure under day light induced slow reduction of vanadium(V) accompanied by color change to brown.

The vibrational spectra of **1**, **2**, and **3** (Supporting Information, Figures 1s−6s) exhibit the expected bands corresponding to ν_{as}(COO), ν_s(COO), ν (C−O_{alc}) (O_{alc} = alcoholic oxygen atom) and to vibrations of organic cations. The spectrum of **1** is profoundly different from the spectra of **2** and **3**. The most striking difference between the spectra of **1** and **2** and **3** occurs in the region of the stretching vibrations of the terminal VO (or VO_2) groups. These bands are generally very strong, both in IR and Raman spectra. Especially in the Raman spectra, the bands corresponding to ν (VO) and ν (VO_2) are usually by far the strongest in the spectra.

As can be seen from Table 3 the spectrum of **1** exhibits two bands characteristic of the VO_2 terminal group while the spectra of **2** and **3** contain only one band corresponding the ν(VO) vibration, which is typically at higher wavenumbers.

Crystal Structures. The coordination geometry about vanadium in these tartrato vanadium(V) complexes is considerably different from the structures found in other vanadium(V) α-hydroxycarboxylato complexes.

The crystal structure of **1** consists of NMe_4^+ cations, $[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{2-}$ (H_2tart^{2-} = $C_4H_4O_6^{2-}$) anions, in an unforeseen D_2 symmetry, and water molecules. The water molecules (defined by OW2, HW2A, and HW2B atoms) are disordered.

Each of the two vanadium atoms of **1** possesses OC-6 coordination geometry with 6 oxygen atoms in the coordination sphere: two terminal (O), two carboxylato (O1), and two hydroxyl oxygen atoms (O2). Thus, two *cis*-VO_2^+ groups are coordinated by two bis(bidentate) tartrato ligands forming a dinuclear complex anion: $[\{VO_2((2R,3R)\text{-}H_2tart)\}_2]^{2-}$ (Figure 1).

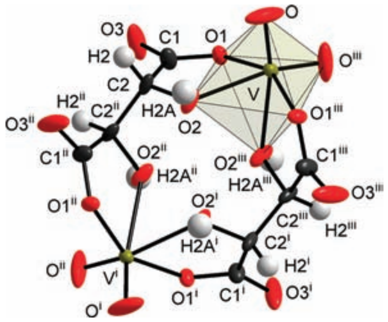

Figure 1. Diamond presentation of the molecular structure of $[\{VO_2((2R,3R)\text{-}H_2tart)\}_2]^{2-}$ anion in **1** with thermal ellipsoid probability 50%. Selected interatomic distances (Å) and bond angles (deg): V−O 1.612(25), V−O1 1.9695(15), V−O2 2.2719(18), O1−V−O1^{iii} 150.97(9), O−V−O2 162.92(11), O−V−O^{iii} 104.9(2), O2−V−O2^{iii} 72.64(9). Symmetry codes: i: x, $1-y$, $2-z$; ii: $1-x$, y, $2-z$; iii: $1-x$, $1-y$, z.

With regard to the space group (*I*222, No. 23), **1** is a chiral non-racemic compound: the complex anion possesses 10 stereogenic centers localized not only at the carbon atoms but also at the hydroxyl oxygen atoms (all of them have *S*-configuration[36]) and the vanadium atoms: both vanadium centers exhibit Δ-configuration (Figure 2).

The distorted octahedron $\{VO_6\}$ exhibits a significant *trans*-influence[37] (V−O2 is 2.2720(17) Å vs V−O1 equal to 1.9695(15) Å) with the deviation of the vanadium atom from the equatorial pseudoplane (least-squares plane) toward the terminal oxygen atom, (O), being 0.3145(3) Å. The pseudoplane was calculated using oxygen atoms coordinated in the equatorial positions: O2, O1, O^{iii}, and O1^{iii} (Figure 1). The angle between the pseudoplanes in the dinuclear complex anion was found to be ≈63.3°.

The crystal structure of **1** consists of hydrophilic and hydrophobic layers parallel to the (001) plane (Figure 3). Hydrophilic layers derive from $[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{2-}$ anions and water molecules interconnected by

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[36] Chirality at the oxygen atoms was recently described: (a) Mikata, Y.; Sugai, Y.; Yano, S. *Inorg. Chem.* **2004**, *43*, 4778–4780. (b) Mikata, Y.; Sugai, Y.; Obata, M.; Harada, M.; Yano, S. *Inorg. Chem.* **2006**, *45*, 1543–1551.

[37] (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth-Heinemann: Oxford, 1998; p 1085(b) Tatiersky, J.; Schwendt, P.; Marek, J.; Sivák, M. *New J. Chem.* **2004**, *28*, 127–133.

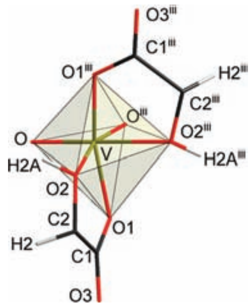

Figure 2. Diamond presentation of Δ-configuration of the vanadium atom in **1**. Symmetry code: iii: 1−*x*, 1−*y*, *z*.

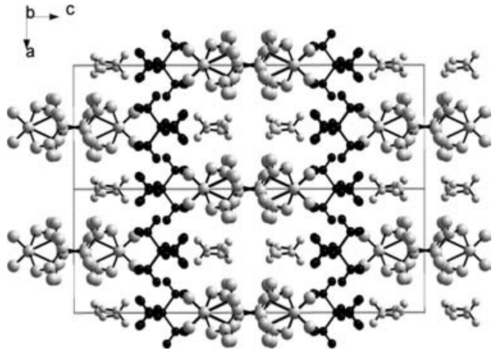

Figure 3. Crystal packing of **1**. Hydrophobic layers consist of NMe_4^+ cations (black), hydrophilic layers consist of $[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{2-}$ anions and water molecules (gray).

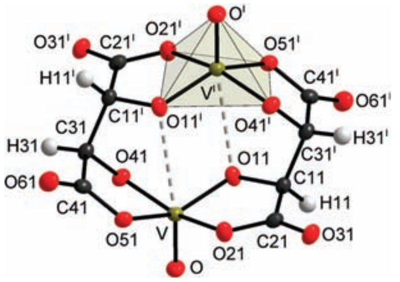

Figure 4. Diamond presentation of the molecular structure of anion in **2** with thermal ellipsoid probability 50%. Selected interatomic distances (Å) and bond angles (deg): V−O 1.5901(13), V−O11 1.8340(13), V−O21 1.9702(18), V−O41 1.8151(19), V−O51 1.9333(14), O−V−O11 106.31(7), O−V−O21 100.43(7), O−V−O41 102.81(7), O−V−O51 108.48(7), O11−V−O51 143.60(6), O21−V−O41 154.55(6). Symmetry code: i: −*x*, 2−*y*, 1−*z*.

a network of hydrogen bonds. The hydrophobic layers arise from the NMe_4^+ cations.

The $[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]^{2-}$ anions in **2** have C_i symmetry. Both vanadium atoms are pentacoordinated by oxygen atoms (SPY-5 coordination geometry, Figure 4): two VO^{3+} groups are coordinated by two bis(bidentate) tartrato ligands forming a dinuclear complex anion.

The geometry of the coordination polyhedron $\{VO_5\}$ can best be described in terms of a square pyramid distorted toward a trigonal bipyramid: the index of trigonality degree (τ)[30] was found to be 0.183. There is a long-range interaction between O11 and the vanadium atom from the opposite polyhedron (V−O11^i is 2.94 Å) which illustrates some tendency of the central atom to achieve octahedral coordination. It must be noted that this interaction is purely electrostatic, and no covalent bond contribution can be expected for this V−O11^i interaction. Generally, V−O distances larger than 2.7 Å have no influence on spectral properties of the complex.[38]

The deviation of the vanadium atoms from the basal pseudoplanes was found to be 0.4698(4) Å. The pseudoplanes were calculated using oxygen atoms coordinated in the base of the pyramid: O11, O21, O41, O51. The distance between the parallel pseudoplanes is 2.50 Å.

The crystal structure of **3** consists of two NEt_4^+ cations and two crystallographically independent $[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]^{2-}$ anions with C_i symmetry ($tart^{4-} = C_4H_2O_6^{4-}$). The molecular structure of the anions in **3** is analogous to those in **2** (Figure 5).

The index of trigonality degree (τ) of the square pyramid $\{VO_5\}$ was found to be 0.179 (for V1) and 0.211 (for V2). The tendency to complete the coordination sphere of the vanadium atoms is very low: V1−O41^i is 3.22 Å, V2−O12^i is 2.80 Å. This is in accordance with the observed significant deviations of vanadium atoms from the basal pseudoplanes: 0.5025(3) Å (for V1) and 0.4702(3) Å (for V2).

The anions of the first crystallographic type are arranged into the layers parallel with the (100) plane. The second type anions are arranged in a similar mode as the first ones, but they are shifted by half of a period (Figure 6). Anions and cations are held together by electrostatic, hydrophilic, and hydrophobic interactions.

Comparison of the structures of **1**−**3** with the structures of dinuclear V(IV)-tartrato complexes is interesting. The structure of the anions in **2** and **3** is very similar to those in $Na_4[(VO)_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]\cdot 12H_2O$.[8] However, the composition and structure of the complex anion in **1** is profoundly different from the composition and structure of the vanadium(IV) complex with an optically active tartrate ligand.[7]

Solution Properties of Vanadium(V) Tartrato Complexes in Acidic Media. The predominant species in mildly acidic medium (pH ≈ 4−6) is $[V_4O_8(tart)_2]^{4-}$. The ^{51}V NMR spectrum of a saturated aqueous solution of **6** (and similarly **4**) exhibited only one signal at −522 ppm. The structure of the tetranuclear anion in solution is very probably the same as in the solid state structure because the Raman spectra do not differ substantially between the solid and the compound in solution (Figure 7). The situation is similar for solutions in CH_3CN. The ^{51}V NMR spectrum of **5** in CH_3CN exhibits only one signal at −497 ppm (Figure 8,c). The Raman spectrum of the same solution exhibits a strong band corresponding to the V=O vibration at 978 cm^{-1} (Table 3).

In more highly acidic solutions (pH ≈ 2.5) an equilibrium among several species exists, the prevailing species being $[V_4O_8(tart)_2]^{4-}$ and a species denoted as V_2L_2.[29] To our surprise, in spite of the different crystal structures of dinuclear vanadium(V) complexes with (2*R*,3*R*)-tartrato and *rac*-tartrato ligands, there is no difference in the ^{51}V NMR spectra of these complexes prepared in situ in aqueous solution at pH ≈ 2.7 (Figure 9). Under the conditions used, according to the NMR spectra, there is approximately 75% vanadium bound in $[V_4O_8(tart)_2]^{4-}$

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(38) Schwendt, P.; Tyršelová, J.; Pavelčík, F. *Inorg. Chem.* **1995**, *34*, 1964–1966.

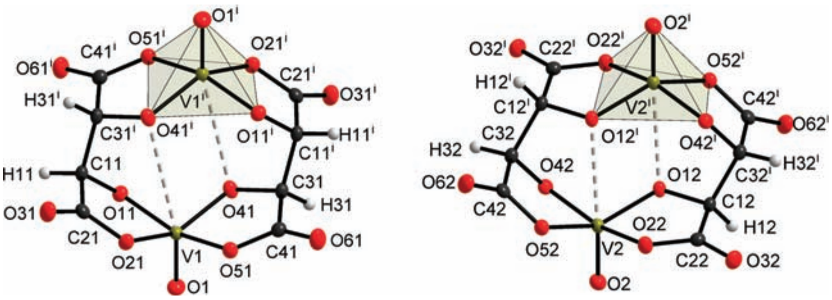

Figure 5. Diamond presentation of the molecular structure of anions of **3** with thermal ellipsoid probability 50%. Selected interatomic distances (Å) and bond angles (deg): V1−O1 1.5959(0), V1−O11 1.8124(2), V1−O21 1.9444(0), V1−O41 1.8271(0), V1−O51 1.9509(1), O1−V1−O11 104.605(1), O1−V1−O21 108.747(1), O1−V1−O41 108.118(1), O1−V1−O51 101.316(1), O11−V1−O51 152.919(2), O21−V1−O41 142.190(3); V2−O2 1.5931(1), V2−O12 1.8428(1), V2−O22 1.9577(1), V2−O42 1.8156(2), V2−O52 1.9509(1), O2−V2−O12 105.620(1), O2−V2−O22 99.682(3), O2−V2−O42 102.556(1), O2−V2−O52 109.573(2), O12−V2−O52 143.356(1), O22−V2−O42 156.010(1). Symmetry codes: i: 2−*x*, −*y*, 1−*z* (left); 1−*x*, −*y*, −*z* (right).

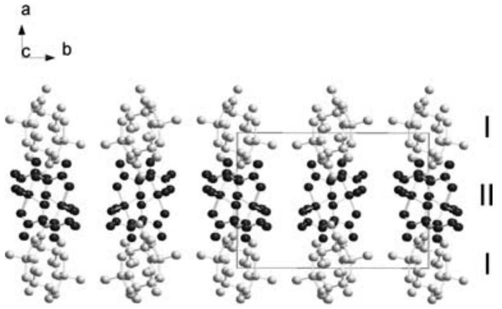

Figure 6. Crystal packing of the **3** (only anions). The first (gray, I) and the second (black, II) crystallographic type of the anions are arranged in the layers parallel with the (100) plane. The hydrophilic layers of both types of anions are parallel with the (010) plane. Cationic (hydrophobic) layers (hidden for clarity) are also parallel with the (010) and are situated between the hydrophilic layers.

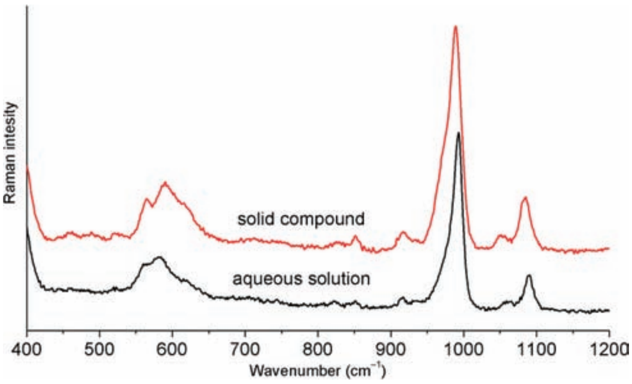

Figure 7. Raman spectra of **6** and of its saturated aqueous solution.

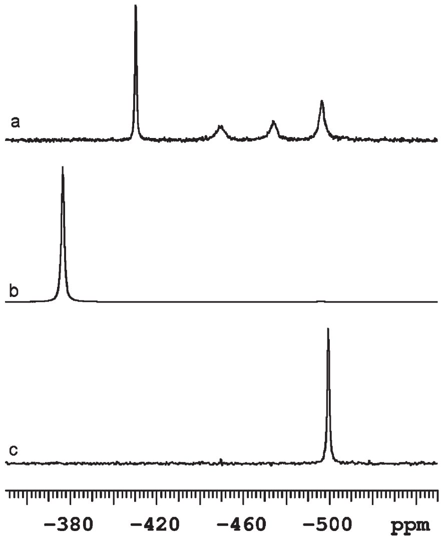

Figure 8. ^{51}V NMR spectra of **1** at 278 K (a), **3** at 278 K (b), and **5** at 295 K (c) in CH_3CN, c = 5.0 mmol/L.

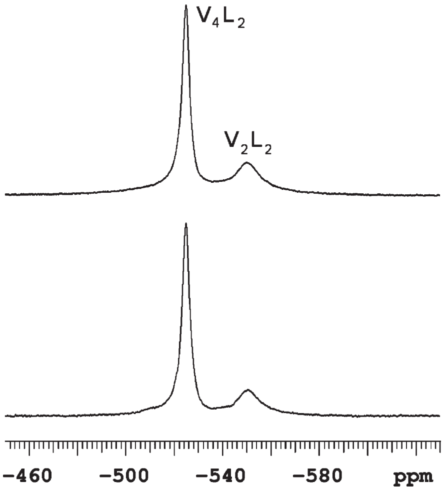

Figure 9. ^{51}V NMR spectra of systems: KVO_3−*rac*-H_4tart−H_2O at ratio n(V)/n(H_4tart) = 1:1, c(V) = 0.10 mol/L, pH = 2.77 (top) and KVO_3−(2*R*,3*R*)-H_4tart−H_2O at ratio n(V):n(H_4tart) = 1:1, c(V) = 0.10 mol/L, pH = 2.75 (bottom), both at 278 K.

and 25% in V_2L_2 species. The ^{51}V NMR spectra of **1**, **2**, and **3** in aqueous solution are indistinguishable.

The explanation for the similar NMR spectra of solutions of **1**, **2**, and **3** in water is provided by the Raman spectra. There is no difference between the Raman spectra from aqueous solutions of complexes prepared in situ with (2*R*,3*R*)-tartaric acid and with *rac*-tartaric acid. Moreover, besides the band at ≈985 cm^{-1} which corresponds to the V=O stretching vibration (evidently because of the presence of $[V_4O_8(\text{tart})_2]^{4-}$ in the solution), the strong bands of the stretching vibrations of the VO_2 group were observed at ≈935 and ≈897 cm^{-1} (Figure 10, Table 3). Figure 10 also illustrates that under the conditions used the V_2L_2 is the dominant species. The compounds **1**−**3** were prepared in water−ethanol medium. This evidence leads to the conclusion that

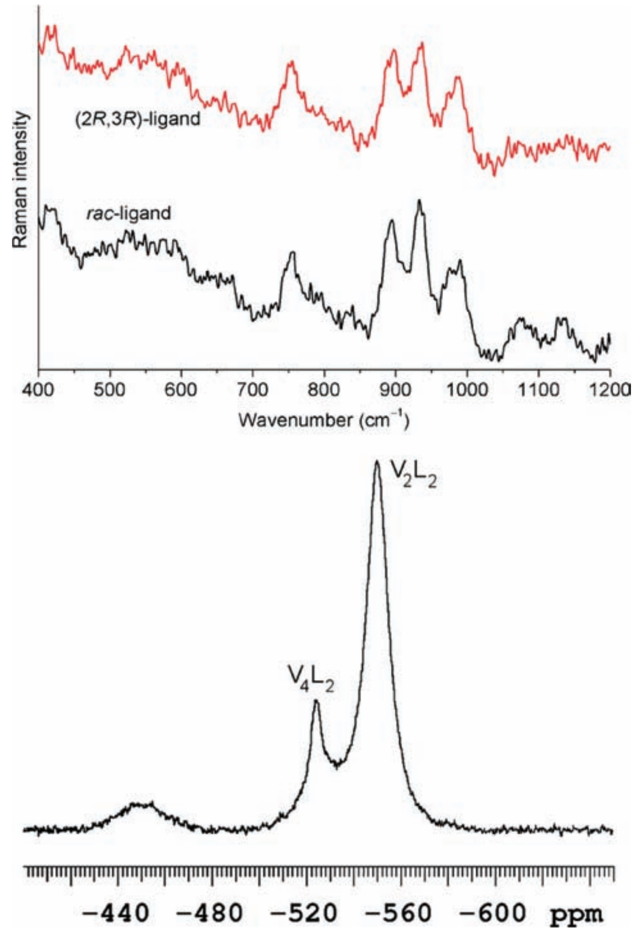

Figure 10. Raman (top) and ^{51}V NMR (bottom) spectra for solution I [4.0 mL (2*R*,3*R*)-H_4tart (c = 1.0 mol/L) + 2.0 mL $NaVO_3$ (c = 0.50 mol/L), pH = 1.71] and solution II [4.0 mL *rac*-H_4tart (c = 1.0 mol/L) + 2.0 mL $NaVO_3$ (c = 0.50 mol/L), pH = 1.71], both at 278 K. The ^{51}V NMR spectra of both solutions are indistinguishable.

$[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{4-}$ ($[V_2O_4((2S,3S)\text{-}H_2tart)_2]^{4-}$) is the prevailing (or only) dinuclear species in aqueous solution and after dissolution of **2** or **3** the reaction (eq 1) takes place:

$$2[V_2O_2((2R,3R)-\text{tart})((2S,3S)-\text{tart})]^{2-} + 4H_2O \rightarrow [V_2O_4((2R,3R)-H_2\text{tart})_2]^{2-} + [V_2O_4((2S,3S)-H_2\text{tart})_2]^{2-} \qquad (1)$$

This is different from the similar V(IV)-tartrato complexes where the *rac*-complex is stable in aqueous solution.[6] Here, the complexes **2** and **3** evidently dissociate in aqueous solution. The vanadium(V) oxoanions and the ligands then reassociate to form a thermodynamically more stable species.

While the $[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]^{2-}$ ion is unstable in aqueous solution, its NMR spectrum indicates it is relatively stable in CH_3CN. The ^{51}V NMR spectrum of **3** in CH_3CN exhibits only one narrow signal at −377 ppm (Figure 11). However, for mixed CH_3CN-H_2O solutions there is an expected shift of the signal corresponding to the $[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]^{2-}$ ion arising from the changing solvent and also the gradual disappearance of this signal with increasing water content (Figure 11). Simultaneously, the intensity of the signals corresponding to the two forms of V_4L_2 complexes (−524 and −539 ppm in H_2O) and to $[V_2O_4((2R,3R \text{ or } 2S,3S)\text{-}H_2tart)_2]^{2-}$ (−550 ppm in water) rises.

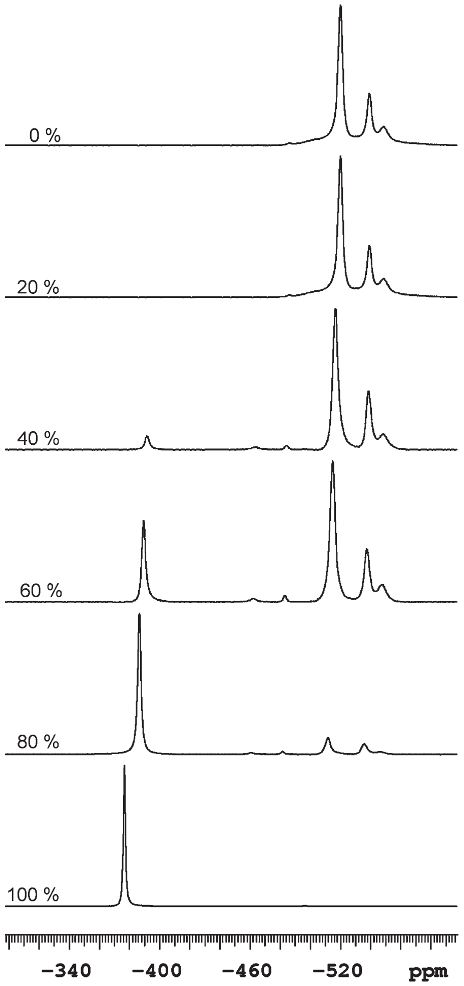

Figure 11. ^{51}V NMR of **3**, c = 5.0 mmol/L in CH_3CN-H_2O mixtures (composition of the mixture is expressed as volume fraction of acetonitrile) at 278 K.

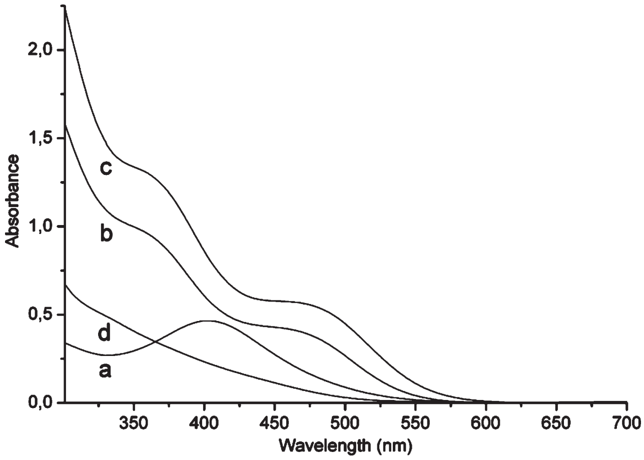

Figure 12. UV−vis spectra: (a) **3** in CH_3CN, c = 0.50 mmol/L; (b) **5** in water, c = 5.0 mmol/L; (c) **5** in CH_3CN, c = 5.0 mmol/L; (d) prepared by mixing of aqueous solutions: 7.50 mL (2*R*,3*R*)-H_4tart (c=1.0 mol/L) + 1.67 mL $NaVO_3$ (c=0.15 mol/L) + 2.20 mL NaOH (c=0.945 mol/L) + water to 50 mL, pH = 2.42. According to ^{51}V NMR spectra, up to 90% of vanadium is bound in the $[V_2O_4((2R,3R)\text{-}H_2tart)_2]^{2-}$ ion under these conditions.

Somewhat surprisingly, complex **1** is unstable in acetonitrile solution. In the NMR spectrum of **1** in CH_3CN we find a signal assigned to V_4L_2 (−497 ppm) and three unidentified signals occurring at −410, −449, and −474 ppm (Figure 8,a). After about 20% of water in the solution the spectrum is a completely changed and it is then not significantly different from the spectrum from an aqueous solution.[39]

UV−vis Spectra. UV−vis spectra of **5** in water and in acetonitrile are essentially identical, exhibiting bands at ≈350 and ≈460 nm (Figure 12b,c). It can be therefore supposed that the tetranuclear structure of $[V_4O_8((2R,3R)\text{-tart})_2]^{4-}$ is preserved in acetonitrile.

The spectrum of **3** dissolved in acetonitrile exhibits a strong band at ≈400 nm ($\varepsilon \approx 920$ mol^{-1} L cm^{-1}, Figure 12a). The comparison with the spectrum of **1** is impossible because **1** is decomposed in acetonitrile. On the other hand the spectrum of an aqueous solution in which the $[V_2O_4((2R,3R)\text{-}H_2\text{tart})_2]^{2-}$ ion is the prevailing species is quite different (Figure 12d), and this supports the view of different solution structures of anions in **1** and **3**.

Concluding Remarks

In a previous paper[29] we were able to successfully identify the main species in mildly acidic solutions of vanadium(V)−tartrate. Here, we concentrated our efforts on the characterization of dinuclear 1:1 vanadium(V) tartrato complexes found in more acidic conditions (pH < 3). We found that the formation of the V_2L_2 complexes is stereospecific. This behavior was similarly found 40 years ago for the formation of the corresponding V(IV) tartrato complexes.[6]

The vanadium(V) tartrato complexes $M_2[V_2O_4((2R,3R)\text{-}H_2\text{tart})_2]\cdot$aq and $M_2[V_2O_2((2R,3R)\text{-tart})((2S,3S)\text{-tart})]$ described here differ in the protonation state of the ligand, in their color, and in their coordination polyhedron (OC-6 vs SPY-5). They also have profoundly different stabilities in aqueous and acetonitrile solutions. In the future an effort will be made to explain the different properties of these complexes using quantum chemical methods.

Acknowledgment. This investigation has been supported by the Ministry of Education of Slovak Republic (Grant VEGA 1/4462/07), Comenius University in Bratislava (Grant UK/203/2009). NMR measurements were performed on the equipment supported by the Slovak State Programme Project No. 2003SP200280203.

Supporting Information Available: IR, Raman spectra (Figure 1s−6s) and crystallographic data for **1**−**3**. This materials are available free of charge via the Internet at http://pubs.acs.org.

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[39] The ^{51}V NMR spectra of **2** and **3** in the mixed ethanol−water media are very similar to the spectra of these compounds in acetonitrile−water solutions (not shown). Similarly, there is a resemblance between the spectra of **1** in acetonitrile−water and ethanol−water media with exception of the solution of **1** in 100% ethanol where the spectrum exhibits signals at −476 (dominant signal), −505, −531, −552, and −595 ppm (minor signals probably due to the complexes with ethanol) and is completely different from the spectrum of **1** in acetonitrile. Generally, the signals in the ^{51}V NMR spectra of complexes **1**, **2**, and **3** in ethanol−water media are broader and less differentiated than in acetonitrile−water media.