Trapping ionic dimers of dinuclear peroxido mandelato complexes of vanadium(V) into cavities constructed from Δ - and Λ -[Ni(phenanthroline)₃]²⁺ cations: a precursor to Ni(VO₃)₂

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Abstract

A nickel–vanadium metal–organic hybrid compound [Ni(phen)₃]₂[(V₂O₂(O₂)₂((*S*)-mand)₂)][(V₂O₂(O₂)₂((*R*)-mand)₂)]·18H₂O (*phen* = 1,10-phenanthroline, *mand*^{2−} = mandelato(2−) ligand, C₆H₅–CO–COO^{2−}) (**1**) was prepared and characterized by spectral methods, X-ray structure analysis and simultaneous DTA and TG measurements. The crystal structure of **1** contains both Δ and Λ enantiomers of the [Ni(phen)₃]²⁺ cations that construct sandwich layers along the crystallographic axis *c*, in between which sit the vanadium(V) complex anions. These are present as ionic dimers in the form of a robust {[(V₂O₂(O₂)₂((*S*)-mand)₂)][(V₂O₂(O₂)₂((*R*)-mand)₂)]}^{4−} species. The two individual anions are coupled by a pair of weak, yet significant attractions between two vanadium atoms and two peroxido ligands of the adjacent anion at V–O distances 2.660 Å. The ⁵¹V NMR spectrum of the compound in DMSO solution revealed a complicated course of decomposition reactions of the anion, which led to formation of the [(V₂O₄(*S,R*-mand)₂]^{2−} anion as a single product. The metal–organic hybrid compound **1** is converted by thermal decomposition into a potential anode material for lithium-ion batteries Ni(VO₃)₂.

Introduction

Nickel vanadates and nickel–vanadium metal–organic hybrid compounds have attracted considerable attention because of their physical and chemical properties, which facilitate technological applications in various fields of materials science. Thus, nickel vanadates have been studied

as a component for electrochemical capacitors [1], as gas sensors [2] and semiconductors [3]. Nickel–vanadium hybrid compounds have also been investigated, e.g. as heterogenous catalysts [4], photocatalysts [5] or magnetic materials [6]. Special interest is focused on nickel vanadates that may be used as anode materials for lithium-ion batteries. The most studied compounds in this respect are Ni₃V₂O₈ [7–11] and a mixed-ion vanadate LiNiVO₄ [12–16]. In fact, the simplest nickel vanadate Ni(VO₃)₂ itself does not suit in such applications; however, synthesis of Ni(VO₃)₂ doped by lithium ions represents a viable option for the development of a different class of lithium-ion batteries [17, 18]. Therefore, the research on innovative methods for the synthesis of nickel vanadates including Ni(VO₃)₂ capable of accommodating lithium ions is ongoing. Peroxido complexes of vanadium may serve as useful precursors in this manner, as has already been shown in the case of the synthesis of Ni₂V₂O₇ by thermal decomposition of [Ni(NH₃)₆][VO(O₂)₂(NH₃)₂]₂ [19]. A notable obstacle is the fact that the final products of a thermal decomposition can scarcely be predicted with certainty. Despite the fact that initial stoichiometry of the coordination compound with *n*(Ni):*n*(V) = 1:2 could favour formation of Ni(VO₃)₂, the calcination product was actually obtained as a mixture of Ni₂V₂O₇ and V₂O₅. Because peroxido complexes of vanadium are a well-investigated

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group of vanadium compounds providing an advantage of relatively low temperatures required for the release of the oxygen atoms of the peroxide group and combustion of the organic components (usually 100–300 °C), new precursors for possible preparation of nickel vanadates are of current interest. Thermal decomposition of vanadium peroxido complexes with transition metal cations has been utilized also for the synthesis of other vanadates, such as $\text{Zn}(\text{VO}_3)_2$ and $\text{Cu}(\text{VO}_3)_2$ [24].

In recent years, we have reported on transition metal–vanadium compounds, comprised of the combinations Mn–V [20], Fe–V, Ni–V [21, 22] and Cu–V [23–29] that were investigated mostly for their chiral properties. In continuation of our studies on stereochemistry of vanadium(V) complexes, we present here the synthesis and characterization of $[\text{Ni}(\text{phen})_3]_2[(\text{V}_2\text{O}_2(\text{O}_2)_2((S)\text{-mand})_2)][(\text{V}_2\text{O}_2(\text{O}_2)_2((R)\text{-mand})_2)] \cdot 18\text{H}_2\text{O}$ ($\text{phen} = 1,10\text{-phenanthroline}$, $\text{mand}^{2-} = \text{mandelato}(2-)$, $\text{C}_6\text{H}_5\text{-CO-COO}^{2-}$).

Experimental

Synthesis and characterization

Materials and methods

The starting materials were obtained from commercial sources: H_2O_2 (35%, p. a., Centralchem), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (p. a., Lachema), KBr (for IR spectra, Lachema), 1,10-phenanthroline (p. a., AFT Bratislava), *rac*-mandelic acid (for synth., Merck), (*S*)-mandelic acid (99%+, Acros Organics), dimethyl sulfoxide (DMSO, p. a., Penta), acetonitrile (99.5%, Centralchem). NH_4VO_3 (purum, Lachema) was purified according to the literature [22].

Elemental analyses C, H, N were determined on a Vario MIKRO cube (Elementar). Vanadium was determined using ICP-MS (Perkin-Elmer Sciex Elan 6000), and nickel was determined using F-AAS (Perkin-Elmer 1100). DTA and TG curves were recorded on an SDT 2960 (TA Instruments) device in static air atmosphere in the temperature range 20–600 °C and with the heating rate 10 °C min^{−1}. UV–Vis spectra in DMSO solutions were measured on a Jasco V-530 (Shimadzu) apparatus in 2-mm quartz cuvettes at ambient temperature in the range 200–1000 nm. Infrared spectra in KBr discs, Nujol mulls or spectra using the ATR technique were recorded on a Nicolet FTIR 6700 spectrometer. ⁵¹V NMR spectra in DMSO solutions were recorded at 298 K on Varian Unity Inova 600 MHz spectrometer operating at 157.68 MHz (⁵¹V); chemical shifts are related to VOCl_3 used as the external standard ($\delta = 0$ ppm).

Synthesis of $[\text{Ni}(\text{phen})_3]_2[(\text{V}_2\text{O}_2(\text{O}_2)_2((S)\text{-mand})_2)][(\text{V}_2\text{O}_2(\text{O}_2)_2((R)\text{-mand})_2)] \cdot 18\text{H}_2\text{O}$ (1) NH_4VO_3 (0.233 g, 2 mmol) was

dissolved in water (15 cm³); subsequently H_2O_2 (30%, 0.5 cm³) and *rac*- H_2mand (0.305 g, 2 mmol) were added. To the red solution so obtained, a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 1 mmol) and *phen* (0.541 g, 3 mmol) in acetonitrile (25 cm³) and water (5 cm³) was added under continuous stirring. The final orange solution was allowed to crystallize at 5 °C, and orange-red block crystals were isolated after 24 h. The compound is insoluble in water and ethanol and partially soluble in DMSO.

Anal. Calc. for $\text{NiV}_2\text{O}_{21}\text{C}_{52}\text{H}_{54}\text{N}_6$ (1259.58 g/mol) (fresh sample): C 49.58; H 4.32; N 6.67; V 8.09; Ni 4.66%; found: C 49.56; H 4.03; N 6.65; V 7.88; Ni 4.34%.

The compound slowly releases molecules of water of crystallization even in a refrigerator. The analysis after storing for 5 months at 5 °C: C 51.43; H 3.31; N 7.25%.

Structure determination details

Single-crystal X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer equipped with Bruker Apex II detector with Mo K α radiation ($\lambda = 0.71073$ nm) at 120 K. Absorption corrections were applied using the program SADABS [30]. The structure was solved with direct methods by using the SHELXT program [31] and refined with SHELXL 2015 [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined with a riding model. The oxygen atoms of water molecules were heavily disordered, and we were obliged to use SQUEEZE programme [33] to expel them to obtain a stable model. The structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC) with the deposition number 1915001. This data can be obtained free of charge under <https://www.ccdc.cam.ac.uk/structures/>.

Results and discussion

Crystal structure of compound 1

Table 1 summarizes crystal structure data and refinement details for compound 1. The asymmetric unit consists of one cation $[\text{Ni}(\text{phen})_3]^{2+}$ and one anion $[(\text{V}_2\text{O}_2(\text{O}_2)_2(m\text{and}))_2]^{2-}$ as well as water molecules of crystallization that were not modelled. Because the compound crystallizes in the space group *P*−1, the asymmetric unit contains only one set of the individual stereoisomers; in the case of our model $[(\text{V}_2\text{O}_2(\text{O}_2)_2((S)\text{-mand})_2)]^{2-}$ and Λ - $[\text{Ni}(\text{phen})_3]^{2+}$ (Fig. 1) with their related enantiomers being generated by a centre of symmetry. The key geometrical parameters of the two ionic components are summarized in Table 2. The Ni–N distances and N–Ni–N angles in the $[\text{Ni}(\text{phen})_3]^{2+}$ cations point to slightly irregular octahedral geometry. The molecular structure of

Table 1 Crystal structure data and refinement details for compound **1**

CCDC code	1915001
Empirical formula	C ₅₂ H ₃₆ N ₆ Ni O ₁₂ V ₂ [+ solvent]
Formula weight	1097.46
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, <i>P</i> − 1
Unit cell dimensions	<i>a</i> = 13.0006(9) Å <i>α</i> = 116.555(2)° <i>b</i> = 15.7426(12) Å <i>β</i> = 93.875(3)° <i>c</i> = 16.0027(12) Å <i>γ</i> = 103.254(2)°
Volume	2796.7(4) Å ³
Z, Calculated density	2, 1.303
Absorption coefficient	0.722 mm ^{−1}
<i>F</i> (000)	1120
Crystal size	0.286 × 0.194 × 0.168 mm
Theta range for data collection	2.347°–27.565°
Limiting indices	−16 ≤ <i>h</i> ≤ 16, −20 ≤ <i>k</i> ≤ 18, −19 ≤ <i>l</i> ≤ 20
Reflections collected/unique	56,503/12,874 [<i>R</i> _{int} = 0.0363]
Completeness to <i>θ</i> = 25.242	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.90 and 0.86
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	12,874/12/658
Goodness of fit on <i>F</i> ²	1.023
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0841
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.0902
Largest diff. peak and hole	0.613 and −0.703 e Å ^{−3}

the [(V₂O₂(O₂)₂(*mand*)₂)]^{2−} anion was previously reported for few vanadium(V) peroxido complexes [29, 34, 35]. Both vanadium atoms adopt pentagonal pyramidal coordination

geometry and are coordinated by one oxido ligand in the apical position as well as two oxygen atoms of the peroxido ligands and one oxygen atom of the carboxylate group of the mandelato ligand in the pentagonal pseudoplane. The oxygen atoms coming from the hydroxyl groups of mandelic acid act as bridging ligands between two vanadium atoms of the anion. The vanadium atoms are displaced from the calculated pentagonal pseudoplanes towards the oxido ligands by 0.4569(4) Å (V1) and 0.3579(3) Å (V2). As noted earlier, the mandelato ligands of the anion have the same configuration (*S*). The partnered anion involving mandelato ligand of the opposite configuration (*R*) is related by a centre of symmetry in the crystal packing and may be actually found in a relatively close distance to the [(V₂O₂(O₂)₂((*S*)-*mand*)₂)]^{2−} anion (Fig. 2). The closest contact between the enantiomers is the V2...O6' interaction at 2.660 Å. This distance is too large to consider it as a regular coordination bond, but still too short to be neglected; especially when in general the atom in the *trans* position towards to oxido ligand of the V=O bond (if present) usually comes from a solvent molecule or other components present in the crystal structure [36]. Therefore, the related enantiomers may be considered as a bulky ionic dimer {[(V₂O₂(O₂)₂((*S*)-*mand*)₂)][(V₂O₂(O₂)₂((*R*)-*mand*)₂)]^{4−} trapped in a cavity that is formed by surrounding [Ni(*phen*)₃]²⁺ cations. In the crystal packing along the crystallographic *c* axis the cations are located in layers above and below the positions of the dimers (Fig. 2). The enantiomers in the two layers have alternate configurations. Interestingly, there is no obvious *π*–*π* stacking between the phenyl groups of the mandelato and phenanthroline ligands. In one of the similar previously studied systems, we employed Δ- and Λ-[Ni(*bpy*)₃]²⁺ cations (*bpy* = 2,2'-bipyridine) and tetranuclear chiral vanadium(V) tartrato complexes [V₄O₈((2*R*,3*R*)-*tart*)₂]

Fig. 1 Molecular structures of [(V₂O₂(O₂)₂((*S*)-*mand*)₂)]^{2−} (left) and Λ-[Ni(*phen*)₃]²⁺ (right) present in compound **1** as revealed by X-ray structure analysis with atom labelling scheme. The displacement

ellipsoids of non-hydrogen atoms are shown at 50% probability level. Colour code: V orange, Ni green, O red, N blue, C black, H white. (Color figure online)

Table 2 Structural parameters of ions $[\text{Ni}(\text{phen})_3]^{2+}$ and $[\text{V}_2\text{O}_2(\text{O}_2)_2(\text{mand})_2]^{2-}$ in **1**

Parameter		Bond length in Å, bond angle in °
$[\text{Ni}(\text{phen})_3]^{2+}$		
Ni(1)–N(1)		2.0850 (17)
Ni(1)–N(2)		2.0860 (16)
Ni(1)–N(3)		2.0672 (16)
Ni(1)–N(4)		2.0851 (16)
Ni(1)–N(5)		2.0722 (17)
Ni(1)–N(6)		2.0951 (17)
N(3)–Ni(1)–N(5)		94.27 (6)
N(3)–Ni(1)–N(1)		91.76 (6)
N(5)–Ni(1)–N(1)		170.89 (7)
N(3)–Ni(1)–N(4)		80.09 (7)
N(5)–Ni(1)–N(4)		94.54 (7)
N(1)–Ni(1)–N(4)		93.22 (6)
N(3)–Ni(1)–N(2)		169.34 (7)
N(5)–Ni(1)–N(2)		94.77 (7)
N(1)–Ni(1)–N(2)		79.98 (7)
N(4)–Ni(1)–N(2)		93.56 (7)
N(3)–Ni(1)–N(6)		96.75 (7)
N(5)–Ni(1)–N(6)		80.09 (7)
N(1)–Ni(1)–N(6)		92.43 (7)
N(4)–Ni(1)–N(6)		173.60 (7)
N(2)–Ni(1)–N(6)		90.37 (7)
$[\text{V}_2\text{O}_2(\text{O}_2)_2(\text{mand})_2]^{2-}$		
V=O	V(1)–O(12)	1.5846 (14)
	V(2)–O(7)	1.5959 (12)
V–O _p	V(2)–O(5)	1.8792 (14)
	V(2)–O(6)	1.8709 (14)
	V(1)–O(10)	1.8543 (15)
	V(1)–O(11)	1.8886 (16)
	V(2)–O(3)	2.0189 (14)
V–O _C	V(1)–O(8)	2.0276 (16)
	V(2)–O(1)	1.9611 (13)
V–O _H	V(2)–O(1)	2.0024 (14)
	V(1)–O(2)	1.9952 (14)
	V(2)–O(2)	1.9878 (13)
O _p –V–O _p	O(6)–V(2)–O(5)	44.80 (6)
	O(10)–V(1)–O(11)	45.00 (7)
V–O _H –V	V(1)–O(1)–V(2)	110.41 (6)
	V(2)–O(2)–V(1)	109.61 (6)
O _H –V–O _C	O(1)–V(1)–O(8)	76.60 (6)
	O(2)–V(2)–O(3)	77.83 (6)
O _H –V–O _H	O(1)–V(1)–O(2)	70.21 (5)
	O(2)–V(2)–O(1)	69.53 (5)

O_p—Oxygen atom of the peroxido ligand, O_H—oxygen atom of the original hydroxy group, O_C—coordinated oxygen atom of the carboxylic group

and $[\text{V}_4\text{O}_8((2S,3S)\text{-tart})_2]$ ($\text{H}_4\text{tart}^{4-}$ = tartaric acid) [22]. In the case where all four chiral components were present in the crystal structure, it was possible to observe a homochiral layers of the cations, while the enantiomers of the anions were not related in a certain interaction and they were alternating along the homochiral layers of the cations. In the crystal structure of **1**, however, the homochiral layers of Δ - and Λ - $[\text{Ni}(\text{phen})_3]^{2+}$ are indeed present, while the anions favour intermolecular interactions and formation of a centrosymmetric entity. We assume that this is a consequence of the bulkiness of the $[\text{Ni}(\text{phen})_3]^{2+}$ cations that enforce squeezing of the anions into cavities; a process that is also supported by an available free coordination site in the *trans* position towards the V=O group. Consequently, the protruding phenyl groups of the chiral mandelato ligands determine the configuration of the cations of the layer with which they interact (or vice versa).

Spectroscopic data

UV–Vis spectra

The UV–Vis spectrum of compound **1** in DMSO exhibits bands due to the π – π^* transitions of the *phen* ligand in the UV region. We assign the band at 417 nm to the $\text{O}_2^{2-} \rightarrow \text{V}$ charge transfer transition [36] and that at 790 nm to the *d*–*d* transition of Ni(II) (Table 3, Fig. 3) [22]. The dominant band in the visible region of the spectrum corresponding to the CT transition in the compound is responsible for the red colour typical for monoperoxido complexes of vanadium(V), while the pink colour expected for the $[\text{Ni}(\text{phen})_3]^{2+}$ cation is entirely suppressed [37].

Infrared spectra

The IR spectrum of compound **1** contains characteristic bands of coordinated *phen* ligands, the bands of the $\text{VO}(\text{O}_2)$ group, as well as the bands of water molecules (Fig. 4). Stretching vibrations of water molecules occur at 3374 and 3280 cm^{-1} . The very strong band corresponding to $\nu(\text{C}=\text{O})$ is observed at 1622 cm^{-1} , and the strong bands assigned to coordinated *phen* molecules at 1516, 1426, 849 and 726 cm^{-1} . The characteristic bands of the $\text{VO}(\text{O}_2)$ group occur at 968–990 cm^{-1} for ($\nu(\text{V}=\text{O})$) and at 929 cm^{-1} for ($\nu(\text{O}_p\text{--O}_p)$ (O_p —oxygen atom of peroxido ligand)).

^{51}V NMR spectra

The decomposition of the complex in solution proceeds with the consecutive release of oxygen from the peroxide group. We investigated the decomposition process in DMSO by

Fig. 2 Schematic representation of the ionic dimer $\{[(V_2O_2(O_2)_2((S)\text{-mand})_2)] [(V_2O_2(O_2)_2((R)\text{-mand})_2)]\}^{4-}$ (upper, H atoms are omitted for clarity) and its position in the crystal packing (lower frame) viewed along the c axis. The enantiomers $\Lambda\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ and $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ are illustrated as blue and green propellers, respectively

Table 3 Electronic spectral data of **1** in DMSO

λ (nm)	Assignment
271	$\pi \rightarrow \pi^*$
297	$\pi \rightarrow \pi^*$
417	CT $O_2^{2-} \rightarrow V$
790	$^3A_{2g} \rightarrow ^3T_{2g}$

Electronic spectra were measured at different concentrations: 7.4×10^{-6} mol/L (bands: 271, 297 nm) and 4.7×10^{-4} mol/L (417, 790 nm)

* stands for “antibonding orbital”

Fig. 3 Electronic spectra of **1** in DMSO measured at various concentrations: 7.4×10^{-6} mol/L (**a**) and 4.7×10^{-4} mol/L (**b, c**)

means of ^{51}V NMR spectroscopy, although due to the complexity of the spectra we were able to make only a tentative assignment of chemical shifts [29, Table 4, Fig. 5]. Based on our previous speciation study of vanadates in DMSO solutions [29], we can rule out the presence of common vanadates as decomposition products in this system as their signals should appear in the region ≈ -545 to -570 ppm (i.e., H_2VO_4^- , $\text{H}_2\text{V}_2\text{O}_7^{2-}$, $\text{V}_4\text{O}_{12}^{4-}$, $\text{V}_5\text{O}_{15}^{5-}$).

The ^{51}V NMR spectrum of the complex in DMSO solution contains nine signals besides several very weak peaks. These nine signals exhibit different behaviour, when the time dependence of the spectra is taken into account:

Fig. 4 IR spectra of compound **1** **a** in KBr disc, **b** ATR

Table 4 ^{51}V NMR spectra of **1** in DMSO. Chemical shifts with the relative intensity in parenthesis

T/h ^a	$\text{VO}(\text{O}_2)\text{M}^b$	$\text{VO}(\text{O}_2)\text{M}^b$	V_2L_2^c	$\text{VO}(\text{O}_2)^d$	$\text{VO}(\text{O}_2)\text{M}^b$	$\text{VO}(\text{O}_2)^d$	$\text{VO}(\text{O}_2)^d$	1	$\text{VO}(\text{O}_2)_2^e$
0	463 (2.3)	495 (9.1)	505 (1.9)	511 (2.7)	522 (6.2)	534 (1.9)	540 w ^f	553 (75)	597 w ^f
3	463 w ^f	495 (19)	505 (4.3)	511 (12.5)	522 (3.9)	534 (2.9)	540 (6)	553 (51)	597 w ^f
6	463 w ^f	495 (19)	505 (12.8)	511 (21.9)	522 (2.4)	534 (3.1)	539 (12.9)	533 (27.9)	597 w ^f
24			504 (90.8)	510 w ^f		534 w ^f	540 w ^f		
48			504 (100)						

M indicates the presence of mandelato ligand in unknown stoichiometry

^aTime after dissolution

^bMonoperoxido mandelato complex of vanadium

^c $[\text{V}_2\text{O}_4(\text{mand})_2]^{2-}$

^dMonoperoxido complex of vanadium (without mandelato ligand)

^eDiperoxido complex of vanadium (without mandelato ligand)

^fw—Very weak signal

Fig. 5 ^{51}V NMR spectra of **1** ($c = 5 \times 10^{-3}$ mol/L) in DMSO: **a** 0 h, **b** 3 h, **c** 6 h, **d** 24 h and **e** 48 h after preparation

- (i) Monotonous decrease of the intensity with time. This is valid for the most intense signal in the spectrum measured immediately after dissolution at -553 ppm (Fig. 5a). We attribute this signal to the original

anion in the compound, which undergoes successive decomposition. Similar behaviour is observed for the weak signal at -597 ppm, which can be assigned to diperoxido species [29, Table 4] and signals at -522 and -463 ppm attributable to monoperoxido mandelato complexes of vanadium.

- (ii) The intensity of signals increases at the beginning, then decreases. This behaviour concerns the signals at -540 , -534 and -511 ppm, which can be assigned to peroxidovanadium species (without mandelic acid) [29] and a signal at -495 ppm attributable to monoperoxido mandelato complexes of vanadium [29].
- (iii) The intensity of only one signal increases continually with time. This signal at -504 ppm can be reliably attributed to the $[\text{V}_2\text{O}_4(\text{mand})_2]^{2-}$ anion (designated as V_2L_2).

Thus, in spite of the complicated course of the decomposition process the whole decomposition reaction corresponds to the release of oxygen from the anion in **1**: $[\text{V}_2\text{O}_2(\text{O}_2)_2(\text{mand})_2]^{2-} \rightarrow [\text{V}_2\text{O}_4(\text{mand})_2]^{2-} + \text{O}_2$. In conclusion, the solvolysis of the complex anion

Fig. 6 DTA and TG curves for **1**

$[\text{V}_2\text{O}_2(\text{O}_2)_2(\text{mand})_2]^{2-}$ provides a rare example in vanadium(V) chemistry, when upon dissolution several species are formed which give rise to a single product. Based on ^{51}V NMR investigations, the ligand–vanadate equilibria are usually complicated, and the presence of vanadate oligomers is common. In the case of compound **1**, however, we observed a completely opposite type of reactivity.

Thermal decomposition

The TG curves of $[\text{Ni}(\text{phen})_3]_2[(\text{V}_2\text{O}_2(\text{O}_2)_2((S)\text{-mand})_2)][(\text{V}_2\text{O}_2(\text{O}_2)_2((R)\text{-mand})_2)] \cdot 18\text{H}_2\text{O}$ proceeds in several steps (Fig. 6). We can propose the release of crystal water (endothermic peak at ≈ 100 °C, calc. mass loss 12.87%, found 9.56%). The difference between calculated and experimental mass loss is due to the instability of the compound (as mentioned in the Experimental section). Moreover, solvent can be liberated also at higher temperatures and an overlap between the processes of the release of the solvent and decomposition of a peroxide group can occur.

Fig. 7 IR spectra of compound **1** after heating at 600 °C (ATR)

The next steps of decomposition that are accompanied by exothermic effects on the DTA curves at ≈ 175 , ≈ 420 and ≈ 504 °C correspond to the decomposition of the peroxidic oxygen and organic ligands. The final product of thermal decomposition is $\text{Ni}(\text{VO}_3)_2$ with a very small admixture of V_2O_5 (calc. residue 20.37%, found 20.61%). Figure 7 features a typical IR spectrum of $\text{Ni}(\text{VO}_3)_2$ [22] with a very weak band of V_2O_5 at ~ 1020 cm^{-1} .

Conclusion

We have reported herein the synthesis and characterization of $[\text{Ni}(\text{phen})_3]_2[(\text{V}_2\text{O}_2(\text{O}_2)_2((S)\text{-mand})_2)][(\text{V}_2\text{O}_2(\text{O}_2)_2((R)\text{-mand})_2)] \cdot 18\text{H}_2\text{O}$ as a new hybrid metal–organic compound comprised of nickel(II) and vanadium(V) coordination entities coupled stereoselectively in the solid state by packing into homochiral layers. The compound provides $\text{Ni}(\text{VO}_3)_2$ as the dominating product of its thermal decomposition. Upon dissolution in DMSO, the compound gives rise to $[\text{V}_2\text{O}_4(\text{mand})_2]^{2-}$ as the single final product.

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