Vanadium-induced formation of thiadiazole and thiazoline compounds. Mononuclear and dinuclear oxovanadium(V) complexes with open-chain and cyclized thiosemicarbazone ligands†

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Received 9th July 2009, Accepted 16th September 2009
First published as an Advance Article on the web 7th October 2009
DOI: 10.1039/b913653c

Reactions of the salicylaldehyde 4-phenylthiosemicarbazone (H_2L) with selected vanadium(IV) and vanadium(V) precursors ([$VO(acac)_2$], [$VO(OAc)_2$], $VOSO_4$, [$V_2O_4(acac)_2$]) were investigated under aerobic conditions in different alcohols (methanol, ethanol, propanol). In all examined cases mononuclear alkoxo vanadium(V) complexes [VOL(OR)] (**1**) (OR = OMe, OEt, OPr) were isolated as major products. On prolonged standing, mother liquids afforded dinuclear vanadium(V) complexes [$V_2O_3(L_{cycl})_2(OR)_2$] (**3**) (OR = OMe, OEt, OPr), where L_{cycl}^- represents 1,3,4-thiadiazole ligand, formed by vanadium-induced oxidative cyclization of H_2L. When [$VO(acac)_2$] or [$V_2O_4(acac)_2$] were used as precursors, in addition to products **1** and **3**, a thiazoline derivative $HL(acac)_{cycl}$ (**2**) was isolated. This compound, formed by a reaction between acetylacetone and H_2L, represented the second type of cyclic product. The products were characterized by IR and NMR spectroscopies, TG analysis, and in some cases by single-crystal X-ray diffraction. To the best of our knowledge, compounds [$V_2O_3(L_{cycl})_2(OR)_2$] represent the first structurally characterized dinuclear vanadium(V) complexes with a thiadiazole moiety acting as a bridging ligand. Complexes **1** and **3**, when dissolved in an appropriate alcohol, underwent substitution of the alkoxo ligand as confirmed by XRPD. The kinetics of reactions in methanolic solutions was qualitatively studied by UV-Vis and ESMS spectrometries. Under the experimental conditions applied, a relatively slow formation of the mononuclear complex [VOL(OMe)] and an even slower formation of the cyclic species **2** were observed, whereas the presence of dinuclear compound [$V_2O_3(L_{cycl})_2(OMe)_2$] in the reaction mixture could not be detected.

Introduction

A growing interest in the coordination chemistry of vanadium is based on the recognition of its importance from a biological and pharmacological perspective.[1] The potential therapeutic use of vanadium compounds in the treatment of diabetes and cancer,[2] as well as their application in catalytic processes,[3] additionally stimulated the expansion of the field. The chemistry of the metal is dominated by oxidation states V(IV) and V(V) which are associated with a variety of cores such as $[VO]^{2+}$, $[VO]^{3+}$, $[VO_2]^+$, $[V_2O_3]^{n+}$ (n = 2, 3, 4), $[V_2O_4]^{2+}$, emphasizing the influence of the reaction conditions: nature of ligands, type of solvent, pH of the reaction medium, *etc.*[4,5]

Thiosemicarbazones continue to draw attention not only as multifunctional ligands,[6] but also because they can undergo ring closure processes by action of bases, acids or oxidants.[7] Reactions may follow different routes depending on the open-chain substrate (thiosemicarbazone) structure as well as the nature of the cyclizing agent. Metal cations represent an interesting class of oxidizing agents.[8] Oxidative cyclization of thiosemicarbazones (**I**) is influenced by the hardness/softness of the metal cation as well as by its oxidizing strength, and can lead to the formation of 1,2,4-triazole-3-thiol (**II**), 1,3,4-thiadiazole-2-amine (**III**), 1,2,4-triazoline-3-thione (**IV**), or 1,3,4-thiadiazoline-2-imine (**V**) derivatives (Scheme 1). Although these cyclizations are well described in the literature, especially those involving Fe(III) or Cu(II) cations, their mechanism is still not clearly resolved.[9] Recently, the field has been enriched by a number of papers reporting on metal-induced cyclizations of thiosemicarbazones involving cations such as Ag(I), Zn(II), Cd(II), *etc.*[10] To the best of our knowledge, only one example of vanadium-induced cyclization of this type involving similar, dithiocarbazate ligand has been reported so far.[11]

Based on previous considerations, we have been interested in exploring reactions of salicylaldehyde 4-phenylthiosemicarbazone (H_2L), a fairly flexible ligand in terms both of coordination and open-chain–ring transformation, with different vanadium precursors. Although vanadium complexes with similar systems, like dithiocarbazate ligands containing an *ONS* donor set, are well described in the literature,[12] papers reporting on corresponding thiosemicarbazone complexes of vanadium are less

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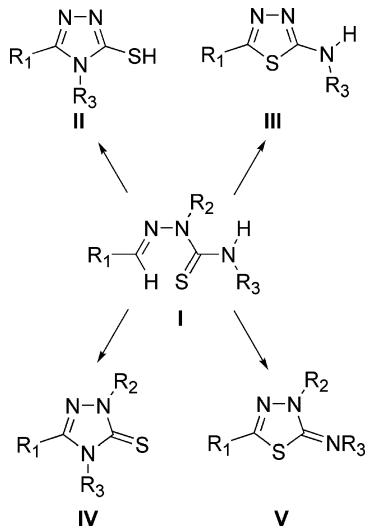
† Electronic supplementary information (ESI) available: IR, ^1H and ^{13}C NMR spectroscopy for compounds **1**, **2** and **3**. Thermogravimetric analysis of the mononuclear and dinuclear vanadium(V) complexes **1** and **3**. Comparison of powder patterns for the mononuclear and dinuclear complexes **1** and **3**. X-Ray crystallographic data for complexes **1b**, **1c** and **3** (molecular structures, selected geometrical parameters, intramolecular hydrogen bonds, intermolecular C–H···O interactions and packing diagrams). Time-dependent UV-Vis spectral changes of the H_2L + $VOSO_4$ reaction mixture. Concentration dependence of the UV spectrum of H_2L solution in methanol. CCDC reference numbers 733234–733239. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b913653c



Scheme 1

numerous.[13,14] Recently, we have reported on two vanadium(v) complexes obtained in the reactions of $[V(acac)_3]$ and two thiosemicarbazone ligands.[14] Herein we report on several synthetic strategies, structural and spectroscopic characterizations, as well as the reactivity of two different types of vanadium(v) complexes: (a) mononuclear alkoxo [VOL(OR)] complexes; (b) dinuclear dialkoxo $[V_2O_3(L_{cycl})_2(OR)_2]$ complexes, where L_{cycl}^- is the thiadiazole ligand formed by oxidative cyclization of H_2L; and (c) thiazoline compound $HL(acac)_{cycl}$ as a product of a heterocyclization reaction between acetylacetone and thiosemicarbazone. As far as we are aware, $[V_2O_3(L_{cycl})_2(OR)_2]$ are the first structurally characterized dimeric vanadium(v) complexes containing a bridging thiadiazole moiety. We have also been interested in finding out how the above-mentioned reactions proceed in solution. For that reason, the time course of some reactions has been followed spectrometrically (UV-Vis, ESMS), and the main products formed under the experimental conditions used have been identified.

Experimental

Materials

Salicylaldehyde, acetylacetone, 4-phenylthiosemicarbazide, V_2O_5, $NaVO_3$, and $VOSO_4{\cdot}5H_2O$ were commercially available and used as received. The ligand H_2L (salicylaldehyde 4-phenylthiosemicarbazone) and $[VO(OAc)_2]$ were prepared according to a literature procedures.[15,16] $[VO(acac)_2]$ was prepared by slight modification of a well-established method, using triethylamine instead of Na_2CO_3.[17] $[V_2O_4(acac)_2]$ was prepared by literature method.[18] The solvents were of reagent grade and distilled before use. Spectroscopic grade methanol (Riedel-de Haën, Spectranal) was used for the UV-Vis and MS measurements.

Syntheses of [VOL(OR)] (1a–1c; R = CH_3, C_2H_5, C_3H_7), $HL(acac)_{cycl}$ (2) and $[V_2O_3(L_{cycl})_2(OR)_2]$ (3a–3c; R = CH_3, C_2H_5, C_3H_7)

General method A: Syntheses of 1, 2, and 3 from $[VO(acac)_2]$. The stoichiometric amount of $[VO(acac)_2]$ (200 mg, 0.75 mmol) was added to alcoholic solution (20 mL) of H_2L (200 mg, 0.74 mmol). The solution rapidly changed color to dark brown and was heated under reflux for additional 2.5 h. Within two days dark brown crystals separated out from the solution (in the case of **1c** the solution was concentrated under reduced pressure to a small volume). The crystals of **1** were filtered off, washed with a small amount of cold alcohol and dried. Mother liquids obtained at this stage were allowed to stand at room temperature and after a few days yielded yellow crystals of compound **2**. The crystals of **2** were filtered off, washed with a small amount of cold alcohol and dried. Prolonged standing of the remaining mother liquids at room temperature (a few weeks) gave the red dimeric vanadium complexes **3**. The crystals of **3** were filtered off, washed with small amount of appropriate alcohol and dried.

Repeated recrystallization of compound **3b** yielded a mixture of **3b** and several crystals of **3b**·0.5EtOH.

*[VOL(OMe)] (**1a**).* Yield: 150 mg (55%). Anal. calcd for $C_{15}H_{14}N_3O_3SV$: C, 49.05; H, 3.84; N, 11.44; S, 8.73; V, 13.87%. Found: C, 48.91; H, 3.69; N, 11.30; S, 8.62; V, 13.41%. IR (KBr, cm^{-1}): 3331 (ν_{N-H}); 1597 ($\nu_{C=N}$); 1318, 756 (ν_{C-S}); 1222 ($\nu_{C-Ophen}$); 980 ($\nu_{V=O}$).

Analytical data were in accordance with those for the previously described compound.[14]

*[VOL(OEt)] (**1b**).* Yield: 143 mg (51%). Anal. calcd for $C_{16}H_{16}N_3O_3SV$: C, 50.40; H, 4.23; N, 11.02; S, 8.41; V, 13.36%. Found: C, 50.29; H, 4.09; N, 10.92; S, 8.36; V, 12.98%. IR (KBr, cm^{-1}): 3332 (ν_{N-H}); 1598 ($\nu_{C=N}$); 1316, 758 (ν_{C-S}); 1222 ($\nu_{C-Ophen}$); 976 ($\nu_{V=O}$).

*[VOL(OPr)] (**1c**).* Yield: 112 mg (38%). Anal. calcd for $C_{17}H_{18}N_3O_3SV$: C, 51.65; H, 4.59; N, 10.63; S, 8.11; V, 12.89%. Found: C, 51.48; H, 4.56; N, 10.55; S, 8.03; V, 12.73%. IR (KBr, cm^{-1}): 3325 (ν_{N-H}); 1599 ($\nu_{C=N}$); 1318, 752 (ν_{C-S}); 1224 ($\nu_{C-Ophen}$); 997 ($\nu_{V=O}$).

*$HL(acac)_{cycl}$ (**2**).* Yield: 10–20 mg (4–8%). Anal. calcd for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.88; N, 11.96; S, 9.12%. Found: C, 64.90; H, 4.81; N, 12.01; S, 8.99%. IR (KBr, cm^{-1}): 1628, 1608, 1576, 1536 ($\nu_{C=N}/\nu_{C=O}$); 1312, 760 (ν_{C-S}).^{1}H NMR ($CDCl_3$, δ ppm): 11.28 (s, 1H, –OH); 8.28 (s, 1H, azomethine), 7.57 (t, 2H, ar), 7.53 (t, 1H, ar), 7.32 (d, 2H, ar), 7.27 (t, 1H, ar), 7.15 (d, 1H, ar), 7.00 (d, 1H, ar), 6.87 (t, 1H, ar), 2.41 (s, 3H, $-CH_3$), 2.28 (s, 3H, $-CH_3$).

The yield for **2** depended on the alcohol used, the lowest being for methanol and the highest for propanol.

Analytical data were in accordance with those for the previously described compound.[14]

*$[V_2O_3(L_{cycl})_2(OMe)_2]$·0.5MeOH (**3a**·0.5MeOH).* Yield: 23 mg (8%). Anal. calcd for $C_{30.5}H_{28}N_6O_{7.5}S_2V_2$: C, 47.94; H, 3.70; N, 11.00; S, 8.39; V, 13.33%. Found: C, 47.90; H, 3.63; N, 11.06; S, 8,43; V, 13.15%. IR (KBr, cm^{-1}): 3244 (ν_{N-H}); 1599, 1563 ($\nu_{C=N}$); 1298, 754 (ν_{C-S}); 1223 ($\nu_{C-Ophen}$); 963 ($\nu_{V=O}$); 710 (ν_{V-O-V}).^{1}H NMR ($CDCl_3$, δ ppm): 9.56 (s, 1H, –NH), 7.43 (t, 1H, ar), 7.36 (t, 2H, ar), 7.31 (d, 1H, ar), 7.21 (d, 1H, ar), 7.13 (t, 1H, ar), 7.06 (d, 2H, ar), 6.84 (t, 1H, ar), 5.48, (s, 3H, $-OCH_3$).

*$[V_2O_3(L_{cycl})_2(OEt)_2]$ (**3b**).* Yield: 12 mg (4%). Anal. calcd for $C_{32}H_{30}N_6O_7S_2V_2$: C, 49.49; H, 3.89; N, 10.82; S, 8.26; V, 13,12%. Found: C, 49.37; H, 3,81; N, 10.69; S, 8.21; V, 12.67%. IR (KBr, cm^{-1}): 3229(ν_{N-H}); 1599, 1564 ($\nu_{C=N}$); 1299, 751 (ν_{C-S}); 1224 ($\nu_{C-Ophen}$); 959 ($\nu_{V=O}$); 714 (ν_{V-O-V}).^{1}H NMR ($CDCl_3$, δ ppm): 9.63 (s, 1H, –NH), 7.41 (t, 1H, ar), 7.37 (t, 2H, ar), 7.30 (d, 1H, ar),

7.17 (d, 1H, ar), 7.13 (t, 1H, ar), 7.07 (d, 2H, ar), 6.83 (t, 1H, ar), 5.95 (q, 1H, –OCH_2CH$_3$), 5.69 (q, 1H, –OCH_2CH$_3$), 1.66 (t, 3H, –OCH$_2$CH_3).

*[$V_2O_3(L_{cycl})_2(OPr)_2$]·0.5PrOH (**3c**·0.5PrOH).* Yield: 94 mg (32%). Anal. calcd for $C_{34.5}H_{38}N_6O_{7.5}S_2V_2$: C, 51.08; H, 4.11; N, 10.07; S, 7.68; V, 12.21%. Found: C, 50.97; H, 4.20; N, 10.14; S, 7.75; V, 11.73%. IR (KBr pellet), cm^{-1}: 3236(ν_{N-H}); 1600, 1564 ($\nu_{C=N}$); 1300, 756 (ν_{C-S}); 1228 ($\nu_{C-Ophen}$); 962 ($\nu_{V=O}$); 710 (ν_{V-O-V}).[1]H NMR ($CDCl_3$, δ ppm): 9.72 (s, 1H, –NH), 7.41 (t, 1H, ar), 7.37 (t, 2H, ar), 7.30 (d, 1H, ar), 7.17 (d, 1H, ar), 7.12 (t, 1H, ar), 7.03 (d, 2H, ar), 6.88 (t, 1H, ar), 5.64 (t, 1H, –OCH_2CH$_2$CH$_3$), 5.99 (t, 1H, –OCH_2CH$_2$CH$_3$), 2.08 (s, 2H, –OCH$_2$CH_2CH$_3$), 1.11 (t, 3H, –OCH$_2$CH$_2$CH_3).

The highest yield for **3c**·0.5PrOH was observed if compound **1c** was not previously isolated from the reaction mixture.

General method B: Syntheses of 1, 2, and 3 from [V_2O_4(acac)$_2$]. H_2L (90 mg, 0.33 mmol) was added to alcoholic solution (10 mL) of [V_2O_4(acac)$_2$] (60 mg, 0.17 mmol). The solution instantaneously changed color to dark brown and was heated under reflux. In the case of **1a** and **1b**, dark brown crystals separated from the solution during heating (after 10–30 min). In the case of propanol as solvent, the solution was concentrated under reduced pressure to a small volume in order to obtain **1c**. The crystals of **1** were filtered off, washed with a small amount of cold alcohol and dried. Mother liquids were allowed to stand at room temperature and, only in the case of propanol, yellow crystals of compound **2** were obtained after a few days. The crystals **2** were filtered off, washed with a small amount of cold propanol and dried. Prolonged standing of the remaining mother liquid at room temperature (a few weeks) gave the red dimeric vanadium complexes **3c**·0.5PrOH. The crystals **3c**·0.5PrOH were filtered off, washed with a small amount of propanol and dried.

*[VOL(OMe)] (**1a**).* Yield: 110 mg (91%).

*[VOL(OEt)] (**1b**).* Yield: 103 mg (82%).

*[VOL(OPr)] (**1c**).* Yield: 91 mg (70%).

*HL(acac)$_{cycl}$ (**2**).* Yield: 21 mg (8%).

*[$V_2O_3(L_{cycl})_2(OPr)_2$]·0.5PrOH (**3c**·0.5PrOH).* Yield: 29 mg (22%).

General method C: Syntheses of 1 and 3 from [VO(OAc)$_2$]. The syntheses were performed by a procedure similar to that described for method A using [VO(OAc)$_2$] (140 mg, 0.76 mmol) instead of [VO(acac)$_2$]. Due to low solubility of [VO(OAc)$_2$] in alcohols heating was prolonged to 4–5 h.

*[VOL(OMe)] (**1a**).* Yield: 143 mg (53%).

*[VOL(OEt)] (**1b**).* Yield: 139 mg (49%).

*[VOL(OPr)] (**1c**).* Yield: 120 mg (41%).

*[$V_2O_3(L_{cycl})_2(OMe)_2$]·0.5MeOH (**3a**·0.5MeOH).* Yield: 12 mg (4%).

*[$V_2O_3(L_{cycl})_2(OPr)_2$]·0.5PrOH (**3c**·0.5PrOH).* Yield: 43 mg (14%).

General method D: Syntheses of 1 and 3 from $VOSO_4 \cdot 5H_2O$. The syntheses were performed by a procedure similar to that described for method A, using $VOSO_4 \cdot 5H_2O$ (190 mg; 0.75 mmol) instead of [VO(acac)$_2$].

*[VOL(OMe)] (**1a**).* Yield: 122 mg (44%).

*[VOL(OEt)] (**1b**).* Yield: 108 mg (39%).

*[VOL(OPr)] (**1c**).* Yield: 91 mg (30%).

*[$V_2O_3(L_{cycl})_2(OPr)_2$]·0.5PrOH (**3c**·0.5PrOH).* Yield: 73 mg (24%).

Analytical and spectral data for all of the isolated products obtained by methods B, C, and D were in agreement with those for products prepared according to method A.

Substitution of the OR group in [VOL(OR)] (1). [VOL(OR)] (0.10 mmol) was dissolved under reflux in about 5–8 mL of appropriate alcohol (R′OH; R′ = CH_3, C_2H_5, C_3H_7). All solutions were filtered and within a few hours they yielded dark brown crystals of [VOL(OR′)] (**1′**). In the case of **1c′**, the solution was concentrated under reduced pressure to a small volume.

***1a′** from **1b**.* Yield: 33 mg (90%).

***1a′** from **1c**.* Yield: 34 mg (93%).

***1b′** from **1a**.* Yield: 31 mg (81%).

***1b′** from **1c**.* Yield: 32 mg (84%).

***1c′** from **1a**.* Yield: 29 mg (73%).

***1c′** from **1b**.* Yield: 29 mg (73%).

Substitution of the OR group in [$V_2O_3(L_{cycl})_2(OR)_2$] (3). [$V_2O_3(L_{cycl})_2(OR)_2$] (0.10 mmol) was dissolved under reflux in about 5–10 mL of appropriate alcohol (R′OH; R′ = CH_3, C_2H_5, C_3H_7). All solutions were filtered and within a few hours they yielded red crystals of [$V_2O_3(L_{cycl})_2(OR')_2$] (**3′**).

***3a′**·0.5MeOH from **3b**.* Yield: 57 mg (75%).

***3a′**·0.5MeOH from **3c**·0.5PrOH.* Yield: 58 mg (76%).

***3b′** from **3a**·0.5MeOH.* Yield: 50 mg (64%).

***3b′** from **3c**·0.5PrOH.* Yield: 52 mg (67%).

***3c′**·0.5PrOH from **3a**·0.5MeOH.* Yield: 70 mg (84%).

***3c′**·0.5PrOH from **3b**.* Yield: 72 mg (86%).

Methods

Elemental analyses (C, H, N, and S) were provided by the Analytical Services Laboratory of the Rudjer Bošković Institute, Zagreb, Croatia. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer Fourier-Transform Spectrum RX1 spectrophotometer in the 4500–450 cm^{-1} region. Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851^e thermobalance using aluminium crucibles under oxygen atmosphere with a heating rate 5 °C min^{-1}. In all experiments the temperature ranged from 25 to 600 °C. The results were processed with the Mettler STAR^e 9.01 software. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AV-600 spectrometer, operating at 600.13 for the ^{1}H and at 150.90 MHz for the ^{13}C resonances. The NMR spectra were recorded in deuterated chlorophorm ($CDCl_3$). For details of IR, ^{1}H and ^{13}C NMR spectroscopy see Table S1 in the ESI.† The UV-Vis absorption spectra were recorded at (25.0 ± 0.1) °C by means of a Varian Cary 5 double-beam spectrophotometer equipped with a thermostating device. Quartz cells of 0.01 cm and 1 cm path lengths were used. Absorbances were sampled at 1 nm intervals. The mass spectra were acquired in the mass range 100–2000 on a LCQ Deca ion trap (ThermoFinnigan, San Jose, CA) operated in the positive ion mode with a spray voltage of 4.5 kV and a tube lens offset of –20 V. The capillary voltage was set to 10 V and the heated capillary temperature to 250 °C. The flow rate was 5 μL min^{-1}.

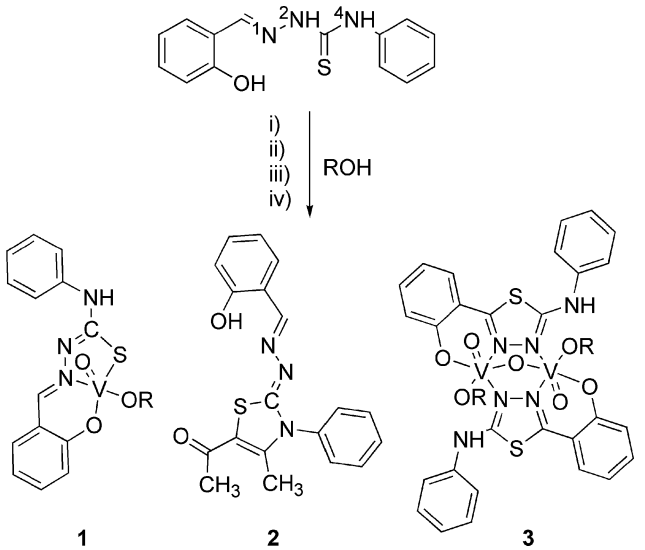
Table 1 Crystallographic data for **1b**, **1c**, **3a**·0.5MeOH, **3b**, **3b**·0.5EtOH, and **3c**·0.5PrOH

	1b	**1c**	**3a**·0.5MeOH	**3b**	**3b**·0.5EtOH	**3c**·0.5PrOH
Chemical formula	$C_{16}H_{16}N_3O_3SV$	$C_{17}H_{18}N_3O_3SV$	$C_{30}H_{26}N_6O_7S_2V_2\cdot 0.5CH_4O$	$C_{32}H_{30}N_6O_7S_2V_2$	$C_{32}H_{30}N_6O_7S_2V_2\cdot 0.5C_2H_6O$	$C_{34}H_{34}N_6O_7S_2V_2\cdot 0.5C_3H_8O$
Formula weight	381.32	395.34	764.59	776.62	799.65	834.72
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	10.8123(2)	15.1837(4)	11.8680(19)	11.4910(9)	11.6448(4)	13.4762(5)
b/Å	9.8588(2)	8.0325(2)	11.963(2)	11.8518(9)	12.1611(4)	17.2325(7)
c/Å	16.0968(4)	16.0582(5)	14.3202(9)	14.7813(13)	14.4691(5)	17.0544(6)
α (°)	90.00	90.00	102.100(10)	92.462(7)	73.441(3)	90.00
β (°)	102.663(2)	114.404(4)	96.852(8)	100.455(7)	84.791(3)	101.835(4)
γ (°)	90.00	90.00	119.640(19)	118.288(8)	62.827(3)	90.00
V/Å^3	1674.12(6)	1783.52(10)	1667.3(6)	1723.8(3)	1745.41(12)	3876.3(3)
Z	4	4	2	2	2	4
T/K	295(2)	133(2)	110(2)	100(2)	120(1)	295(2)
Data total/unique	10935/2925	9284/3124	19578/5847	12872/5869	15723/7536	16269/6706
R_{int}	0.0151	0.0204	0.0183	0.1016	0.0251	0.0474
R^a [$I > 2\sigma(I)$]	0.0266	0.0299	0.0323	0.0588	0.0349	0.0409
$R_w{}^b$ (all data)	0.0741	0.0806	0.0932	0.1126	0.0913	0.0999

^{a} $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

X-Ray diffraction experiments

The single-crystal X-ray data were collected by an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction was performed using the CrysAlis software package.[19] For solution, refinement, and analysis of the structures the programs integrated in the WinGX system were used.[20] The structures were solved by direct methods (SHELXS-97)[21] and refined by the full-matrix least-squares method based on F^2 against all reflections (SHELXL-97).[21] The non-hydrogen atoms were refined anisotropically with restraints on ADPs and geometrical parameters of the disordered atoms. Hydrogen atoms attached to the nitrogen atoms (except for H23N in **3b** and H3N in **1b** and **1c**) were refined isotropically with the restrained N–H distance, whereas all other H atoms were refined using the riding model. Geometrical calculations were performed using PLATON[22] and the figures were made using ORTEP-3.[23] The crystallographic data are summarized in Table 1. X-Ray powder diffraction experiments were performed on a Philips PW 3710 diffractometer, Cu-Kα radiation, flat plate sample on zero background in Bragg–Brentano geometry (40 kV and 40 mA). The patterns were collected in the angle region between 4° and 50° (2θ) with a step size of 0.02° and 1.5 s per step.



Scheme 2 Reactions of H_2L and different vanadium precursors: (i) [VO(acac)$_2$]: **2**; **1a** and **3a** (R = CH_3); **1b** and **3b** (R = C_2H_5), **1c** and **3c** (R = C_3H_7); (ii) [VO(OAc)$_2$]: **1a** and **3a** (R = CH_3); **1b** (R = C_2H_5); **1c** and **3c** (R = C_3H_7); (iii) $VOSO_4\cdot 5H_2O$: **1a** (R = CH_3); **1b** (R = C_2H_5); **1c** and **3c** (R = C_3H_7); (iv) [V_2O_4(acac)$_2$]: **2**; **1a** (R = CH_3); **1b** (R = C_2H_5); **1c** and **3c** (R = C_3H_7).

Results and discussion

Reactions of salicylaldehyde 4-phenylthiosemicarbazone and vanadium(IV) precursors ([VO(acac)$_2$], [VO(OAc)$_2$], $VOSO_4\cdot 5H_2O$) in different alcohols (Scheme 2) gave mononuclear vanadium(V) complexes [VOL(OR)] (**1**) as major products in low to moderate yields (30–55%). Prolonged standing of mother liquids in some cases yielded dinuclear vanadium(V) complexes [$V_2O_3(L_{cycl})_2(OR)_2$] (**3**). When [VO(acac)$_2$] was used as starting material, in addition to products **1** and **3**, thiazoline derivative $HL(acac)_{cycl}$ (**2**) was obtained. In the reactions with [V_2O_4(acac)$_2$] as vanadium(V) precursor, mononuclear vanadium(V) complexes [VOL(OR)] (**1**) were obtained in much higher yields than when vanadium(IV) precursors were used. In these reactions, thiazoline compound **2** and dinuclear vanadium(V) complex [$V_2O_3(L_{cycl})_2(OPr)_2$] (**3c**) were isolated only from propanolic solution.

A survey of recent literature shows that among various vanadium precursors [V_2O_4(acac)$_2$] has been seldom used.[24,25] This relatively underexplored precursor is easily accessible from $NaVO_3$. It is stable and soluble in a variety of organic solvents, and therefore quite applicable as a starting material. The results reported herein show that mononuclear alkoxovanadium(V) complexes **1** were formed in significantly higher yields when synthesized

from $[V_2O_4(acac)_2]$ than from more common precursors such as $[VO(acac)_2]$ or $VOSO_4$. This interesting finding can be related to the maintenance of the oxidation state, for both the starting and the resulting complexes contain vanadium(V). We therefore believe that the use of $[V_2O_4(acac)_2]$ as a precursor for the targeted synthesis of vanadium(V) complexes is advantageous because of its good solubility in organic solvents, which is a common restriction for vanadates, and preservation of the oxidation state in comparison with the vanadium(IV) starting compounds.

Formation of the thiazoline derivative $HL(acac)_{cycl}$ (2)

It was mentioned earlier that in the synthesis involving $[VO(acac)_2]$ the thiazoline derivative $HL(acac)_{cycl}$ (**2**) was isolated in addition to products **1** and **3**. The formation of **2** was attributed to a heterocyclization reaction between acetylacetone (from vanadium precursor) and H_2L. It has to be pointed out that **2** could not have been obtained solely by the reaction of H_2L and acetylacetone, indicating that the reaction was influenced by the presence of vanadium. We reported in our previous paper[14] that the product **2** was detected in the reaction of $[V(acac)_3]$ and H_2L. As in both syntheses, from $[V(acac)_3]$ or $[VO(acac)_2]$, vanadium was oxidized, we were interested to find out whether the formation of the thiazoline compound **2** was coupled to the oxidation process. Thus, instead of vanadium(IV), we used a vanadium(V) precursor. $[V_2O_4(acac)_2]$ was chosen since Grybos *et al.*[26] demonstrated that the final product of $[VO(acac)_2]$ oxidation in methanol was [VO(OH)(OMe)(acac)], which could be obtained simply by dissolving $[V_2O_4(acac)_2]$ in the same alcohol. Our concern was to establish whether having the same vanadium(V) species in the solution, that is [VO(OH)(OMe)(acac)], and not having all the side products of the oxidation process, would affect the course of the cyclization reaction and consequently its final products. The fact that compound **2** was isolated from the propanolic solution showed that the formation of thiazoline compound **2** was independent of the initial oxidation state of vanadium. As H_2L was needed for the formation of the monomeric complexes **1** and the thiazoline compound **2**, the absence of **2** in the case of methanolic and ethanolic solutions was attributed to the observed higher yields of mononuclear complexes **1**. On the basis of several control experiments which included attempted synthesis from $VOSO_4$ or NH_4VO_3 and H_2L and Hacac, but failed to yield desired $HL(acac)_{cycl}$, we believe that the initial attachment of the acetylacetone moiety to the vanadium atom was essential for the formation of **2**.

Dinuclear complexes $[V_2O_3(L_{cycl})_2(OR)_2]$ (3) – formation of the thiadiazole ligand

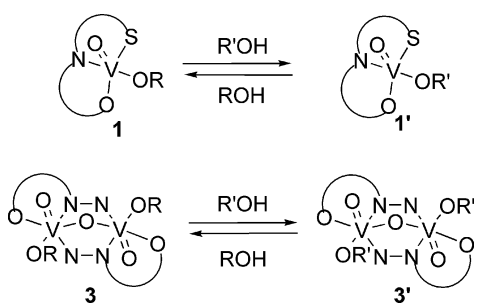
As already stated, on prolonged standing mother liquids yielded, in some cases, dinuclear complexes $[V_2O_3(L_{cycl})_2(OR)_2]$ (**3**) containing the coordinated thiadiazole ligand (L_{cycl}^-). Complexes **3** were isolated in various yields, depending on the alcohol used, and, especially in propanolic solutions, depended on the previous isolation and yields of mononuclear complexes **1**. The relationship between the yields of complexes **1** and **3** indicated that the presence of **1** was important to the formation of **3**. However, we were able to establish that complexes **1**, once isolated and redissolved in their parent alcohols, were stable in solution for weeks and did not undergo any transformation, *i.e.* that the formation of **3** was not due solely to the conversion of **1** (Fig. S1, ESI†). Additionally, by employing synthetic procedures with precursors that did not contain the acetylacetonate ligand ($[VO(OAc)_2]$, $VOSO_4$) we established that the formation of the thiadiazole ring and complexes **3** was not coupled to the cyclization reaction leading to the thiazoline product $HL(acac)_{cycl}$. The coordinated thiadiazole ligands (L_{cycl}^-) in **3** were formed by vanadium-induced oxidative cyclization of salicylaldehyde 4-phenylthiosemicarbazone. Like in the case of formation of the thiazoline compound, all experimental data indicated that the reaction was influenced by vanadium in oxidation state V. This finding is in agreement with the literature data and is supported by numerous examples of cyclization reactions induced by high-valent metal cations (Fe^{3+}, Cu^{2+}).[8,9] In the present case, formation of the 1,3,4-thiadiazole ring seems to be induced by an attack of vanadium(V) acting as Lewis acid on the imine nitrogen atom, followed by the ring closure, and finally by the electron abstracting-dehydrogenation step.[8,9a] Thiadiazole anions (L_{cycl}^-) formed in that way, act as bridging ligands through the nitrogen atoms of the thiadiazole rings and coordinate to the vanadium atoms of $[V_2O_3]^{4+}$ core forming **3**.

Repeated recrystallization of compound **3b**, in the attempt to obtain good-quality single crystals, yielded a mixture of **3b** and several crystals suitable for X-ray diffraction but slightly differing in morphology from those of **3b**. By structural analysis crystals were determined to be pseudo-polymorphs of **3b**, namely **3b**·0.5EtOH. For **3b** the unsolvated form was apparently the dominant one, whereas in the case of methoxo and propoxo dinuclear complexes the solvated crystals, **3a**·0.5MeOH and **3c**·0.5PrOH, were favored.

Alkoxo subsitution reactions of the vanadium(V) complexes

Rather poor yields of methoxo and ethoxo dinuclear vanadium(V) complexes led us to attempt to prepare products **3a** and **3b** by substitution of the alkoxo ligand in $[V_2O_3(L_{cycl})_2(OPr)_2]$ (**3c**), obtained in notably higher yields.

The substitution reactions tend to allow a better insight into the properties of the explored systems, and can be valuable in assessing their stability. Therefore, we tested the ability of both mononuclear **1** and dinuclear **3** complexes to undergo replacement of alkoxo ligands (Scheme 3). All substituted derivatives (**1′** or **3′**) were prepared in satisfying yields, simply by dissolving the starting alkoxo complex (**1** or **3**) in appropriate alcohol (R′OH). By following the same routine the substituted derivatives (**1′** or **3′**) could be converted back to their starting alkoxo complexes (**1** or **3**), thus making transformation reversible. The purity of



Scheme 3 R′OH (R = CH_3, C_2H_5, C_3H_7).

all products was confirmed by XRPD analysis, and no mixture was detected (Fig. S2 and S3 in ESI†). This very facile exchange of alkoxo ligands could be utilized as an elegant method for obtaining various alkoxide complexes from a single [VOL(OR)] or similar alkoxo-type precursor.

Crystal structure descriptions

(a) Mononuclear alkoxo [VOL(OR)] complexes 1b and 1c. The molecular structures of [VOL(OEt)] (**1b**) and [VOL(OPr)] (**1c**) are shown in Fig. 1, and the selected geometrical parameters are given in Table S2 in ESI.† The vanadium(v) ions in both structures are pentacoordinated by an oxo oxygen atom, a doubly deprotonated tridentate thiosemicarbazonato ligand and by an alkoxo group in a distorted tetragonal-pyramidal geometry. In both molecules, coordination of the thiosemicarbazonato ligand through the imine nitrogen N(1), sulfur S(1) and deprotonated phenolic oxygen O(2) atoms leads to formation of five- and six-membered rings. The coordination sphere is completed by an oxygen atom O(3) of the alkoxo moiety and an oxo group O(1) in the apical position. The vanadium atoms are shifted by 0.5147(3) Å for **1b**, and by 0.5335(3) Å for **1c** above the basal plane defined by N(1), S(1), O(2), and O(3). The degree of distortion from an ideal tetragonal-pyramidal geometry is indicated by τ value of 0.30 for **1b** and 0.38 for **1c** (Table S2). The thiosemicarbazonato ligand comprises three planar fragments: salicyl [O(2), C(1)–C(6)], central thiosemicarbazonyl [C(7), N(1), N(2), C(8) and N(3)] and phenyl [C(9)–C(14)] part. The salicyl and thiosemicarbazonyl fragments are not completely coplanar, as indicated by the dihedral angles of 13.84(14)° for **1b** and 15.32(14)° for **1c**. Additionally, in **1b** the phenyl part is inclined for 16.18(15)° to the thiosemicarbazonyl part of the ligand, while in **1c** the angle amounts to 10.52(15)°. The bond lengths given in Table S2 and the planarity suggest a certain degree of π delocalization along the thiosemicarbazonyl backbone of the ligand.

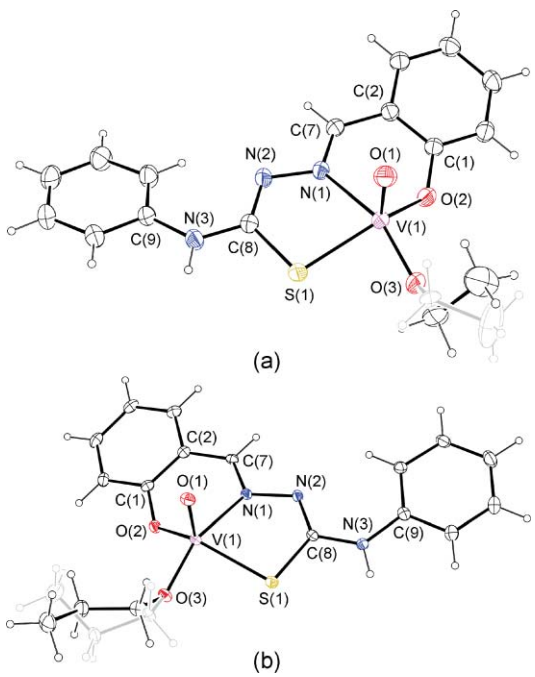


Fig. 1 Molecular structures with the atom-numbering scheme and displacement ellipsoids drawn at a 30% probability level for: (a) [VOL(OEt)] (**1b**) and (b) [VOL(OPr)] (**1c**). The disordered alkoxo groups in the positions with lower occupancies are shown in gray; refined occupancy for the major site of the disordered alkoxo group is 0.715(13) in **1b** and 0.557(5) in **1c**. Full atom-numbering scheme for **1b** and **1c** is given in Fig. S4 in ESI.†

In the crystal of **1b**, the molecules form infinite one-dimensional chains by N(3)–H(3N)···O(1) hydrogen bonds (Table S3 and Fig. S5 in the ESI†). The same kind of architecture is observed in the crystal structure of **1c**, provided over a different array of N(3)–H(3N)···O(2) hydrogen bonds (Table S3 and Figure S6 in the ESI†). Both hydrogen bonds form one-dimensional networks which can be described with a graph set notation C(6).

(b) Dinuclear dialkoxo $[V_2O_3(L_{cycl})_2(OR)_2]$ complexes 3a, 3b and 3c. Hemi-solvates of dinuclear dialkoxo $[V_2O_3(L_{cycl})_2(OR)_2]$ complexes (**3a**·0.5MeOH, **3b**·0.5EtOH, and **3c**·0.5PrOH) as well as the pseudo-polymorph of **3b** with no solvent molecules were analyzed by single-crystal X-ray diffraction (Fig. 2 and Fig. S7 in the ESI†).

All dinuclear dialkoxo complexes **3** have analogous molecular structures: two singly deprotonated molecules of the 1,3,4-thiadiazole derivative (L_{cycl}^-) and two alkoxo groups are bound to the dinuclear $[V_2O_3]^{4+}$ core. Each vanadium(v) atom [V(x); x = 1 or 2] is coordinated by a terminal oxo group O(x1), O(x2) and N(x1) atoms of the same ligand L_{cycl}^-, N(y2) atom (where y = 3 – x) from another anionic ligand L_{cycl}^-, O(x3) atom from an alkoxo group, and the bridging O(4) atom. Altogether, the two V(v) are bridged by an oxo group and two 1,3,4-thiadiazole rings of L_{cycl}^-. The values of equivalent bond lengths and angles of the two halves of dinuclear molecules are very similar (Table S4 in the ESI†): the largest difference in equivalent bond length in the same structure is between the two V(x)–N(y2) bonds in **3a** [0.046(3) Å]. Each V atom is in a highly distorted octahedral environment with the terminal oxygen O(x1) and N(y2) atoms being in the apical positions. The axial V(x)–N(y2) bonds are significantly longer (by ~0.2 Å) than the equatorial V(x)–N(x1) which can be attributed to the *trans*-effect of the terminal oxo group. Also, vanadium atoms are shifted out of the mean basal plane defined by O(x2), O(x3), N(x1), and O(4) towards the terminal oxo group by ~0.3 Å (Table S4). Therefore, the coordination number of each vanadium atom is actually 5+1. Intramolecular N(x3)–H(x3N)···O(y2) hydrogen bonds (Table S5) additionally stabilize the observed molecular geometry of $[V_2O_3(L_{cycl})_2(OR)_2]$. An angle between the planes of two 1,3,4-thiadiazole rings in the same molecule of the complex amounts to ~80° (Table S4 in the ESI†).

As far as we are aware, the only structurally characterized vanadium complex with 1,3,4-thiadiazole ligand is the mononuclear oxovanadium(v) complex $[VOL^1(L^1_{cyclic})]$.[11] In the complex, the 1,3,4-thiadiazole ligand (L^1_{cyclic}) formed by cyclization of *S*-methyl 3-((2-hydroxyphenyl)methyl)dithiocarbazate (H_2L^1), binds in a bidentate fashion utilizing a deprotonated phenolic group and a thiadiazole N atom closer to the phenoxo group. The octahedral coordination around V is realized through the O, N, S atoms of the dianionic, tridentate ligand (L^1). The V–N(thiadiazole) bond [2.342(2) Å] in $[VOL^1(L^1_{cyclic})]$ is *trans* to the terminal oxo group, so it is considerably longer than the corresponding V(x)–N(x1) bonds [2.157(6)–2.1914(17) Å] in $[V_2O_3(L_{cycl})_2(OR)_2]$ complexes. On the other hand, the V–O(phenoxo) bond [1.823(1) Å] in $[VOL^1(L^1_{cyclic})]$ is significantly shorter than the corresponding

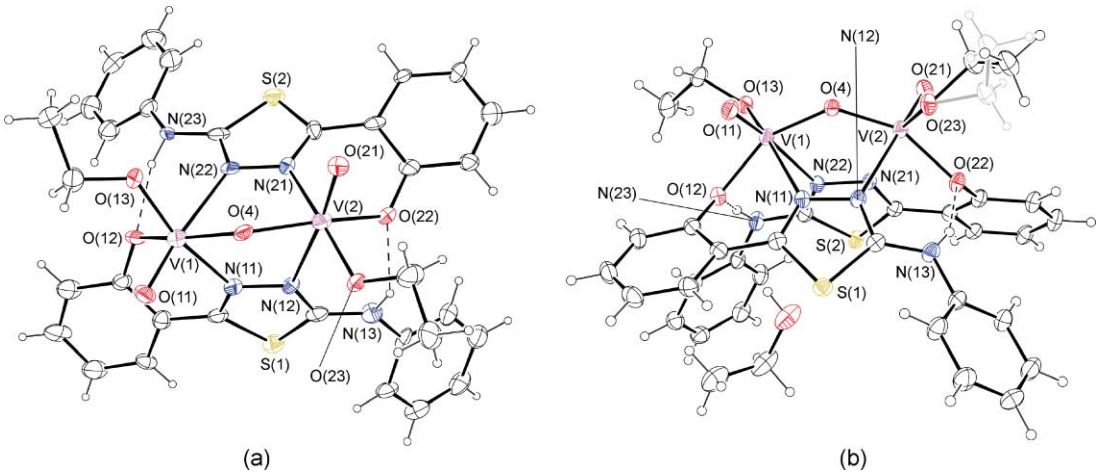


Fig. 2 Crystallographic asymmetric units of (a) **3b** and (b) **3b**·0.5EtOH. Molecules of the dinuclear $[V_2O_3(L_{cycl})_2(OR)_2]$ complex are shown in different relative views. Displacement ellipsoids are drawn at the probability level of 30%. In **3b**·0.5EtOH the disordered ethoxo group in the position with lower occupancy is shown in gray; refined occupancies for the major site is 0.747(6). Hydrogen bonds are denoted by dashed lines. Molecular structures for all dinuclear complexes **3** are presented in Fig. S7 in the ESI†.

V(*x*)–O(*x*2) bonds [1.946(2)–1.9668(17) Å] in $[V_2O_3(L_{cycl})_2(OR)_2]$ complexes, while being more similar to the V–O(alkoxo) bonds [1.7672(15)–1.7900(1) Å].

In the analyzed crystal structures, the $[V_2O_3(L_{cycl})_2(OR)_2]$ molecules are packed by a plethora of $\pi\cdots\pi$ interactions, C–H$\cdots\pi$ and C–H$\cdots$O hydrogen bonds (Tables S6 in the ESI†) thus forming voids at certain crystallographic inversion centers with volumes of 84 Å^3 in **3a**·0.5MeOH, 29 Å^3 in **3b**, 101 Å^3 in **3b**·0.5EtOH, and 125 Å^3 in **3c**·0.5PrOH (Fig. S8–S11 in the ESI†). In the structures of hemi-solvates, each such void is filled with a molecule of the crystallization solvent, which makes only van der Waals interactions with the adjacent molecules, and its orientation is evenly disordered around the crystallographic inversion center. The voids in the crystal structure of **3b** are too small to accommodate an ethanol molecule.

Spectrometric study of reactions in methanolic solutions

The time course of a reaction between H_2L and $[VO(acac)_2]$ in methanol was studied by means of UV-Vis spectrometry.

As already mentioned, in the methanolic solution of $[VO(acac)_2]$, vanadium(IV) undergoes oxidation by molecular oxygen, and the final, stable product is [VO(OH)(OMe)(acac)].[26] In order to simplify the system investigated, we used the $[VO(acac)_2]$ solution sufficiently aged to have a UV spectrum that did not change with time, *i.e.* most of the vanadium was in the V(V) form. Upon mixing of equimolar amounts of reactants ($c = 2.5 \times 10^{-5}$ mol dm^{-3}) in methanol a new band (shoulder) centered at ≈400 nm emerged (Fig. 3a). The time-dependent spectral changes were accompanied by the occurrence of a well-defined isosbestic point at 360 nm, and could be attributed to a rather slow formation of the monomeric complex. This conclusion was supported by a resemblance between the spectrum of the "final" reaction mixture (recorded approximately 18 h after mixing of the reactants) and the sum of Hacac and [VOL(OMe)] spectra (Fig. 3b). It should be noticed that the intersection of the H_2L and [VOL(OMe)] spectra (Fig. 4) lies at a wavelength which corresponds exactly to the position of the above-mentioned isosbestic point.

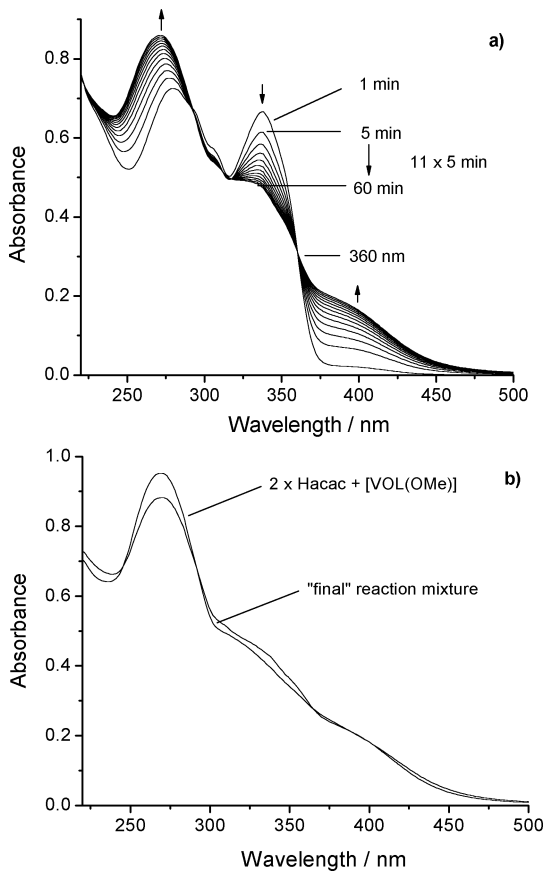


Fig. 3 (a) Time dependence of the UV-Vis absorption spectra of an equimolar solution of H_2L and $[VO(acac)_2]$ ($c = 2.5 \times 10^{-5}$ mol dm^{-3}). Spectra are labeled with the approximate times after mixing of H_2L and $[VO(acac)_2]$. Solvent: methanol; $l = 1$ cm; $\vartheta = 25.0 \pm 0.1$ °C. (b) Comparison of the UV-Vis spectrum of reaction mixture recorded ≈18 h after mixing of the reactants with the sum of Hacac and [VOL(OMe)] spectra.

Comparable results were obtained when the reaction with H_2L was conducted with $[V_2O_4(acac)_2]$ or $VOSO_4$ instead of

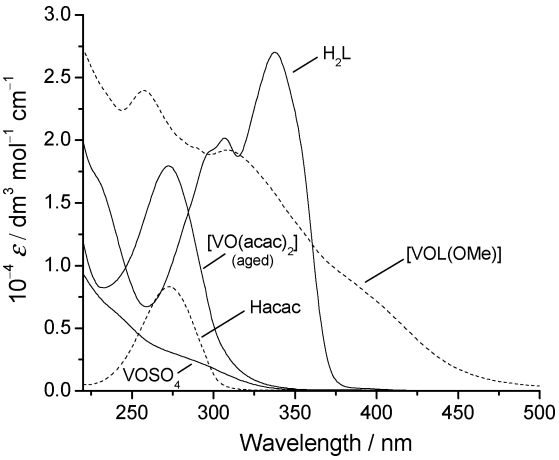


Fig. 4 Molar absorption coefficients of methanol solutions of H_2L, [VO(acac)$_2$] (aged), $VOSO_4$, Hacac, and [VOL(OMe)].

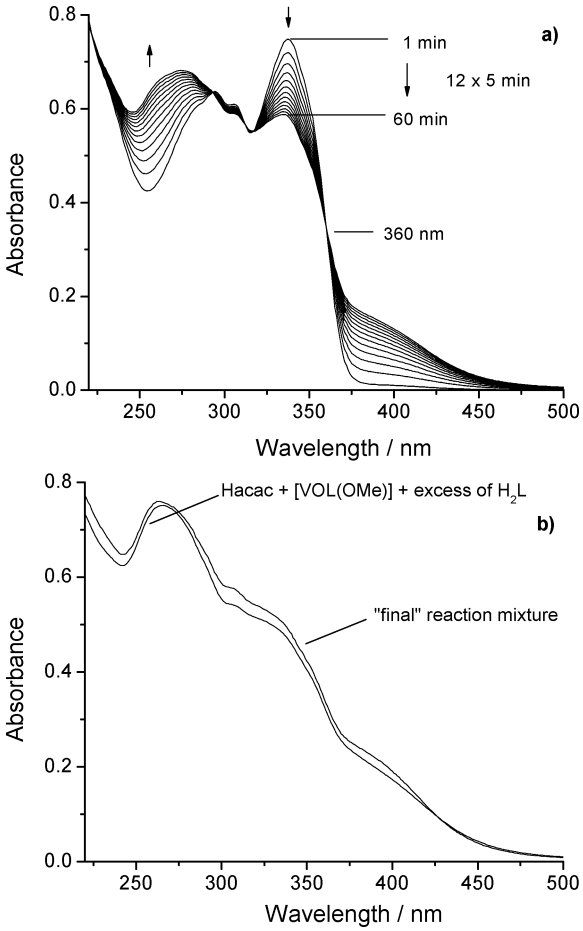


Fig. 5 (a) Time dependence of the UV-Vis absorption spectra of a solution of H_2L ($c = 2.75 \times 10^{-5}$ mol dm^{-3}) and [V_2O_4(acac)$_2$] ($c = 1.19 \times 10^{-5}$ mol dm^{-3}). Spectra are labeled with the approximate times after mixing of H_2L and [V_2O_4(acac)$_2$]. Solvent: methanol; $l = 1$ cm; $\vartheta = 25.0 \pm 0.1$ °C. (b) Comparison of the UV-Vis spectrum of reaction mixture recorded ≈18 h after mixing of the reactants with the sum of Hacac and [VOL(OMe)] spectra (spectral contribution of a stoichometric excess of H_2L is added).

[VO(acac)$_2$]. The spectra recorded after mixing of the reactants were again characterized by a neat isosbestic point located at 360 nm (Fig. 5a and S12a), and the "final" reaction mixture spectrum resembled that of [VOL(OMe)] (Fig. 5b and S12b).

In the above UV-Vis experiments significant spectral changes were observed until approximately 1 h after mixing of the reactants. After that the spectrum of the reaction mixture remained almost unchanged for quite a long time. In order to find out whether any other reaction product besides [VOL(OMe)] could be detected in solution, an analogous experiment was conducted with the 100 times higher initial H_2L and [VO(acac)$_2$] concentrations using 0.01 mm optical cells. The reaction taking place at room temperature was followed for more than three months. As can be seen in Fig. 6, after a rather long time new bands centered at 326 nm, 376 nm, and 394 nm appeared. From comparison with the spectrum of thiazoline compound **2** in methanol (Fig. 7), the appearance of the bands was obviously attributable to the formation of that species. However, to no significant extent could the presence of dinuclear compound **3** (its spectrum is also shown in Fig. 7) be detected under the conditions used. Detailed kinetic investigations are in progress in order to shed more light on the mechanisms of the reactions studied.

The speciation in the methanolic solution of H_2L and [VO(acac)$_2$] over an hour after mixing of the reactants was additionally confirmed by electrospray mass spectrometry. The spectra were collected at different times after mixing of equimolar amounts of reactants ($c = 2.5 \times 10^{-5}$ mol dm^{-3}). The results are summarized in Table 2. As can be seen, in addition to the signals assigned to the H_2L and its monomeric complex with vanadium, the peaks corresponding to dimeric species were also observed. To check the existence of a dimerization equilibrium in the methanolic solution of H_2L, the concentration dependence of its UV spectrum

Table 2 ESMS data for H_2L solution and H_2L + [VO(acac)$_2$] reaction mixture in methanol

				t^a/min		
m/z		Solution		3	30	60
Exp.	Calc.	H_2L	Reaction mixture H_2L + [VO(acac)$_2$]	Relative intensity/%		
272.1	272.1	$[H_2L + H]^+$	$[H_2L + H]^+$	6	<6	<6
294.0	294.1	$[H_2L + Na]^+$	$[H_2L + Na]^+$	100	100	100
368.0	368.0		[VOL(OMe) + H]$^+$	4	16	22
564.8	565.1	$[2H_2L + Na]^+$	$[2H_2L + Na]^+$	38	15	18
639.4	639.1		[VOL(OMe) + H_2L + H]$^+$	21	22	28
660.7	661.1		[VOL(OMe) + H_2L + Na]$^+$	13	41	47

[a] Approximate times after mixing of H_2L and [VO(acac)$_2$].

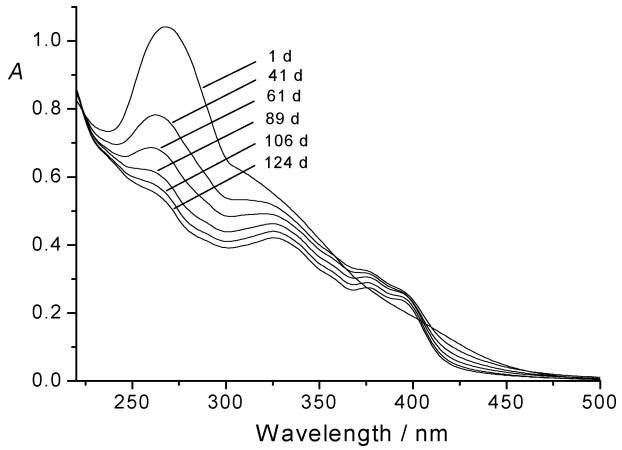


Fig. 6 Time dependence of the UV-Vis absorption spectra of an equimolar solution of H_2L and $[VO(acac)_2]$ ($c = 2.64 \times 10^{-3}$ mol dm^{-3}). Spectra are labeled with the approximate times after mixing of H_2L and $[VO(acac)_2]$. Solvent: methanol; $l = 0.01$ cm; $\vartheta = 25.0 \pm 0.1$ °C.

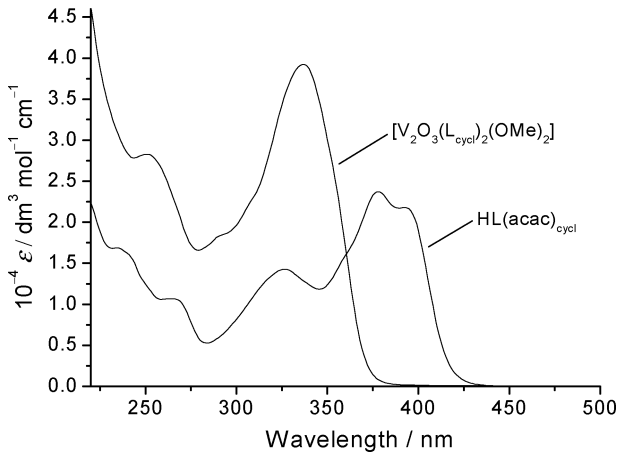


Fig. 7 Molar absorption coefficients of methanol solutions of $HL(acac)_{cycl}$ and $[V_2O_3(L_{cycl})_2(OMe)_2]$.

was measured. It was found that in the concentration range (1×10^{-5}–1×10^{-4}) mol dm^{-3} the recorded spectra obeyed the Beer–Lambert law almost perfectly (Fig. S13 in the ESI†). Accordingly, it could be concluded that a dimer of H_2L was not present in the solutions, and that the dimeric species detected in MS spectra were nonspecific adducts.

Conclusions

New mononuclear thiosemicarbazonato complexes, [VOL(OR)] (**1**), and dinuclear vanadium(v) complexes, $[V_2O_3(L_{cycl})_2(OR)_2]$ (**3**) were synthesized and characterized in the solid state and in the solution. 1,3,4-Thiadiazole anion (L_{cycl}^-) in **3** was formed by oxidative cyclization of the thiosemicarbazone ligand (H_2L). To the best of our knowledge, complexes $[V_2O_3(L_{cycl})_2(OR)_2]$ (**3**) are the first structurally characterized dinuclear vanadium(v) complexes in which a thiadiazole moiety acts as a bridging *ONN* ligand. When acetylacetonato complexes of vanadium(iv) or vanadium(v) were used as precursors, the reaction mixtures also yielded the thiazoline compound $HL(acac)_{cycl}$ (**2**) as a result of a heterocyclization reaction between acetylacetone and thiosemicarbazone. On the basis of all experimental data it was concluded that both cyclization reactions were triggered by the presence of vanadium in the highest oxidation state, which is consistent with the literature data.[8,9] It was also revealed that the two cyclization processes were not mutually reliant. Although the observed facts pointed to a connection between compounds **1** and **3**, we established that the formation of **3** was not exclusively product of conversion of **1**.

The UV-Vis study of reactions of H_2L with $[VO(acac)_2]$, $VOSO_4$, or $[V_2O_4(acac)_2]$ in methanol revealed a relatively slow formation of the mononuclear complex [VOL(OMe)] at 25 °C. When $[VO(acac)_2]$ was used as reactant that was corroborated by ESMS measurements. With sufficiently high reactant concentrations a very slow formation of thiazoline compound $HL(acac)_{cycl}$ could also be observed, whereas the formation of the third expected reaction product, that is dinuclear complex $[V_2O_3(L_{cycl})_2(OMe)_2]$, was not detected. These results were in accordance with the time sequence of precipitation of products in the preparation experiments.

Among various synthetic strategies described in this work the best yields for the [VOL(OR)] complexes were obtained with $[V_2O_4(acac)_2]$ as a precursor. Hence, this seldom used starting material might be reconsidered as a much better alternative for the targeted synthesis of vanadium(v) complexes than the commonly used $[VO(acac)_2]$ or $VOSO_4 \cdot 5H_2O$.

The mononuclear and dinuclear complexes underwent a reversible substitution of the alkoxo ligand when dissolved in appropriate alcohol. An important feature of the substitution reactions is that they can serve as a simple general method for the preparation of various alkoxovanadium complexes from a single [VOL(OR)] type precursor.

Acknowledgements

This research was supported by the Ministry of Science, Education and Sports of the Republic of Croatia (Grants No. 119–1191342–1082, 119–1193079–1084, 119–1191342–2960). We thank Prof. Boris Kamenar and Prof. Dubravka Matković-Čalogović for helpful discussions, Ms Dubravka Šišak for preliminary X-ray crystallographic analyses of crystals of **3b**, as well as Dr Vesna Gabelica and Ms Dubravka Gembarovski for ESMS measurements.

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