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Complexation between vanadium (V) and phenyllactate: Synthesis, spectral studies and crystal structure of $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$, [3-phlact = 3-phenyllactato(2−)]

P. Schwendt [a,*], M. Ahmed [a], J. Marek [b]

[a] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, SK-84215 Bratislava, Slovak Republic
[b] Laboratory of Functional Genomics and Proteomics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic

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Abstract

The peroxo complexes formed by vanadium (V) in the presence of rac- or *S*-3-phenyllactic acid as heteroligand, $M_2[V_2O_2(O_2)_2(rac\text{-3-phlact})_2]\cdot nH_2O$ ($M^+ = K^+$ (**1**), NMe_4^+ (**3**), NBu_4^+ (**6**)), $M_2[V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot nH_2O$ ($M^+ = K^+$ (**7**), NH_4^+ (**8**), NMe_4^+ (**9**), NEt_4^+ (**10**), NPr_4^+ (**11**), NBu_4^+ (**12**)), $(NH_4)_4[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 2H_2O\cdot 2CH_3OH\cdot 2H_2O_2$ (**2**), $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ (**4**) and $(NPr_4)(NH_4)_3[V_2O_2(O_2)_2(rac\text{-3-phlact})_2]_2\cdot 7H_2O$ (**5**) were isolated from H_2O/methanol solutions. All complexes were characterized by elemental analysis, IR, UV–Vis and ^{51}V NMR spectroscopies. The molecular structure of $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ (**4**) was determined by X-ray crystallography. The complex crystallizes as racemic compound with alternating $[V_2O_2(O_2)_2(R\text{-3-phlact})_2]^{2-}$ and $[V_2O_2(O_2)_2(S\text{-3-phlact})_2]^{2-}$ anions in the structure. Coordination geometry around the central vanadium atoms is pentagonal pyramidal, which is typical for hexacoordinate oxoperoxovanadium (V) complexes.

Keywords: Crystal structure; Peroxo phenyllactato complexes of vanadium (V); IR spectra; ^{51}V NMR spectra

1. Introduction

The past decade has seen a vast increase in interest in the biological influences of vanadium [1–3]. Much of the impetus toward vanadium biochemical research derives from the fact that a number of vanadium complexes have insulin-mimetic or insulin-enhancing properties. Since discovery of the insulin mimetic effect of vanadium (V) compounds [4], the structure and reactivity of vanadium (V) complexes with biologically important ligands have been intensively studied [5].

Vanadium (V) peroxo complexes have been the object of intense investigations, due both to their biological relevance (insulinmimetic and antitumour activities [6–10], functional models for the haloperoxidase enzymes [11–13]) and their application in oxidation of several substrates, such as benzene and other aromatics, alkenes, allylic alcohols, sulfides, halides and primary and secondary alcohols [14]. Peroxovanadium complexes with α-hydroxycarboxylic acids have been the object of special interest, since the anions of these acids are known to exist in biological media and to be involved in many basic biochemical processes (Krebs cycle, Cori cycle, photorespiration, and others [15]). The monoperoxovanadium complexes of citric, malic, tartaric, glycolic,

* Corresponding author. Fax: +421 2 6029 6273.
E-mail address: peter.schwendt@fns.uniba.sk (P. Schwendt).

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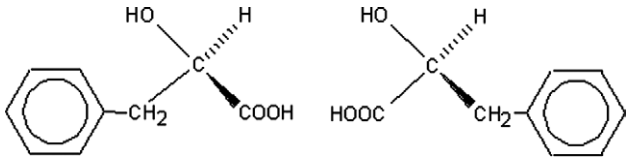


R-3-Phenyllactic acid *S*-3-Phenyllactic acid

Scheme 1.

mandelic and α-hydroxyhippuric acids were isolated and characterized [10,15–25].

3-Phenyllactic acid (Scheme 1) and its derivatives have found broad application in the production of many chiral pharmaceutical and agricultural products. 3-Phenyllactic acid has recently been found in the cultures of *Lactobacillus plantarum* that show antifungal activity in sourdough breads [26]. 3-Phenyllactic acid has also been reported to be one of the most abundant aromatic acids to which antibacterial properties have been attributed to occur in several honeys with different geographical origins [27,28].

The present work deals with the synthesis, spectroscopic study and crystal structure of the peroxovanadium (V) complexes with 3-phenyllactic acid. To our knowledge, only one crystal structure containing coordinated 3-phenyllactato ligand has been reported yet, namely (salen)Ti(*R*-3-phlact) (salen = *N*,*N*′-ethylene-bis(salicylideneaminate)) [29]. The structural parameters of α-hydroxycarboxylatoperoxovanadates are compared and their characteristic structural features are discussed.

2. Experimental

All chemicals were of analytical grade and used as supplied by Aldrich.

2.1. Physical measurements and analytical methods

UV–Vis spectra were recorded using a JASCO V-530 spectrophotometer. FT-IR measurements were taken on a Nicolet 750 Magna spectrometer using Nujol mulls. ^{51}V NMR spectra were measured on a Varian Gemini 2000 spectrometer operating at 78.94 MHz, the chemical shifts were referenced to $VOCl_3$ as external standard. Carbon, hydrogen and nitrogen were estimated on a Carlo Erba CHN-analyser. Peroxidic oxygen was determined by titration with $KMnO_4$. Vanadium (V) was determined by titration with $FeSO_4$.

2.2. X-ray structure determination

Low-temperature X-ray measurements were made on a KUMA KM4 + CCD diffractometer with monochromated (monochromator Enhance, Oxford Diffraction, UK) Mo K_α radiation using rotation method with ω-scan technique. Cell parameters and an orientation matrix for data reduction were obtained from all strong reflections. For data collection, cell refinement and data reduction, we used the CrysAlis (Oxford Diffraction, 2002) software package. Data were not corrected for absorption effects. All calculations for structure solution and refinement were done using the SHELX-97 program [30].

2.3. Syntheses

2.3.1. $K_2[V_2O_2(O_2)_2(rac\text{-}3\text{-}phlact)_2]\cdot 2H_2O$ (**1**)[1]

A solution of KVO_3 (0.138 g, 1 mmol) in 5 ml water was mixed with a solution of *rac*-3-H_2phlact acid (0.166 g, 1 mmol) in 5 ml methanol. After cooling (0 °C) of the resulting solution, H_2O_2 (30%, 0.1 ml) was added under constant stirring. Light red crystals were isolated after 4 days standing at 5 °C. *Anal.* Calc. for $K_2C_{18}H_{20}O_{14}V_2$: C, 33.8; H, 3.1; O_2^{2-}, 10.0; V, 15.9. Found: C, 33.3; H, 3.0; O_2^{2-}, 10.2; V, 15.5%.

2.3.2. $(NH_4)_4[V_2O_2(O_2)_2(R\text{-}3\text{-}phlact)_2][V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 2H_2O\cdot 2CH_3OH\cdot 2H_2O_2$ (**2**)[2]

NH_4VO_3 (0.117 g, 1 mmol) and *rac*-3-H_2phlact acid (0.166 g, 1 mmol) were dissolved in 5 ml water and 10 ml methanol. After cooling of the solution, H_2O_2 (30%, 0.1 ml) was added under continuous stirring. The red crystals were isolated after 3 days standing at 5 °C. *Anal.* Calc. for $C_{19}H_{32}N_2O_{16}V_2$: C, 35.3; H, 5.0; N, 4.3; O_2^{2-}, 10.0; V, 15.8. Found: C, 37.2; H, 4.4; N, 4.2; O_2^{2-}, 10.3; V, 16.1%.

2.3.3. $(NMe_4)_2[V_2O_2(O_2)_2(rac\text{-}3\text{-}phlact)_2]\cdot 1.5H_2O$ (**3**)

NH_4VO_3 (0.117 g, 1 mmol) was dissolved under stirring in a NMe_4OH solution (25%, 0.36 ml, 1 mmol) and 5 ml water. NH_3 was removed from the solution by boiling. After cooling of the resulting solution, H_2O (5 ml), H_2O_2 (30%, 0.1 ml), *rac*-3-H_2phlact acid (0.166 g, 1 mmol) and methanol (5 ml) were added. The red solution obtained was allowed to crystallize at 5 °C. The red crystals were isolated after few days. *Anal.* Calc. for $C_{26}H_{43}N_2O_{13.5}V_2$: C, 44.5; H, 6.2; N, 4.0; O_2^{2-},

[1] We use the *rac*-3-phlact formula, when racemic ligand was used in the synthesis, but without knowledge what enantiomers are bound in the structure.

[2] X-ray structure of this compound was solved: $a = 17.3196(13)$ Å, $b = 17.4775(7)$ Å, $c = 17.7981(14)$ Å, $\beta = 114.697(9)°$, $Z = 4$, space group $P2_1/n$, $D_c = 1.600$ g/cm^3. Some of the solvent molecules were found to be disordered with two main positions and occupancy factors around 0.5. Due to disorder, the final *R* factors were high ($R_1(I > 2\sigma_1) = 0.0787$), nevertheless, the results confirmed the expected connectivity, racemic character of the compound and the presence of CH_3OH, H_2O_2 and H_2O molecules in the structure.

9.1; V, 14.5. Found: C, 44.6; H, 5.8; N, 3.8; O_2^{2-}, 8.9; V, 14.8%.

*2.3.4. $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-}3\text{-}phlact)_2][V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 6H_2O$ (**4**)*

To a solution of NH_4VO_3 (0.117 g, 1 mmol) in 5 ml H_2O, NEt_4OH (35%, 0.42 ml, 1 mmol) was added. The solution was heated for a short time, cooled and then H_2O_2 (30%, 0.1 ml) was added. Finally, *rac*-3-H_2phlact acid (0.166 g, 1 mmol) in 5 ml methanol was added under vigorous stirring. The obtained solution was allowed to crystallize (5 °C), the red crystals of **4** were isolated after 4 days. *Anal.* Calc. for $C_{44}H_{76}N_4O_{30}V_4$: C, 39.3; H, 5.7; N, 4.2; O_2^{2-}, 9.5; V, 15.1. Found: C, 39.3; H, 5.4; N, 3.8; O_2^{2-}, 9.2; V, 14.9%.

*2.3.5. $(NPr_4)(NH_4)_3[V_2O_2(O_2)_2(rac\text{-}3\text{-}phlact)_2]_2\cdot 7H_2O$ (**5**)*

NH_4VO_3 (0.234 g, 2 mmol) was dissolved in a stirred NPr_4OH (1 mol dm^{-3}, 2 ml)/H_2O (5 ml) mixture. NH_3 was partially removed from the solution by brief boiling. After cooling to the room temperature, H_2O_2 (0.2 ml, 30%) and *rac*-3-H_2phlact acid (0.332 g, 2 mmol) in methanol (5 ml) were added. The red solution obtained was allowed to crystallize at 5 °C. The red crystals were isolated after three days. *Anal*. Calc. for $C_{48}H_{86}N_4O_{31}V_4$: C, 40.6; H, 6.1; N, 3.9; O_2^{2-}, 9.0; V, 14.4. Found: C, 40.5; H, 6.0; N, 3.5; O_2^{2-}, 9.3; V, 14.1%.

*2.3.6. $(NBu_4)_2[V_2O_2(O_2)_2(rac\text{-}3\text{-}phlact)_2]\cdot H_2O$ (**6**)*

The compound was prepared by the same procedure as for **3**, but using NBu_4OH solution (40%, 0.65 ml, 1 mmol). *Anal.* Calc. for $C_{50}H_{90}N_2O_{13}V_2$: C, 58.3; H, 8.8; N, 2.7; O_2^{2-}, 6.2; V, 10.0. Found: C, 58.1; H, 9.0; N, 2.6; O_2^{2-}, 6.4; V, 10.2%.

*2.3.7. $K_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 5H_2O$ (**7**)*

Prepared by the same procedure as for **1**, but using *S*-3-H_2phlact acid (0.166 g, 1 mmol). *Anal*. Calc. for $K_2C_{27}H_{36}O_{20}V_2$: C, 31.1; H, 3.8; O_2^{2-}, 9.2; V, 14.7. Found: C, 31.2; H, 3.4; O_2^{2-}, 9.0; V, 14.8%.

*2.3.8. $(NH_4)_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 0.5H_2O$ (**8**)*

NH_4VO_3 (0.234 g, 2 mmol) was dissolved in diluted H_2O_2 (0.5 ml 30% in 10 ml H_2O) under cooling in ice bath, *S*-3-H_2phlact acid (0.332 g, 2 mmol) was dissolved in 5 ml H_2O and 5 ml methanol and added under stirring to the solution of peroxovanadate. The red crystals of **8** were crystallized within 3 days standing at 5 °C. *Anal.* Calc. for $C_{18}H_{25}N_2O_{12.5}V_2$: C, 37.8; H, 4.4; N, 4.9; O_2^{2-}, 11.2; V, 17.8. Found: C, 37.6; H, 4.5; N, 5.0; O_2^{2-}, 10.9; V, 17.4%.

*2.3.9. $(NMe_4)_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 3H_2O$ (**9**)*

NH_4VO_3 (0.234 g, 2 mmol) was dissolved under stirring in a NMe_4OH solution (25%, 0.72 ml, 2 mmol) and NH_3 was removed from the solution by brief boiling. After cooling of the resulting solution, H_2O (5 ml), H_2O_2 (30%, 0.2 ml), *S*-3-H_2phlact acid (0.332 g, 2 mmol) and methanol (5 ml) were added. The red solution obtained was allowed to crystallize at 5 °C. The red crystals were isolated after few days. *Anal.* Calc. for $C_{26}H_{46}N_2O_{15}V_2$: C, 42.9; H, 6.4; N, 3.8; O_2^{2-}, 8.8; V, 14.0. Found: C, 42.4; H, 5.9; N, 4.4; O_2^{2-}, 9.1; V, 14.2%.

*2.3.10. $(NEt_4)_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 0.5H_2O$ (**10**)*

The same procedure was followed as for **9**, except that NEt_4OH solution (35%, 0.84 ml, 2 mmol) was used in place of the NMe_4OH solution. *Anal.* Calc. for $C_{34}H_{57}N_2O_{12.5}V_2$: C, 51.3; H, 7.2; N, 3.5; O_2^{2-}, 8.0; V, 12.8. Found: C, 51.9; H, 7.7; N, 3.8; O_2^{2-}, 8.3; V, 13.1%.

*2.3.11. $(NPr_4)_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 4H_2O$ (**11**)*

NPr_4OH (1 mol dm^{-3}, 2 ml, 2 mmol) was added to a solution of NH_4VO_3 (0.234 g, 2 mmol) in 5 ml H_2O. The ammonia was removed from the resulting solution by boiling. The solution was cooled and added to a solution of H_2O_2 (30%, 0.2 ml). A solution of *S*-3-H_2phlact acid (0.332 g, 2 mmol) in 5 ml methanol was then added under vigorous stirring. The obtained solution was allowed to crystallize, the red crystals of **11** were obtained within a few days. *Anal.* Calc. for $C_{42}H_{80}N_2O_{16}V_2$: C, 51.9; H, 8.3; N, 2.9; O_2^{2-}, 6.6; V, 10.5. Found: C, 51.8; H, 8.5; N, 2.6; O_2^{2-}, 6.9; V, 10.2%.

*2.3.12. $(NBu_4)_2[V_2O_2(O_2)_2(S\text{-}3\text{-}phlact)_2]\cdot 2H_2O$ (**12**)*

Prepared by the same procedure as for **11**, but using NBu_4OH (40%, 1.3 ml, 2 mmol). *Anal*. Calc. for

Table 1
Characteristic IR bands (cm^{-1}) for the vanadium (V) oxo peroxo *rac*-3-phenyllactato complexes (**1**–**6**)

1	2	3	4	5	6	Assignment
3642 s	3469 b	3343 b	3435 b	3520 m	3527 s	$\nu(H_2O)$ or
3553 m	3297 m, 3160 m	3235 sh		3435 m	3440 m, 3293 w	ν(NH)
1645 s, 1623 s	1645 vs	1662 vs	1652 vs	1633 vs	1634 vs	$\nu_{as}(COO^-)$
1394 s, 1377 s	1376 s	1380 m, 1360 s	1375 vs	1377 vs	1379 vs	$\nu_s(COO^-)$
980 vs	982 s	982 s	982 s	983 s	990 vs, 980 s	ν(V=O)
923 vs	923 s	954 m, 933 vs	929 s	929 s	931 vs	$\nu(O_p\text{–}O_p)$
562 s	567 m	576 m, 541 s	575 m	582 m	581 s	$\nu(V\text{–}O_p)$

Table 2
Characteristic IR bands (cm^{-1}) for the vanadium (V) oxo peroxo *S*-3-phenyllactato complexes (**7**–**12**)

7	8	9	10	11	12	Assignment
3641 s	3445 m	3480 w	3533 s, 3440 m	3531 m	3527 s	$\nu(H_2O)$ or
3550 m			3289 sh	3438 m	3439 m	ν(NH)
1645 s, 1621 s	1667 m, 1614 vs	1661 vs	1635 vs	1636 vs	1634 vs	$\nu_{as}(COO^-)$
1377 vs	1378 vs	1375 s	1378 vs	1378 vs	1379 vs	$\nu_s(COO^-)$
979 s	977 m	983 s	989 vs	988 s	990 vs	ν(V=O)
924 s	938 s, 927 s	954 m, 932 vs	933 vs	934 vs	931 vs	$\nu(O_p–O_p)$
562 m	545 s	579 m, 540 m	582 m, 540 m	580 m, 540 m	583 s, 539 m	$\nu(V–O_p)$

$C_{50}H_{92}N_2O_{14}V_2$: C, 57.3; H, 8.9; N, 2.7; O_2^{2-}, 6.1; V, 9.7. Found: C, 57.0; H, 8.8; N, 2.5; O_2^{2-}, 6.4; V, 10.1%.

3. Results and discussion

3.1. Syntheses

The red or light red peroxo complexes of vanadium (V) of composition $M_2[V_2O_2(O_2)_2(rac\text{-3-phlact})_2]\cdot nH_2O$ ($M^+ = K^+$ (**1**), NMe_4^+ (**3**), NBu_4^+ (**6**)), $M_2[V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot nH_2O$ ($M^+ = K^+$ (**7**), NH_4^+ (**8**), NMe_4^+ (**9**), NEt_4^+ (**10**), NPr_4^+ (**11**), NBu_4^+ (**12**)), $(NH_4)_4[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 2H_2O\cdot 2CH_3OH\cdot 2H_2O_2$ (**2**), $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ (**4**) and $(NPr_4)(NH_4)_3[V_2O_2(O_2)_2(rac\text{-3-phlact})_2]_2\cdot 7H_2O$ (**5**) were obtained by crystallization from the MVO_3–H_2phlact–H_2O_2–H_2O–CH_3OH and NH_4VO_3–H_2phlact–NR_4OH–H_2O_2–H_2O–CH_3OH systems (R = Et, Me, Bu, Pr). The complexes decompose slowly at room temperature both in the solid state and solution.

3.2. Infrared spectroscopy

The infrared spectra for complexes **1**–**12** are listed in Tables 1 and 2. The spectra exhibit strong absorptions for the carbonyl of the carboxylate group in both the asymmetric and symmetric vibration regions. Asymmetric stretching vibrations $\nu_{as}(COO^-)$ appeared in the region from 1667 to 1614 cm^{-1}, whereas the corresponding symmetric stretches $\nu_s(COO^-)$ were present in the range 1394–1360 cm^{-1}. For all of the complexes studied here, the difference between the asymmetric and symmetric stretches, $\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$, was greater than 200 cm^{-1}, indicating that the carboxylate group in the phenyllactate ligand was coordinated to vanadium in a monodentate fashion [31]. This was further confirmed by the X-ray crystal structure of **4**. The spectra also exhibit characteristic bands of the $VO(O_2)$ group [32,33]. The bands at 990–977 cm^{-1} were assigned to V=O stretches, in agreement with a double bond character of this bond, the bands at 954–923 cm^{-1} were assigned to the peroxo O_p–O_p stretches and the V–O_p stretching vibrations were observed at 583–539 cm^{-1}.

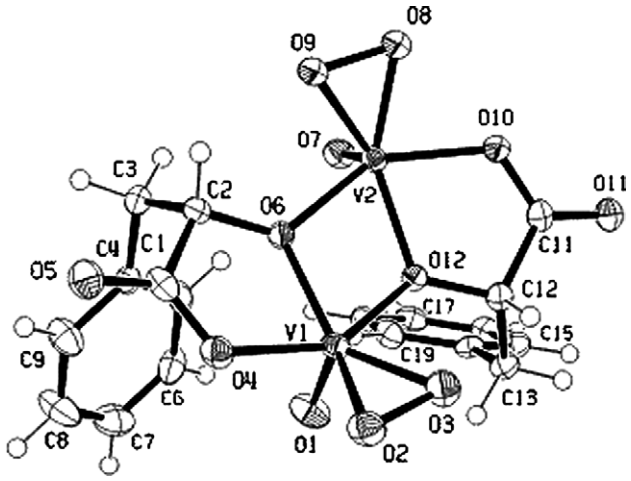


Fig. 1. The structure of the $[V_2O_2(O_2)_2(S\text{-3-phlact})_2]^{2-}$ anion in **4** at the 50% probability level.

Table 3
Crystal data and structure refinement for $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ (**4**)

Formula	$C_{44}H_{76}N_4O_{30}V_4$
Crystal system	orthorhombic
Space group	*Pbcn*
T (K)	120(2)
a (Å)	10.0312(4)
b (Å)	29.4515(11)
c (Å)	19.7814(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	5844.1(4)
Z	4
D_{calc} (g/cm^3)	1.524
λ (Å)	0.71073
Crystal size (mm)	$0.30\times0.20\times0.20$
θ Range (°)	2.90–25.00
Index ranges	$-11 \leqslant h \leqslant 11$, $-35 \leqslant k \leqslant 34$, $-23 \leqslant l \leqslant 19$
Reflections collected	29 340
Independent reflections [R_{int}]	5127 [0.0683]
Goodness-of-fit on F^2	1.223
Final R indices ($I > 2\sigma_1$)	$R_1 = 0.0631$, $R_{w2} = 0.1084$
R indices (all data)	$R_1 = 0.0838$, $R_{w2} = 0.1170$
Largest difference in peak and hole (e Å^{-3})	0.307 and −0.250
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5127/9/411

3.3. Crystal structure

The ORTEP diagram of the anion in **4** is shown in Fig. 1. Crystal data and structure refinement for $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ are shown in Table 3. The selected interatomic distances and angles, listed in Table 4, are in the expected ranges. The structure of the anion can be described as a dimer of two oxoperoxovanadium (V) units with two *R* (or *S*)-3-phenyllactate ligands. The 3-phenyllactate(2−) anion exhibits a chelating bonding mode via two oxygens, one belonging to a monodentate carboxylate and another to the adjacent deprotonated alcoholic group. The latter donor behaves as a monoatomic bridge and coordinates simultaneously to two metal centres, giving a central V_2O_2 rhomboid ring. The V_2O_2 core is nonplanar and the V=O groups are *cis*-oriented in relation to the V_2O_2 core [15] (vide infra). The coordination environment around each vanadium can be described as a distorted pentagonal pyramid. The equatorial planes are occupied by the peroxo groups (O(2), O(3), O(8), O(9)), both bridging hydroxyl oxygen atoms (O(6), O(12)), and the oxygen atoms (O(4), O(10)) from the monodentate carboxylic

Table 4
Selected bond lengths (Å) and angles (°) for $(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$ (**4**)

V(1)–O(1)	1.590(3)
V(1)–O(3)	1.863(3)
V(1)–O(2)	1.885(3)
V(1)–O(6)	1.964(3)
V(1)–O(12)	1.998(2)
V(1)–O(4)	2.016(3)
V(2)–O(7)	1.583(3)
V(2)–O(8)	1.863(3)
V(2)–O(9)	1.880(3)
V(2)–O(12)	1.983(3)
V(2)–O(10)	2.019(3)
V(2)–O(6)	2.020(2)
O(2)–O(3)	1.428(4)
O(8)–O(9)	1.433(4)
O(1)–V(1)–O(3)	106.69(15)
O(1)–V(1)–O(2)	100.85(14)
O(3)–V(1)–O(2)	44.80(11)
O(1)–V(1)–O(6)	106.54(14)
O(3)–V(1)–O(6)	138.77(12)
O(2)–V(1)–O(6)	145.59(12)
O(1)–V(1)–O(12)	95.59(12)
O(3)–V(1)–O(12)	82.62(11)
O(2)–V(1)–O(12)	127.38(11)
O(6)–V(1)–O(12)	70.50(10)
O(1)–V(1)–O(4)	96.78(13)
O(2)–V(1)–O(4)	79.13(12)
O(6)–V(1)–O(4)	77.34(11)
O(12)–V(1)–O(4)	147.65(11)
O(7)–V(2)–O(12)	103.89(12)
O(8)–V(2)–O(12)	145.06(11)
O(9)–V(2)–O(12)	142.82(11)
O(7)–V(2)–O(10)	97.80(13)
O(8)–V(2)–O(10)	78.21(11)
O(9)–V(2)–O(10)	122.30(11)
O(12)–V(2)–O(10)	77.23(10)
O(7)–V(2)–O(6)	98.35(12)
O(8)–V(2)–O(6)	126.20(12)
O(9)–V(2)–O(6)	82.35(11)
O(12)–V(2)–O(6)	69.67(10)
O(10)–V(2)–O(6)	145.76(11)
O(3)–O(2)–V(1)	66.77(16)
O(2)–O(3)–V(1)	68.43(16)
V(1)–O(6)–V(2)	107.68(12)
O(9)–O(8)–V(2)	68.12(15)
O(8)–O(9)–V(2)	66.86(15)
V(2)–O(12)–V(1)	107.81(12)

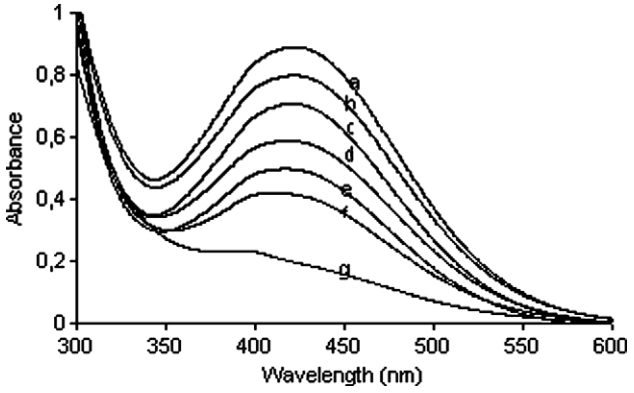


Fig. 2. UV–Vis spectra of 10^{-3} mol dm^{-3} $(NMe_4)_2[V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 3H_2O$ (**9**) in MeCN at $T = 278$ K and 30 min (a), 1 d (b), 2 d (c), 4 d (d), 5 d (e), 6 d (f), 10 d (g) after dissolution.

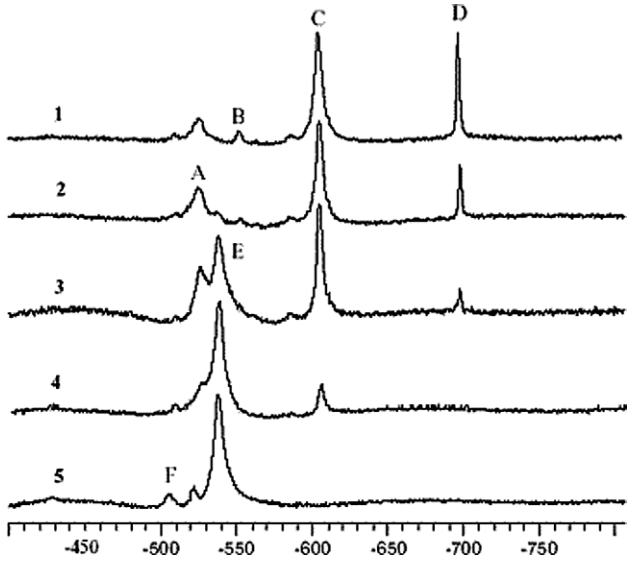


Fig. 3. Time dependence of the ^{51}V NMR spectra of the aqueous solutions of vanadium (V) peroxo *rac*-3-phenyllactato complexes. Solution prepared by mixing of aqueous NH_4VO_3, *rac*-3-phlact and H_2O_2 [$c(V) = c(rac\text{-3-phlact}) = c(H_2O_2) = 0.02$ mol dm^3] at $T = 278$ K. 1, 40 min; 2, 8 h; 3, 24 h; 4, 2 days after preparation; 5, solution prepared by mixing of aqueous NH_4VO_3 and *rac*-3-phlact [$c(V) = c(rac\text{-3-phlact}) = 0.02$ mol dm^{-3}], 30 min after preparation. For **A**–**F** see text.

group. The axial positions are taken by the double bonded oxygen atoms (O(1), O(7)). The length of the VO (alcoholate) bonds (2.000, 1.967, 2.026 and 1.988 Å) supports the view that the hydroxyl groups are deprotonated. Formation of the $[V_2O_2(O_2)_2(R\text{-3-phlact})(S\text{-3-phlact})]^{2-}$ stereoisomer was not observed, the complex crystallizes as a racemic compound.

3.4. Solution spectra

The UV–Vis spectra of **9** (and similarly of other prepared complexes) in MeCN solution (Fig. 2) exhibit a LMCT band at 424 nm, which is characteristic for the vanadium (V) monoperoxo complexes [34,35].

The ^{51}V NMR spectra of oxo peroxo complexes of vanadium (V) with α-hydroxycarboxylates and other ligands have been currently studied [20,21,36–45]. In the presence of hydrogen peroxide and *rac*-3-phenyllactic acid in aqueous solution, vanadium (V) can form several complexes (Fig. 3, spectra 1–4). The chemical shift $\delta = -604$ ppm can be assigned to the dinuclear monoperoxo vanadium complex **C**, $[V_2O_2(O_2)_2(rac\text{-3-phlact})_2]^{2-}$, which is probably the species with the same structure as found in the solid state. We tentatively assign the signal **B** at −552 ppm to a monomeric monoperoxo species $[VO(O_2)(rac\text{-3-phlact})(H_2O)]^-$ [38,39]. The species **A** is attributed to the intermediate decomposition product $[V_2O_3(O_2)(rac\text{-3-phlact})_2]^{2-}$ (resulting from the decomposition of **C** by release of one oxygen atom from the two peroxo groups). For the $[V_2O_3(O_2)(rac\text{-3-phlact})_2]^{2-}$ ion, we should expect two ^{51}V NMR signals: one for the vanadium atom in the dioxo moiety, observed at −524 ppm, and the second one for the vanadium atom in the intact $VO(O_2)$ moiety. The latter signal, lacking in the spectra, is probably hidden in the signal at −604 ppm. The complex **A** converts into an oxovanadium complex of *rac*-3-phlact acid **E** $[V_2O_4(rac\text{-3-phlact})_2]^{2-}$ (−537 ppm) by release of the second active oxygen atom. The identity of the **E** species was confirmed by the in situ measurement (Fig. 3, spectrum 5). The ^{51}V NMR spectra also exhibit peaks of $H_xV_{10}O_{28}{}^{(6-x)-}$ (**F**) at about −521, −506 and −427 ppm and $[VO(O_2)_2(H_2O)]^-$ (**D**) at about −697 ppm.

3.5. Characteristic features of the crystal structures of α-hydroxycarboxylatooxoperoxovanadates

The structure of all structurally characterized α-hydroxycarboxylatooxoperoxovanadates (V) listed in Table 5 consists of dinuclear anions and counter cations. The characteristic structural feature of anions is the central rhombic V_2O_2 core. All α-hydroxycarboxylato ligands are coordinated to the central atom via monodentate carboxylic and hydroxylic groups, the latter forming a bridge between two vanadium centres. The citrato, malato and α-hydroxyhippurato ligands are coordinated to the vanadium atom as tridentate ligands using the oxygen atoms of carboxylic groups (from COOH or CO) as the third donor atom.

The coordination number of the central atom varies between 6 (pentagonal pyramidal geometry) and 7 (pentagonal bipyramidal structure). With exception of the citrato, malato and α-hydroxyhippurato complexes mentioned above, the pentagonal bipyramidal arrangement is achieved by bonding of a water molecule or exceptionally by bonding of a molecule of α-hydroxycarboxylic acid. The geometric parameters of the V_2O_2 core in various compounds are similar (Table 6).

The V_2O_2 core is planar or nonplanar in dependence on the type of the α-hydroxycarboxylato ligands (chiral

Table 5
Structurally characterized α-hydroxycarboxylatooxoperoxovanadates (V)

No.	Complex[a]	Ref.
1	$(NBu_4)_2[V_2O_2(O_2)_2(S\text{-lact})_2]\cdot 2H_2O$	[15]
2	$(NBu_4)_2[V_2O_2(O_2)_2(R\text{-lact})(S\text{-lact})]\cdot 2H_2O$	[15]
3	$(NH_4)_2[V_2O_2(O_2)_2(H_2cit)_2]\cdot 2H_2O$	[23]
4	$K_4[V_2O_2(O_2)_2(R\text{-mal})(S\text{-mal})]\cdot 4H_2O$	[24]
5	$(NH_4)_4[V_2O_2(O_2)_2(R\text{-mal})(S\text{-mal})]\cdot 3H_2O$	[24]
6	$K_2[V_2O_2(O_2)_2(R\text{-Hmal})(S\text{-Hmal})]\cdot 2H_2O$	[24]
7	$(NBu_4)_4[V_2O_2(O_2)_2(S\text{-mand})_2][V_2O_2(O_2)_2(R\text{-mand})_2]\cdot(R\text{-H}_2\text{mand})(S\text{-H}_2\text{mand})$	[18]
8	$K_4[V_2O_2(O_2)_2(R\text{-lact})_2][V_2O_2(O_2)_2(S\text{-lact})_2]$	[19]
9	$K_2[\{VO(O_2)(RR\text{-H}_2\text{tart})\}_2(\mu\text{-H}_2O)]\cdot 5H_2O$	[17]
10	$(NBu_4)_2[V_2O_2(O_2)_2(glyc)_2]\cdot H_2O$	[20]
11	$(NMe_4)_4[V_2O_2(O_2)_2(R\text{-mand})_2][V_2O_2(O_2)_2(S\text{-mand})_2]\cdot 13H_2O$	[21]
12	$(NMe_4)_2(NH_4)_2[V_2O_2(O_2)_2(R\text{-mand})_2(H_2O)][V_2O_2(O_2)_2(S\text{-mand})_2(H_2O)]\cdot 4H_2O$	[21]
13	$(NEt_4)_2[V_2O_2(O_2)_2(R\text{-mand})_2]$	[21]
14	$(NPr_4)_2[V_2O_2(O_2)_2(R\text{-α-hhip})(S\text{-α-hhip})]\cdot 5H_2O$	[22]
15	$(NBu_4)_2[V_2O_2(O_2)_2(R\text{-α-hhip})(S\text{-α-hhip})]\cdot 5H_2O$	[41]
16	$(NEt_4)(NH_4)_3[V_2O_2(O_2)_2(R\text{-3-phlact})_2][V_2O_2(O_2)_2(S\text{-3-phlact})_2]\cdot 6H_2O$	this work
17	$(NH_4)_6[V_2O_2(O_2)_2(cit)_2]\cdot 4.5H_2O$	[25]

[a] glyc = glycolato $(C_2H_2O_3)^{2-}$, cit = citrato $(C_6H_4O_7)^{4-}$, mal = malato $(C_4H_3O_5)^{3-}$, lact = lactato $(C_3H_4O_3)^{2-}$, mand = mandelato $(C_8H_6O_3)^{2-}$, tart = tartrato $(C_4H_2O_6)^{4-}$, α-hhip = α-hydroxyhippurato $(C_9H_7NO_4)^{2-}$, 3-phlact=3-phenyllactato $(C_9H_8O_3)^{2-}$.

Table 6
Geometric parameters of the V_2O_2 core in α-hydroxycarboxylatooxoperoxo-vanadates (V)

Complex no.[a]	Space group	*d*(V–O) (Å)	∠OVO (°)	∠VOV (°)	Geometry[b]	Chirality[c]	T[d]	CN[e]
1	$P2_1$	1.918(6) 2.037(5) 1.927(6) 2.049(6)	69.8(3) 69.3(2)	109.4(3) 109.3(3)	NP	CH (*SS*)	B	6
2	$P2_1/n$	2.025(6) 1.927(6)	70.0(3)	110.0(3)	P	CH (*RS*)	A	6
3	$P2_1/n$	1.992(2) 2.034(2)	72.45(8)	107.15[f]	P	ACH	A	6
4	$P2_1/c$	2.005(2) 2.025(2)	72.30(8)	107.70[f]	P	CH (*RS*)	A	7
5	$P\bar{1}$	1.987(3) 2.026(3)	71.6(2)	108.4[f]	P	CH (*RS*)	A	7
6	$P2_1/c$	1.986(2) 2.021(2)	71.43(9)	108.57[f]	P	CH (*RS*)	A	6
7	*Pbcn*	1.979(2) 2.000(2)	69.57(10)	105.58(10)	NP	CH (*SS*) (*RR*)	B	6
8	$C2/c$	1.957(3) 2.000(3)	70.0(1)	109.9(1)	NP	CH (*SS*) (*RR*)	B	6
9	$C222_1$	2.010(5) 2.015(5) 2.026(5) 2.003(5)	70.3(2) 69.9(2)	101.0(2) 101.6(2)	NP	CH (*RRRR*)[g]	B	7
10	$P2_1/n$	1.923(4) 2.011(4)	69.7(2)	110.3(2)	P	ACH	A	6
11	$C2/c$	1.975(4) 2.035(3) 1.967(3) 1.990(4)	69.25(14) 70.32(14)	109.92(16) 108.44(15)	NP	CH (*SS*) (*RR*)	B	6
12	$P2_1/c$	1.9747(19) 2.0004(19) 1.9871(19) 2.0211(19) 1.9979(19) 2.006(2) 1.9977(19) 2.0056(19)	70.04(8) 69.38(8) 70.31(8) 70.33(8)	109.39(9) 109.73(9) 103.16(8) 103.75(8)	NP	CH (*SS*) (*RR*)	B	6, 7
13	$P2_12_12_1$	1.975(2) 2.018(19) 1.954(2) 2.042(2)	68.44(8) 68.35(8)	108.59(9) 110.44(10)	NP	CH (*RR*)	B	6
14	$P\bar{1}$	2.032(4) 2.037(4) 2.032(4) 2.042(4) 2.289(4) 2.292(4)	70.98(14) 70.89(14)	108.79(19) 109.34(19)	P	CH (*RS*)	A	7
15	$P2_1/c$	2.0330(15) 2.0403(15) 2.0244(14) 2.0301(15)	70.54(7) 72.05(7)	109.46(7) 107.95(7)	P	CH (*RS*)	A	7

(*continued on next page*)

Table 6 (*continued*)

Complex No.[a]	Space group	*d*(V–O) (Å)	∠OVO (°)	∠VOV (°)	Geometry[b]	Chirality[c]	T[d]	CN[e]
16	*Pbcn*	1.967(3) 2.000(3) 2.026(3) 1.988(3) 1.968(3) 2.002(3) 2.023(3) 1.986(3)	70.55(11) 69.61(11) 70.53(11) 69.73(11)	107.63(12) 107.87(12) 107.68(12) 107.79(12)	NP	CH (*SS*) (*RR*)	B	6
17	*C*2/*c*	2.013(3) 2.055(3)	73.44(11)	106.56(11)	P	ACH	A	7

[a] Numbering according to Table 5.
[b] Planarity of the V_2O_2 core: P, planar; NP, nonplanar.
[c] Chirality of the ligands: ACH, achiral ligand; CH, chiral ligand with combination of enantiomers in the anion in parentheses.
[d] Types according to Fig. 4.
[e] Coordination number.
[f] Calculated value.
[g] Two chiral centres in one ligand, i.e., four chiral centres in a dinuclear anion.

or achiral) and on the combination of ligand enantiomers in the dinuclear anion (*RR*, *SS* or *RS*) (Fig. 4).

For all complexes given in Table 5, the previously formulated rule on the geometry of the V_2O_2 core [15] (Fig. 4, Table 6) is valid. The different arrangement of the $[V_2O_2(O_2)_2(\text{ligand})_2]^{n-}$ anions in dependence on the enantiomers of a ligand present in the dinuclear anion can be attributed in large part to the steric demands of the ligand. With ligands containing the bulky benzene ring in the proximity of the OH group, in spite of racemic ligand used in the synthesis, the $[V_2O_2(O_2)_2(\text{R-ligand})_2]^{n-}$ and $[V_2O_2(O_2)_2(\text{S-ligand})_2]^{n-}$ isomers can only be obtained. This is the case of mandelic acid (one C atom between benzene ring and the donor oxygen atom of the hydroxylic group) and 3-phenyllactic acid (two C atoms – Scheme 2). On the other hand, with α-hydroxyhippuric acid, in which the aromatic ring is relatively distant from the hydroxylic group, $[V_2O_2(O_2)_2(\text{R-ligand})(\text{S-ligand})]^{2-}$ isomer was formed. Using lactic acid as a heteroligand, both isomers $M_2[V_2O_2(O_2)_2(S\text{-lact})_2]$ and $M_2[V_2O_2(O_2)_2(R\text{-lact})(S\text{-lact})]$ were prepared [15].

The deviation of the vanadium atoms from the least squares pentagonal plane (Table 7) depends on the structural type (**A** and **B**) and on the coordination number of vanadium. The deviation is smallest for the seven coordinated vanadium atoms in the structures with a planar V_2O_2 core (≈0.24–0.29 Å) and largest for the six coordinated vanadium atoms in mandelato complexes (≈0.31–0.49 Å, the V_2O_2 core is nonplanar).

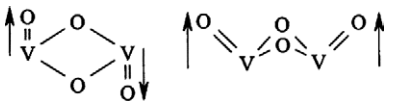
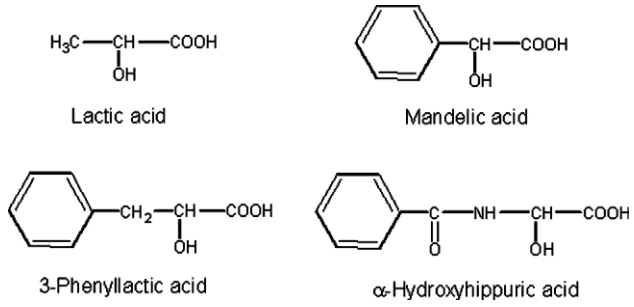


Fig. 4. Structural types of the α-hydroxycarboxylatooxoperoxovanadates. **A** (left) – planar V_2O_2 group for *RS* combination of a chiral ligand or some achiral ligands (glycolato-, citrato-), **B** (right) – for *RR* or *SS* combination of the chiral ligand.



Scheme 2.

Table 7
The deviations of the vanadium atoms from the least squares pentagonal plane in complexes **9** and **12**–**15**

Complex no.	V1	V2	V3	V4
9	0.3688	0.3501		
12	0.4588	0.3166	0.3383	0.3464
13	0.4302	0.4858		
14	0.2720	0.2879	0.2850	0.2612
15	0.2423	0.2462		
16	0.3745	0.3845	0.3744	0.3859

4. Supplementary material

Supplementary data are available from CCDC 12 Union Road, Cambridge, CB 2 1EZ, UK on request quoting the deposition number CCDC 247261.

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