

Synthesis and X-ray structural characterization of tris(L-glycinato)vanadium(III) and *trans*-tetraquadichlorovanadium(III) chloride

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Abstract

Despite the importance of V^{III} in biology, only three V^{III} complexes of naturally occurring amino acids have been structurally characterized. We report the structure of the first vanadium complex incorporating a glycine ligand, [V(Gly)₃] · 2DMSO, which crystallizes in a monoclinic system with space group *Cc*, *a* = 8.9186(5) Å, *b* = 21.5347(9) Å, *c* = 9.9064(5) Å and β = 110.536(3)°. The X-ray structural data show the central V^{III} metal octahedrally coordinated by three bidentate glycinato ligands arranged a *mer* configuration, with both Δ and *A* enantiomers present in the unit cell. The bulk sample was isolated as [V(Gly)₃] · DMSO · NaCl. Structural comparisons are made with the corresponding homoleptic glycinato complexes of Co^{III}, Cr^{III} and Ni^{II}. The structure of *trans*-[V(OH)₂(Cl)₂]Cl · 2H₂O has also been re-determined. This latter complex crystallizes in a monoclinic system in the *P2(1)/c* space group, *a* = 6.4381(9) Å, *b* = 6.3843(9) Å, *c* = 11.7980(17) Å and β = 98.057(2)°. The vanadium atom lies at a crystallographic inversion centre within the distorted octahedron formed by the four water and two chloride ligands.

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1. Introduction

Vanadium is a metal of environmental, biological and pharmacological relevance. It is commonly found in iron ores, clays, basalts and oils [1], and is the most abundant transition metal in the aquasphere [1]. Vanadium is found in nitrogenases in azotobacteria (V^{II}/V^{III}), haloperoxidases in marine algae (V^V), as amavadin in the mushroom *Amanita muscaria* (V^{IV}), as V^{III} in the marine fanworm *Pseudopotamilla ocellata* and as V^{III}/V^{IV} in ascidians [1,2].

There is also considerable interest in therapeutic applications of vanadium complexes for treating cancer and especially diabetes [3]. The relative ease with which vanadium is converted among a range of oxidation states is a dominant feature of vanadium coordination chemistry. However, much of the research on the coordination chemistry of this metal has focused on the +4 and +5 oxidation states despite the importance of V^{III} and V^{II} in biology, since these complexes are readily probed using conventional field EPR and ⁵¹V NMR spectroscopy and do not require strictly anaerobic conditions.

One area of V^{III} chemistry of fundamental biological importance concerns its coordination to amino acids. There have been numerous reports on the formation of V^{III}/amino acid complexes in aqueous solution [4–12].

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However, although a large number of amorphous amino acid complexes of vanadium(III) complexes have been isolated [5,8,10], only a handful of V(III)/amino acid complexes have been structurally characterized by X-ray diffraction: $[\text{V}_2(\text{L-His})_4(\mu\text{-O})] \cdot 2\text{H}_2\text{O}$ [4,13], $\text{Na}[\text{V}(\text{L-Cys})_2] \cdot 2\text{H}_2\text{O}$ [6], $[\text{V}(\text{L-Pro})_3] \cdot \text{DMSO}$ and $[\text{V}(\text{D-Pro})_3] \cdot \text{DMSO}$ [5]. Herein we report the synthesis and X-ray structural characterization of the homoleptic V^{III} complex of the structurally simplest amino acid glycine, $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$. We have also re-determined the structure of *trans*- $[\text{V}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$.

2. Results and discussion

Crystals of $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ formed upon reacting VCl_3 with 3.3 equiv. of sodium glycinate in dry DMSO solution under strictly anaerobic conditions. The color of the solution changed from brown to dark purple over a period of 90 min, upon which the volume was reduced and the solution filtered to remove excess sodium glycinate. A mixture of purple and colorless crystals grew, from which a purple plate was removed for crystallographic studies. The colorless crystals were presumed to be sodium chloride. Since an insufficient amount of crystals were

obtained, the procedure was repeated and a product precipitated which elemental analysis showed to be consistent with the formulation $[\text{V}(\text{Gly})_3] \cdot \text{DMSO} \cdot \text{NaCl}$ (see Section 3 for further details).

A thermal ellipsoid plot of $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ is shown in Fig. 1. Crystallographic data and selected bond lengths and angles are given in Tables 1 and 2, respectively. The asymmetric unit contains one molecule of $\text{V}(\text{Gly})_3$ and two DMSO solvent molecules. The vanadium atom resides in a distorted octahedral environment, coordinated by three bidentate glycinato ligands, each coordinated to the metal center via the nitrogen and a carboxylate oxygen. The ligands are arranged in a *mer* configuration with both Δ and Λ enantiomers present in the unit cell. The O–V–N bond angle, where O and V are atoms from the same ligand, are significantly smaller than the ideal octahedral angle of 90° (79.64, 87.18 and 81.34° , Table 1). The V–O and V–N bond distances are similar to those reported for $[\text{V}^{\text{III}}(\text{L-Cys})_2]^-$ (2.02 and 2.13 Å, respectively) [6]. They are also similar to the Cr–O and Cr–N bond lengths of $[\text{Cr}^{\text{III}}(\text{Gly})_3]$, Table 3. The extended packing array of $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ is shown in Fig. 1. The complex is overall neutral in charge and spaces in between the complex units are occupied by a bilayer of DMSO molecules,

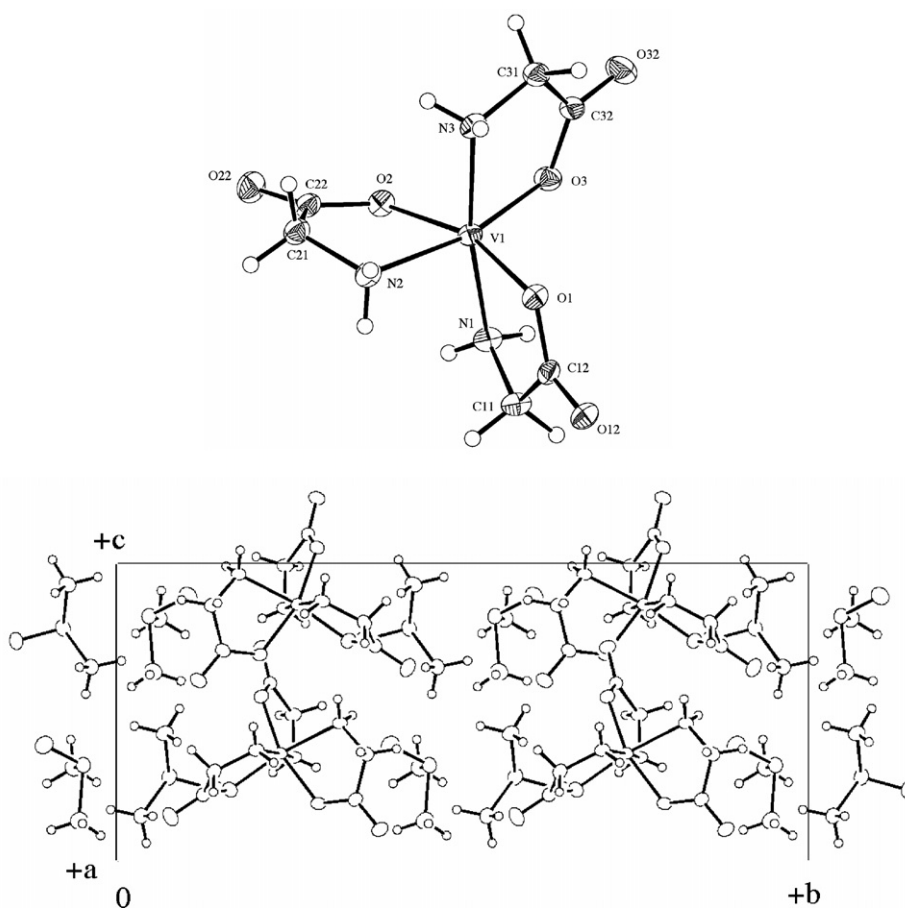


Fig. 1. Upper figure: Thermal ellipsoid plots (30% probability) of the core of *mer* $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ with labeling of selected atoms. Hydrogen atoms are drawn as circles with small radii. Lower figure: Unit cell packing diagram of $\text{C}_{10}\text{H}_{24}\text{N}_3\text{O}_8\text{S}_2\text{V}$ projected down the *a* axis.

Table 1
Crystallographic data for $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ and $\text{trans-}[\text{V}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

Complex	$[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$	$\text{trans-}[\text{V}(\text{OH}_2)_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$
Chemical formula	$\text{C}_6\text{H}_{12}\text{N}_3\text{O}_6\text{V} \cdot 2(\text{C}_2\text{H}_6\text{OS})$	$\text{C}_{13}\text{H}_{12}\text{O}_6\text{V}$
M_r	429.39	269.39
T (K)	200(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	Cc	$P2(1)/c$
a (Å)	8.9186(5)	6.4381(9)
b (Å)	21.5347(9)	6.3843(9)
c (Å)	9.9064(5)	11.7980(17)
β (°)	110.536(3)	98.057(2)
V (Å ³)	1781.71(16)	480.14(12)
Z	4	2
D_{calc} (g cm ⁻³)	1.601	1.836
μ (mm ⁻¹)	0.834	1.848
Reflections collected	12164	3571
Independent reflections	3969	938
R [$I > 2\sigma(I)$]		0.0476
$R_w(F^2)$ [$I > 2\sigma(I)$]		0.1378
R (all data)		0.0487
$R_w(F^2)$ (all data)		0.1380
R [$I > 3\sigma(I)$]	0.0326	
R_w [$I > 3\sigma(I)$]	0.0289	
GOF	1.0830	1.343

Table 2
Selected bond lengths (Å) and angles (°) for $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$

V1–O1	1.959(2)	V1–N1	2.125(2)
V1–O2	1.984(2)	V1–N2	2.155(3)
V1–O3	1.952(2)	V1–N3	2.138(3)
O1–V1–O2	160.75(9)	O3–V1–N2	167.28(10)
O1–V1–O3	103.96(9)	O1–V1–N3	97.24(10)
O2–V1–O3	92.34(9)	O2–V1–N3	95.26(10)
O1–V1–N1	79.64(9)	O3–V1–N3	81.34(9)
O2–V1–N1	90.22(9)	N1–V1–N3	170.27(12)
O3–V1–N1	90.41(10)	N1–V1–N2	97.73(12)
O1–V1–N2	87.18(9)	N2–V1–N3	91.29(11)
O2–V1–N2	77.94(9)		

Table 3
Selected bond lengths (Å) and angles (°) for homoleptic glycine complexes of first row transition metals

	$[\text{V}^{\text{III}}(\text{Gly})_3]^{\text{a}}$	$[\text{Cr}^{\text{III}}(\text{Gly})_3]$ [17]	$[\text{Co}^{\text{III}}(\text{Gly})_3]$ [14]	$[\text{Ni}^{\text{II}}(\text{Gly})_3]^-$ [16]
M–O	1.95–1.98	1.96–1.97	1.88–1.93	2.04–2.06
M–N ^b	2.13–2.16	2.06–2.07	1.92–1.95	2.09–2.10
O–M–N ^b	77.9–81.3	81.6–82.0	85.0–87.1	81.0–82.1

^a This work.

^b O and N from the same Gly ligand.

which are hydrogen bonded to the amine groups on the glycinato ligands.

To our knowledge $[\text{V}(\text{Gly})_3] \cdot 2\text{DMSO}$ is the first example of a structurally characterized vanadium complex

incorporating glycine. There are, however, several reports concerning formation of V^{III} /glycine complexes [9–12]. UV–Vis titration studies support formation of a 1:1 V^{III} /glycine complex in acidic solution [9]. Castillo and co-workers report that $[\text{V}(\text{Gly})_3]$ is formed upon the addition of 3 mol equiv. glycine to an aqueous solution of VCl_3 , although the complex was not characterized [10]. They also isolated a compound described as $[\text{V}(\text{GlyH})_3\text{Cl}_3]$ (a species with monodentate coordination of GlyH to V^{III} via the nitrogen atom), upon dissolving the former complex in 2 M HCl. Recent potentiometric studies also provide support for the formation of $\text{V}(\text{Gly})_3$ in aqueous solution [12], although another study highlights the difficulties in obtaining reliable data for these systems due to the ease of hydrolysis of V^{III} in aqueous solution [11]. We made several attempts to crystallize glycine complexes of V^{III} from aqueous solution, without success. However given that $[\text{V}^{\text{III}}(\text{L-Cys})_2]^-$ crystallizes from aqueous solution [6], it seems reasonable that $[\text{V}(\text{Gly})_3]$ is also formed.

Crystallographically characterized homoleptic metal complexes of glycine are surprisingly uncommon, with structures reported for $\text{Co}^{\text{III}}(\text{Gly})_3$ in both the *fac* and *mer* configurations [14,15], *fac* $\text{Ni}^{\text{II}}(\text{Gly})_3$ [16] and *fac* $\text{Cr}^{\text{III}}(\text{Gly})_3$ [17] only. Table 3 summarizes M–O and M–N bond distances and the O–M–N bond angle (where O and N from the same Gly ligand) for these complexes, which belong to the first row of the transition series. As the effective nuclear charge increases across the period, the M–O and especially the M–N bond distance shortens for the +3 metal complexes. Shortening of the metal–ligand bonds leads to an increase in the O–M–N angle, as expected from a geometric point of view. The M–O and M–N bond lengths of $[\text{Ni}^{\text{II}}(\text{Gly})_3]^-$ are significantly shorter compared with its closest neighbor $[\text{Co}^{\text{III}}(\text{Gly})_3]$, due to the lower oxidation number of the metal center and hence the lower effective nuclear charge. This results in a decrease in the O–M–N bond angle, as expected.

A limited number of V^{III} structures with purely water and halide ligands have been reported. Two structures of $[\text{V}(\text{OH}_2)_6]^{3+}$ species have been determined: a double salt incorporating a hydrated hydroxonium ion as a triflate salt [18] and alums of $[\text{V}(\text{OH}_2)_6]^{3+}$ with the composition $\text{M}(\text{I})\text{V}(\text{III})(\text{XO}_4) \cdot 12\text{H}_2\text{O}$ (M(I) = K, Rb, or Cs; X = S or Se) [19]. Recently we crystallized and structurally characterized a series of trinuclear and tetranuclear V^{III} complexes of acetate and related carboxylate ligands from acidic aqueous solution [20]. In several crystallization attempts of V^{III} /carboxylate complexes, crystals of $\text{trans-}[\text{V}(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ were instead obtained. Although the $\text{trans-}[\text{V}(\text{OH}_2)_4\text{Cl}_2]^+$ cation is not abundant in these solutions, favorable crystallization of the chloride salt of this cation drives the reaction to produce significant amounts of $\text{trans-}[\text{VCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals. The structure of this complex has been determined previously by Smith et al. [21]; however, we felt that it was worthy of re-examination as the earlier report estimated the intensities visually, and the data was from a twinned crystal

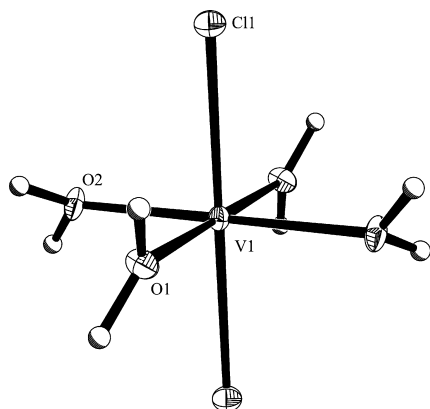


Fig. 2. Thermal ellipsoid plots (30% probability) of the cation from *trans*-[V(OH₂)₄Cl₂]Cl · 2H₂O with labeling of selected atoms.

using Cu-K α as the radiation source. Our data was obtained from a single crystal using Mo K α radiation and an array detector.

A crystal of *trans*-[V(OH₂)₄Cl₂]Cl · 2H₂O was selected from an acidic aqueous solution of VCl₃ and phthalic acid (see Section 3). The thermal ellipsoid plot is shown in Fig. 2. Crystallographic data and selected bond distances and angles are given in Tables 1 and 4, respectively. The V^{III} center is coordinated by four water molecules and two *trans* chloride ligands in a distorted octahedral geometry, with the V–Cl bond longer than either V–O bond. The vanadium atom sits at an inversion centre. The bond lengths and angles agree well with the previously reported structure, although the variance between the V–O bond distances is smaller in this more recent structural elucidation (see Table 4). Smith et al. also reported on the structure of the *trans*-[V(OH₂)₄Cl₂]⁺ ion in the salt Cs₂[V(OH₂)₄Cl₂]Cl₃ [22]. Interestingly, in spite of the different packing and hydrogen bonding present in the lattice, the bond lengths are remarkably similar in both structures, with V–O and V–Cl lengths shortening by only 0.01 Å in the cesium structure. In contrast, the arrangement of water molecules in the cesium salt is in a rectangular configuration with an acute O–V–O bond angle of 81.2(2)°. These differences most likely result from changes in packing between the two solids. The structure of the isomorphous bromo complexes *trans*-[V(OH₂)₄Br₂]Br · 2H₂O and cesium

trans-[V(OH₂)₄Br₂]Br₃ have also been reported [21,22]. The V–OH₂ bond lengths in these latter complexes are remarkably similar to those observed for the isomorphous chloro complexes, indicating that the donor properties of the *cis* halides have little effect on the V–O bond distance in these cations.

In summary, we report the crystal structure of the tris-glycinato complex of vanadium(III). The vanadium atom resides in a distorted octahedral environment, and the bidentate amino acid ligands chelate in a *mer* configuration. In addition, we have re-elucidated the structure of the *trans*-[V(OH₂)₄Cl₂]Cl · 2H₂O salt, a common by-product of aqueous reactions using VCl₃ as a starting material. We are continuing our work investigating the biologically relevant chemistry of V^{III} and the structures of the coordination complexes of this metal ion.

3. Experimental

Materials: Unless otherwise stated, chemicals were of reagent grade purity or better, obtained from commercial suppliers and used without further purification. All experiments were conducted under an atmosphere of N₂ or argon using standard schlenk techniques. Infra red spectra were recorded on either a Perkin Elmer Spectrum I spectrophotometer or a Bruker Tensor 27 spectrophotometer as KBr disks at room temperature. Elemental analyses were performed by the analytical service of the Research School of Chemistry, Australian National University.

3.1. Synthesis of sodium glycinate, NaGly

Na metal (3.29 g, 0.14 mol, rinsed in petroleum ether) was added in small pieces to dry MeOH (~50 mL) under argon with stirring. The solution was filtered (Schlenk apparatus) and glycine (10.0 g, 0.13 mol) added to yield a white solid. The white solid was collected by filtration, washed with MeOH (~20 mL) and dried overnight under vacuum (0.01 mbar) at ~100 °C. Microanalytical data: *Anal.* Calc. for C₂NO₂H₄Na: Na, 23.69; C, 24.75; H, 4.15; N, 14.43. Found: Na, 24.02; C, 24.49; H, 3.98; N, 14.04%. The IR spectrum was in good agreement with that reported in the literature [23].

3.2. Synthesis of [V(Gly)₃] · 2DMSO

VCl₃ (0.23 g, 1.47 mmol) was suspended in dry DMSO (30 mL) and stirred for 30 min. The suspension was filtered into a flask containing 3.3 equiv. NaGly (0.47 g, 4.85 mmol). After 90 min of stirring the color changed from greenish-brown to plum colored. The solution was reduced in volume under reduced pressure and filtered to remove excess NaGly. The concentrated solution was left sitting at room temperature and after several days a mixture of purple and colorless crystals were obtained. A purple plate crystal measuring 0.15 × 0.12 × 0.06 mm was removed for X-ray crystallography.

Table 4

Selected bond lengths (Å) and angles (°) for comparison of the *trans*-[V(OH₂)₄Cl₂]Cl · 2H₂O structures and the *trans*-[V(OH₂)₄Cl₂]⁺ core of Cs₂[VCl₂(OH₂)₄]Cl₃

This work		Previous work ³⁶	Cs ₂ [VCl ₂ (OH ₂) ₄]Cl ₃ ³⁷
V1–O1	2.000(4)	2.024(5)	1.983(10)
V1–O2	1.993(4)	1.961(7)	
V1–Cl1	2.3712(13)	2.361(2)	2.361(2)
O1–V1–O2	89.51(18)	88.6(2)	81.2(2)
O1–V1–Cl	87.79(14)	87.9(1) ^a	91.1(1)
O2–V1–Cl	89.70(13)	87.4(2) ^a	

^a These angles have been converted to allow for comparison with the present work.

3.3. Synthesis of $[V(\text{Gly})_3] \cdot \text{NaCl} \cdot \text{DMSO}$

The method above was repeated and a powder was isolated instead of crystals. The powder was washed with hot EtOH (3×30 mL) to remove excess NaCl. The powder was dried *in vacuo* for 4 h. Yield 0.24 g (17%). Microanalytical data: *Anal.* Calc. for $[V(\text{Gly})_3] \cdot \text{NaCl} \cdot \text{DMSO}$; $\text{C}_8\text{H}_{18}\text{N}_3\text{ClNaO}_7\text{SV}$: C, 23.5; H, 4.4; N, 10.3; Cl, 8.7. Found: C, 23.6; H, 4.5; N, 10.2; Cl, 8.5%. IR (KBr): 3434 m, 3269 m, 3080 m, 1651 s, 1538 m, 1405 m, 1360 m, 1320 m, 1261 w, 1133 w, 1028 m, 973 m, 802 w, 737 w, 675 w, 586 w.

3.4. Crystallization of $\text{trans-}[V(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

Phthalic acid (0.72 g, 4.3 mmol) was added to a solution of VCl_3 (0.92 g, 5.9 mmol) in water (~ 6 mL) with stirring, causing the solution to change from brown to green. The solution was heated under reflux for 20 min, then slowly cooled the solution to room temperature and the solution filtered. The solvent was reduced under reduced pressure (~ 1 mL) until crystals appeared. The solution was heated gently until all solid had re-dissolved, and the flask placed in a dewar of hot (~ 70 °C) water, causing the solution to change from green to brown. Green crystals deposited upon slow cooling of the solution to room temperature. A crystal measuring $0.2 \times 0.2 \times 0.06$ mm was removed for X-ray diffraction studies. The product proved to be heat sensitive in the crystalline form. Yield 80 mg, 7%. Microanalytical data: *Anal.* Calc. for $\text{trans-}[V(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, $\text{VCl}_3\text{H}_{12}\text{O}_6$: C, 0.00; H, 4.56; Cl, 40.07; V, 19.20. Found: C, 0.90; H, 4.22; Cl, 39.93; V, 19.11%. Selected IR data (cm^{-1} , KBr): 3333 (br s), 3028 (br s), 1603 (s), 1458 (w), 1421 (w), 1263 (w), 1064 (m), 802 (m), 749 (m), 501(m), 478 (m), 348 (m).

4. X-ray crystallography experiments

X-ray diffraction data for $[V(\text{Gly})_3] \cdot 2\text{DMSO}$ were measured at 200 K on a Nonius KappaCCD diffractometer using Mo $\text{K}\alpha$ radiation. Intensity data were collected with ϕ and ω scans, and corrected for absorption analytically. The structure was solved with use of SIR92 and refined using the CRYSTALS software package. Non-hydrogen atoms were refined with anisotropic displacement parameters while hydrogen atoms were refined positionally but with isotropic displacement parameters held fixed at appropriate values. Restraints were applied to distances and angles involving hydrogen atoms bonded to carbon atoms.

X-ray diffraction data for $\text{trans-}[V(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operating at 2000 W. The crystal was mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystal. 1818 frames were collected with a scan width of 0.3° in ω . Analyses of the

data sets showed negligible decay during data collection. The data were corrected for absorption with the SADABS program. The structure was refined using the Bruker SHELXTL Software Package (version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged. Hydrogen–oxygen bond lengths were restrained to ideal values (0.95 Å) on the water molecules and the hydrogen atoms were refined isotropically.

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Appendix A. Supplementary material

CCDC 659004 and 418528 contain the supplementary crystallographic data for $[V(\text{Gly})_3] \cdot 2\text{DMSO}$ and $\text{trans-}[V(\text{OH}_2)_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre and The Inorganic Crystal Structure Database via www.ccdc.cam.ac.uk/data_request/cif and http://www.fiz-karlsruhe.de/crystal_structure_dep.html. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2007.11.025](https://doi.org/10.1016/j.ica.2007.11.025).

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