Vanadium(v) complexes of mandelic acid†

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New vanadium complexes of mandelic acid (NMe4)2[V2O4(Ir)-mand]2 [V2O4(IS)-mand]2 (1), (NMe4)2- [V2O4(IS)-mand]2H2O (2), (NEt4)2[V2O4(IS)-mand]2H2O (3), (PPPh4)2[V2O4(Ir)-mand]2H2O(C2H2COCH3)2H2O (4), and (NH4)2[NEt4][V2O4(IR)-mand]2H2O (5) (mand2- = mandelato ligand) have been synthesized and characterized by single crystal X-ray diffraction and FT-IR spectroscopy. The band assignment in the IR spectra was corroborated by DFT calculations. While the structures of 1–4 comprise the expected dinuclear [V2O4(mand)2]2- (V2L2) anions, the structure of [V2O4(IR)-mand]2H2O (5) (V3L2) in 5 is unique and represents a new structural type in vanadium(v) chemistry. Solution studies of vanadium with mandelic acid by 51V NMR revealed the presence of two dominant species V2L2 and V3L2 in aqueous solutions and increasing fraction of V3L2 species at slightly acidic pH (pH ≈ 6).

Introduction

Vanadium participates in an essential way in several biochemical processes. This element was found at the active centre of some enzymes, including vanadium dependent nitrogenases or vanadium haloperoxidases which enable halogenation of organic compounds.1 On the other hand α-hydrocarboxylic acids are also involved in many basic biochemical processes (such as the Krebs cycle, Cori cycle, photorespiration and others).2 Due to the importance of both vanadates and α-hydrocarboxylic acids the mutual interaction of these groups of compounds was intensively studied.3–5 51V NMR studies revealed complex equilibria involving several species of different nuclearities; however, solid state investigations confirmed with certainty only dinuclear complexes.6 The dominant components in the vanadate–α-hydrocarboxylic acid system, apart from common vanadates, are the dinuclear and trinuclear complexes of the composition V2L2 and V3L2 (L = anion of the α-hydrocarboxylic acid) accompanied by a mononuclear complex VL7. Several dinuclear vanadium(v) complexes with α-hydrocarboxyloxytalo ligands were also reported in the solid state: {NH4}2[V2O4(glyc)2], Rb2[V2O4(glyc)2], Na2[V2O4(mlact)2], 7H2O, Na2[V2O4(mlact)2]·2H2O,11 (NBu4)2[V2O4(mlact)2]·2H2O,12 (NH4)2[V2O4(ethyl)]2·H2O,13 and Cs2[V2O4((S)-lact)]2·2H2O,14† and a richer series of vanadium complexes with α-hydrocarboxylic acids with more than one carboxyl group such as malic,14 citric,15–23 homocitric24 and tartaric acid.25–28 The crystal structures confirmed the composition and geometry as were proposed by 51V NMR spectroscopy; however, the V3L2 complexes do not have a model compound with a solved crystal structure. In this list, mandelato complexes are obviously missing. Mandelic acid is a common chiral aromatic α-hydrocarboxylic acid (Scheme 1). Isolation of non-peroxido vanadium(v) complexes of mandelic acid was, so far, not possible mainly due to its strong reduction potential towards V(V). In this work we augment the family of vanadium(v) complexes of α-hydrocarboxylic acids by mandelato complexes. We present the synthesis and characterization of dinuclear V2L2 complexes and a trinuclear V3L2 complex which revealed a surprising structure not identical to the previously proposed geometry.

Experimental

Materials and methods

All chemicals were of analytical grade and used as received. Stock aqueous solutions of (NMe4)VO3 and (NEt4)VO3 (1 mol dm−3) were prepared by dissolution of V2O5 in conc. (NMe4)OH and (NEt4)OH, adjustment of the pH to 8.0 and dilution. Elemental analyses (C, H, and N) were performed on a Vario MIKRO cube (Elementar).

† Abbreviations of ligands: glyc2- = glycylato, lact2- = lactato, mlact2- = methyl-lactato, ethl2- = 2-ethyl-2-hydroxybutanoato.

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The phase problem was solved by direct methods (SHELXS) 29 with and refined by full-matrix least-squares based on \( F^2 \) (SHELXL). 10 All non-hydrogen atoms were refined with no restraints and with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined as riding atoms. Graphics were obtained with DIAMOND. 31 In the case of compound 5 we were forced to use SQUEEZE to expel cations and present only the structure of the anionic component of the compound. Crystal structure data and refinement details are summarized in Table S1 (see ESIF).

Calculation of infrared spectra

The molecular structure of \([V_2O_4((S)\text{-mand})_2]^{2-}\) from compound 2 has been optimized at the DFT level with the BP86 functional 32,33 using tight convergence criteria and an ultrasoft integration grid in vacuo. We have employed the all-electron Wachters+ [14s11p6d3f] [8s6p4d1f] basis set 34,35 for the vanadium atom and the 6-31+G(d,p) basis set 36,37 for the remaining atoms. Afterwards, harmonic vibrational frequencies were calculated. Quantum chemical calculations were performed using the Gaussian 09 Revision D.01 program 38 and for subsequent potential energy distribution (PED) analysis the VEDA4 program was utilized. 39

Syntheses

\([\text{NMe}_4]_2[V_2O_4((R)\text{-mand})_2] \cdot [V_2O_4((S)\text{-mand})_2] \) (1). To 9.4 mL of acetone, 0.4 mL of aqueous \( \text{rac-H}_2\text{mand} \) (0.5 mol dm\(^{-3}\); 0.2 mmol) and 0.2 mL of \( \text{NMe}_4\text{VO}_3 \) (1 mol dm\(^{-3}\); 0.2 mmol) were added. The solution was kept at \( -20 \) °C. After two weeks, yellow needle-like crystals of 1 were isolated. Yield: 50 mg (40% based on V). Analytical data for \( C_{26}H_{34}N_2O_{14}V_2 \) in % (calc. %): C 46.05 (46.91), H 6.24 (5.91), N 4.58 (4.56), V 16.3 (16.6).

\([\text{NMe}_4]_2[V_2O_4((S)\text{-mand})_2] \cdot 2\text{H}_2\text{O} \) (2). To 9.5 mL of acetone, 0.3 mL of aqueous \( (S)\text{-H}_2\text{mand} \) (0.5 mol dm\(^{-3}\); 0.15 mmol) and 0.2 mL of \( \text{NMe}_4\text{VO}_3 \) (1 mol dm\(^{-3}\); 0.2 mmol) were added. The solution was kept at \( -20 \) °C. After six weeks, yellow needle-like crystals of 2 were isolated. Yield: 25 mg (20% based on V). Analytical data for \( C_{26}H_{34}N_2O_{12}V_2 \) in % (calc. %): C 45.10 (45.58), H 6.05 (6.06), N 4.59 (4.43).

\([\text{NET}_4]_2[V_2O_4((S)\text{-mand})_2] \cdot 3\text{H}_2\text{O} \) (3). To 100 mL of acetone, 5 mL of \( \text{NET}_4\text{VO}_3 \) (1 mol dm\(^{-3}\); 5 mmol) and 5 mL of \( (S)\text{-H}_2\text{mand} \) (1 mol dm\(^{-3}\); 5 mmol) were added. The solution was kept at \( -20 \)°C. After one day, yellow plate-like crystals of 3 were isolated. Yield: 69 mg (20% based on V). Analytical data for \( C_{32}H_{54}N_2O_{14}V_2 \) in % (calc. %): C 50.49 (51.61), H 7.40 (7.31), N 3.73 (3.76).

\([\text{PPh}_4]_2[V_2O_4((R)\text{-mand})_2] \cdot (S\text{-mand})_2] \cdot 2\text{H}_2\text{O} \) (4). To 9.4 mL of acetone, 0.4 mL of aqueous \( \text{rac-H}_2\text{mand} \) (0.5 mol dm\(^{-3}\); 0.2 mmol), 0.2 mL of \( \text{NMe}_4\text{VO}_3 \) (1 mol dm\(^{-3}\); 0.2 mmol) and 0.225 g of \( \text{PPh}_4\text{Cl} \) (0.6 mmol) were added. The solution was kept at \( -20 \)°C. After one month yellow needle-like crystals of 4 were isolated. Yield: 44 mg (17% based on V). Analytical data for \( V_2P_2C_70H_{68}O_{14} \) in % (calc. %): C 63.77 (64.82), H 4.92 (5.28), V 8.5 (7.9).

\([\text{NH}_4]_2[\text{NET}_4]_2[V_2O_4((R)\text{-mand})_2] \cdot (S\text{-mand})_2] \cdot 2\text{H}_2\text{O} \) (5). The pH of an aqueous solution of \( \text{NET}_4\text{VO}_3 \) (1.5 mL; \( c = 1 \) mol dm\(^{-3}\); 1.5 mmol) was adjusted to 9.0 with concentrated \( \text{NH}_3 \). Afterwards, the solution was mixed with 1.2 mL of aqueous solution of \( \text{rac-H}_2\text{mand} \) (1.2 mmol; \( c = 1 \) mol dm\(^{-3}\)) and concentrated. The obtained solution acetone (35 mL) was added. The resulting solution was allowed to crystallize at \( -20 \)°C. After 3 weeks light yellow crystals in the form of rectangular plates were isolated. Yield: 117 mg (11% based on V). Analytical data for \( C_{20}H_{36}N_2O_{15}V_3 \) in % (calc. %): C 33.35 (33.77), H 6.46 (5.10), N 6.02 (5.91), V 21.89 (21.48).

The \([\text{NET}_4]_2[V_2O_4(\text{mlact})]_2 \cdot 2\text{VO}_3(\text{OH})_2 \) (type \( V_2L_2 \)) complex was obtained in the mixture with \([\text{NET}_4]_2[V_2O_4(\text{mlact})]_2 \) (type \( V_2L_3 \)). Attempts to isolate the \( V_2L_2 \) complex in a form suitable for X-ray studies failed. The proposed structure of this complex we discussed in the text.

Results and discussion

Crystal structures

The prepared dinuclear mandelato complexes can be divided into two groups. For compounds 1-3 we observed that the central \( V_2O_4 \) unit binds always to the mandelato anion of the same configuration. Thus, racemic compound 1 contains both enantiomers \([V_2O_4((S)\text{-mand})_2]^{2-}\) and \([V_2O_4((R)\text{-mand})_2]^{2-}\) related in the crystal packing by the center of symmetry (Fig. 1), while compounds 2 and 3 contain only the \([V_2O_4((S)\text{-mand})_2]^{2-}\) anion. The \([V_2O_4((R)\text{-mand})_2]^{2-}\) anion in 4 contains both enantiomers of the racemic mandelatic acid (Fig. 2). Because of the \( C_1 \) symmetry it is a meso-anion. It can be concluded from the stereochemical point of view that the formation of vanadium(\( V_2O_4 \)) mandelato complexes is not stereospecific, because it is possible to obtain the chiral anion (1) and the achiral compound in complex (4) starting from a racemic precursor of \( \text{rac-mandelic acid} \). Table 1 summarizes geometrical data for the anions in all compounds. As confirmed by the calculation of \( \tau \) parameters in...
pentacoordinated systems, the vanadium atoms V1 and V2 form slightly distorted tetragonal pyramidal coordination geometry and are displaced above the calculated plane by about 0.5 Å. Axial positions are occupied by oxido ligands O1 and O2, respectively. The tetragonal pseudoplane is completed by one oxido ligand (O3, and O4, resp.), and one oxygen atom from the carboxylate anion (O6, and O9, resp.) and the two vanadium atoms are connected by hydroxylate oxygen atoms O5 and O8.

Compound 5 is the first isolated vanadium(V) complex of an α-hydroxycarboxylic with the stoichiometry V₃L₂. Previous attempts to clarify the structure of such complexes relied mostly on ⁵¹V NMR spectroscopy. The proposed structure is shown in Scheme 2. However, the X-ray structure analysis of 5 revealed a different structure (Fig. 3). The [V₃O₇((R)-mand)((S)-mand)]³⁻ anion contains both enantiomers of rac-mandelic acid. Unlike in Scheme 2, all vanadium atoms are pentacoordinated. Two oxido ligands always occupy the axial positions and one equatorial position. The central vanadium atom V1 is further coordinated by two oxygen atoms coming from the hydroxylate group and the oxido ligand, O1. The oxygen atom, O1, represents an unexpected feature of the anion as it was not expected in V₃L₂ complexes. The bridging μ₂-O1 ligand is connecting all three vanadium atoms of the anion. The coordination of the V2 atom is completed by the chelating mandelato ligand that coordinates through one hydroxylato (O2) and one carboxylate (O3) oxygen.

| Compound bond lengths and δ in Å | 1     | 2     | 3     | 4*   |
|----------------------------------|-------|-------|-------|------|
| V=O                             | 1.6206(12) | 1.621(4) | 1.622(3) | 1.6213(9) |
| V2-O2                           | 1.6213(13) | 1.613(4) | 1.617(3) | 1.6248(8) |
| V1-O3                           | 1.6305(12) | 1.617(4) | 1.628(3)  | —   |
| V2-O4                           | 1.6308(13) | 1.617(4) | 1.636(3) | —   |
| V-O₉ₖ                           | V1-O5   | 1.9730(10) | 1.957(3) | 1.954(3) | V1–O3' 1.9636(8) |
| V2-O5                           | 2.0438(11) | 2.017(3) | 2.033(3) | V1–O3 2.0319(8) |
| V1-O8                           | 2.0280(11) | 2.015(3) | 2.032(3) | 1.9637(8) |
| V2-O8                           | 1.9690(11) | 1.969(3) | 1.980(3) | —   |
| V–O₉₉                           | V1–O9   | 1.9714(11) | 1.960(4) | 1.965(3) | V1–O4 1.9775(9) |
| V2–O6                           | 1.9711(12) | 1.989(3) | 1.957(3) | —   |
| δₒ V₁                          | 0.2    | 0.38  | 0.11  | 0.15 |
| δₒ V₂                          | 0.527  | 0.533 | 0.487 | 0.513 |
| δₒ V₃                          | 0.04   | 0.15  | 0.18  | —   |
| δₒ V₄                          | 0.565  | 0.535 | 0.533 | —   |

O₉₆ – oxygen atom from the original alcoholic group, O₉₇ – oxygen atom from the original carboxylic acid group. τ – parameter calculated from two bond angles in the tetragonal pseudoplane as (α – β)/60; τ = 0 tetragonal pyramidal geometry, τ = 1 trigonal bipyramidal geometry. δ – displacement of the V atom from the ideal plane calculated from the positions of four atoms forming the tetragonal pseudoplane. * – only symmetrically independent bond parameters of the anion are given.
atomic. Key structural parameters of \([\text{V}_2\text{O}_7(\text{(R-mand)})\text{[(S-mand)]}]^{3-}\) are summarized in Table 2.

The triangular center \([\text{V}_3\text{O}_7\text{O}_2]\) has been known in several vanadium(III) complexes. However, most of these compounds exhibit \(D_{3h}\) symmetry, or at least approximate \(C_3\) axis passing through the \((\mu_{3-O})\) atom.\(^{40}\) In the case of anion \([\text{V}_2\text{O}_7(\text{(R-mand)})\text{[(S-mand)]}]^{3-}\), the geometry around the O atom is different and it lies in the symmetry plane of the \(C_3\) symmetry.

In conclusion, the molecular structure of \([\text{V}_3\text{O}_7(\text{O}_2)\text{[(S-mand)]}]^{3-}\) differs from the proposed one\(^{7}\) in: (1) the absence of bridging OH\(^-\) groups between V1 and V2 atoms, (2) the presence of a bridging \((\mu_{2-O})\) ligand connecting all vanadium atoms, (3) the coordination number of the central vanadium atom; and (4) the overall symmetry \(C_3\).

### Infrared spectroscopy

The selected characteristic bands in the IR spectra of the prepared mandelato complexes and their assignment are summarized in Table 3 (the spectra are shown in Fig. S1–S10 (ESI†)).

| Characteristic group | Wavenumbers in cm\(^{-1}\) |
|---------------------|---------------------------|
| \(\nu(\text{V}^-\text{O})\) | 921 (s) 928 (vs) 935 (s) 925 (s) 910 (s) |
| \(\nu(\text{C}^-\text{O})_\text{h}\) | 1048 (m) 1059 (s) 1061 (m) 1063 (m) 1072 (m) |
| \(\nu(\text{C}^-\text{O})_\text{co}\) | 1315 (m) 1323 (s) 1304 (m) 1298 (s) |
| \(\nu(\text{C}^-\text{O})_\text{hun}\) | 1332 (m) 1329 (m) 1329 (m) 1308 (s) |
| \(\nu(\text{C}^-\text{O})_\text{hun} - \text{uncoordinated} (\text{C}^-\text{O})\) groups | 1654 (vs) 1655 (vs) 1655 (v) 1651 (s) 1672 (vs) |

O\(_h\) – oxygen atom from the original alcoholic group, O\(_c\) – oxygen atom of bridging OH/C\(_0\) ones (Table 4) and enable reliable band assignment as shown in the positions of four atoms forming the tetragonal pseudoplane.

The selected characteristic bands in the IR spectra of the prepared compounds and their assignment are summarized in Table 3 (the spectra are shown in Fig. S1–S10 (ESI†)). All compounds exhibit typical strong bands corresponding to \(\nu(\text{V}^-\text{O})\) vibrations in the region around 930 cm \(^{-1}\) as well as to \(\nu(\text{C}^-\text{O})_\text{h}\), \(\nu(\text{C}^-\text{O})_\text{co}\) and \(\nu(\text{C}^-\text{O})_\text{hun}\) (for symbols see Table 2) vibrations of the coordinated carboxylato ligand.

Theoretical calculations are very helpful for more precise band assignment using PED analysis that allows decomposing complicated vibrational movement of the molecule into several components. Thus, we employed this method for band assignment of the model \([\text{V}_2\text{O}_7(\text{(S-mand)})\text{]}^{2-}\) anion from compound 2. The theoretical values are in good agreement with experimental ones (Table 4) and enable reliable band assignment as shown in Table 3. We recently employed DFT calculations of IR spectra for several chiral and non-chiral vanadium(\(\nu\)) complexes using similar basis sets and methods demonstrating that the interpretation of IR spectra of distinct geometries may be performed reliably using theoretical calculations.\(^{31-43}\)

### Solution studies of vanadate with mandelic acid

The \(^{51}\)V NMR spectra have been measured for a number of nonperoxido vanadium(\(\nu\)) \(\nu\)-hydroxycarboxylato complexes.\(^{7,13,44-47}\) The only published data on nonperoxido vanadium(\(\nu\)) complexes with mandelic acid\(^{44}\) supposed the existence of complexes, "a" of the \(n(V):n(\text{L}) = 1:1\) type with a signal at \(-532\) ppm and, "b" with unknown stoichiometry, the signal for which appeared at \(-548\) ppm. Studied \(\nu\)-hydroxycarboxylic acids can be divided into two groups: The first one consists of the \(\nu\)-hydroxycarboxylic acids containing one carboxylic acid group and one alcoholic group, e.g. glycolic, lactic and mandelic acids. The second group involves \(\nu\)-hydroxycarboxylic acids with more than one carboxyl and hydroxyl groups, such as citric,\(^{45}\) glyceric or malic acids.\(^{44}\) Accordingly, the anions of \(\nu\)-hydroxycarboxylic acids of the second group can act as flexi-dentate ligands and have greater protonation variability in complexes. The most thorough studies\(^{7,46}\) devoted to \(\nu\)-hydroxycarboxylic acids of the first group suggested the existence of two dominant complexes with \(\text{V}_2\text{L}_2\) and \(\text{V}_3\text{L}_2\) stoichiometries (\(L\) represents the \(\nu\)-hydroxyxybcarbolyato-(2−) ligand). While the \(\text{V}_2\text{L}_2\) complex gives rise to one \(^{51}\)V NMR signal, the trinuclear complex exhibits different peaks for the central and “peripheral” vanadium atoms. Besides the signals of the \(\text{V}_2\text{L}_2\) and \(\text{V}_3\text{L}_2\) complexes, very weak signals of other species (\(\text{VL}\) and \(\text{V}\text{L}_3\)) have also been observed. The \(^{53}\)V NMR investigation we performed in the \(\text{H}_3\text{VO}_4/\text{rac-H}_2\text{mand-H}_2\text{O}\) system agrees with the general picture of the composition of complexes obtained by Tracey et al.\(^{7,47}\) and Pettersson et al.\(^{46}\) Summarized data from so far studied systems are given in Table 5.

In the \(^{53}\)V NMR spectrum of the \(\text{NMe}_4\text{VO}_3/\text{rac-H}_2\text{mand-H}_2\text{O}\) system (Fig. 4), it is possible to identify two groups of species. Besides various vanadates (\(\text{V}_1: \text{H}_2\text{VO}_4\), \(\text{V}_2: \text{H}_2\text{V}_2\text{O}_7\), \(\text{V}_3: \text{V}_2\text{O}_12\), \(\text{V}_4: \text{V}_2\text{O}_15\), and \(\text{V}_{10}: \text{H}_2\text{V}_{10}\text{O}_{28}\)), two broader peaks are present. The signal at \(-533\) ppm corresponds mainly to the \(\text{V}_2\text{L}_2\) complex and the signal at \(-551\) ppm arises from the central vanadium atom of the \(\text{V}_3\text{L}_2\) complex. The common signal of the two peripheral vanadium atoms of the \(\text{V}_3\text{L}_2\) complex is evidently overlapped by the signal at \(-533\) ppm. This overlapped signal is sometimes observed as a downfield
Table 4  Selected infrared bands for \( [\text{V}_2\text{O}_4((S)\text{-mand})\text{]}^{2-} \)

| Calculated wavenumbers with rel. intensity in parentheses | Experimental wavenumbers | Band assignment with PED |
|-----------------------------------------------------------|--------------------------|--------------------------|
| 3096 (9)                                                  | 2962 m                   | \( \nu(\text{C-H}) \)ar 92% |
| 3080 (11)                                                 | 2888 m                   | \( \nu(\text{C-H}) \)ar 92% |
| 1653 (9)                                                  | 1659 vs                  | \( \nu(\text{C-O}) \)un 83% |
| 1651 (100)                                                | 1336 m-s                 | \( \delta(\text{HCC}) \)ar 64% |
| 1299 (12)                                                 | 1323 s                   | \( \nu(\text{C-O}) \)ar 66% |
| 1293 (52)                                                 | 1084 m                   | \( \nu(\text{C-O}_\text{H}) \)37% \( \delta(\text{HCC}) \)ar 21% |
| 1082 (11)                                                 | 1059 s                   | \( \nu(\text{C-O}_\text{H}) \)37% \( \delta(\text{HCC}) \)ar 21% |
| 1051 (15)                                                 | 928 vs                   | \( \delta(\text{OCO}) \)91% (mean) |
| 968 (17), 964 (10), 953 (16), 951 (21)                   | 765 s                    | tors(\text{HCCC})_s 36%, tors(\text{CCCC})_s 18% |
| 768 (8)                                                   | 696 m                    | tors(\text{HCCC})_s 44%, tors(\text{CCCC})_s 39% |
| 705 (11)                                                  | 622 w                    | \( \delta(\text{OC}_2\text{C}_\text{C}_\text{H}) \)23%, \( \nu(\text{C}_\text{C}-\text{C}_\text{H}) \)12% |
| 675 (5)                                                   | 537 w                    | \( \delta(\text{OC}_2\text{C}_\text{C}_\text{H}) \)18% |
| 556 (6)                                                   | 444 s                    |             |
| 420 (15)                                                  |                         |             |

Relative intensities are given on the scale of 0–100, the bands with intensities < 5 were not included. \( \text{ar} \) – aromatic circle, \( \text{un} \) – uncoordinated \( \text{C-O} \) group, \( \text{co} \) – coordinated \( \text{C-O} \) group, \( \text{C}_\text{H} \) – carbon atom from the carboxylic acid group, \( \text{C}_\text{H}_\text{C} \) – carbon atom from the original alcoholic group.

Table 5  \( ^{51}\text{V} \) NMR chemical shifts of \( \alpha \)-hydroxy-carboxylato vanadium(v) complexes in aqueous solutions, and ionic strength 1.0 mol dm\(^{-3}\) NaCl. Chemical shifts are given in ppm.

| \( \text{V}_2\text{L}_2^{2-} \) | \( \text{V}_3\text{L}_2^{2-} \) |
|-------------------------------|--------------------------|
| \( \text{C}-\text{H} \) | \( \nu(\text{C-O}) \) |
| \( \text{V}_2\text{L}_2^{2-} \) | \( \text{V}_3\text{L}_2^{2-} \) |
| 533 ppm | 533 ppm |
| 533 ppm | 533 ppm |
| 533 ppm | 533 ppm |

Conclusions

In spite of the fact that the aqueous mandelic acid–vanadate system is prone to redox reactions, we succeeded in the synthesis of new vanadium(v) mandelo complexes by crystallization at...
−20 °C in acetone–water solvent. Dinuclear chiral [V₂O₆(mandelate)]²⁻ ([V₂L₂]) complexes in 1, 2 and 3 contain only one enantiomer of the mandelate anion regardless of whether chiral or racemic mandelic acid was used in the synthesis. On the other hand, the dinuclear achiral [V₂O₆([R]-mandate)([S]-mandate)]²⁻ anion in 4 comprises both enantiomers of the mandelato ligand. The [V₂O₆([R]-mandate)([S]-mandate)] ([V₂L₂]) anion in 5 possesses several unique structural features. To the best of our knowledge, it is the first vanadium(v) trinuclear complex with a triangular {[V₃µ₃O]} centre. The symmetry of the anion is C₃ and it contains both enantiomers of mandelate. The solution studies confirmed the expected similarity of the mandelic acid–vanadate system in acid aqueous solutions to systems with other 3-hydroxy-carboxylic acids.

Conflicts of interest

There are no conflicts to declare.

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