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Lipophilic chloro-oxo-bis(hydroxamato)vanadium(V) complexes: synthesis methods and structure

Valeriy I. Dzyuba [a], Lyudmila I. Koval [a,*], Olherd O. Shtokvysh [a], Volodymyr V. Trachevskii [b], Vasyl I. Pekhnyo [a]

[a] V.I. Vernadskii Institute of General and Inorganic Chemistry, Ukrainian National Academy of Sciences, prospect Palladina 32-34, 03680 Kyiv, Ukraine
[b] Technical Centre of NAS of Ukraine, Ukrainian National Academy of Sciences, vul. Pokrovs'ka 13, 04070 Kyiv, Ukraine

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ABSTRACT

New methods for the synthesis of vanadium(V) complexes with hydrophobic alkyl- and aryl-substituted hydroxamic acids as well as hydrophilic ones have been developed. A number of novel coordination compounds of the general formula VOL_2Cl (where HL is *N*-phenylaceto-, *N*-methylbenzo-, *N*-methyldecano- or *N*-methylacetohydroxamic acid) have been synthesized. Complexes of the above formula with alkyl substituents on the ligands have been obtained for the first time. All the compounds obtained have been characterized by UV–Vis, IR, ^1H and ^{51}V NMR spectroscopy. Studies using the ^{51}V NMR method showed the presence of two forms of the complexes in solution, which coalesce with increasing temperature. Chloro-oxo-bis(*N*-methylacetohydroxamato)vanadium(V) has been characterized by X-ray crystallography. The effect of the electron donating properties of the ligand substituents on the structure of the complexes is discussed.

1. Introduction

A series of vanadium(V) complexes with monodentate and polydentate ligands have the ability to catalyze the oxidation of organic substrates, using aqueous H_2O_2 as an oxidant [1–3]. N-substituted hydroxamato complexes of vanadium(V) are used as effective homogeneous catalysts for the selective oxidation of aromatic, heterocyclic, carbocyclic and aliphatic hydrocarbons with hydrogen peroxide. The oxidation process proceeds at moderate temperatures with a high yield of the desired product [4]. The action of the vanadium hydroxamato complexes in biochemical systems has been noted [5]. Vanadium(V) and (IV) complexes containing various organic ligands have been tested for their insulin-mimetic activity, with positive results [6–12]. It is widely accepted that lipophilic compounds have better cellular permeability than hydrophilic ones. A number of vanadyl and vanadate (chloro-oxo) complexes with hydroxamic acids as suitable hydrophobic ligands showed considerable glucose-lowering activity in tests on experimental diabetic mice [13]. The presence of aliphatic substituents on the hydroxamic acids results in their high lipophilicity, both as proligands and for their coordination compounds [14]. Chloro-oxo-bis(hydroxamato)vanadium(V) complexes with alkyl substituents on the coordination fragment are not known as yet, possibly due to the lack of suitable methods for the preparation of these compounds.

The present article describes methods, developed by us, for the synthesis of vanadium(V) complexes with hydroxamic acids containing aliphatic substituents, both at the nitrogen atom and at the carbonyl carbon atoms, taking into account that the developments could be further used in applied chemistry. The following novel coordination compounds have been synthesized and investigated: chloro-oxo-bis(*N*-phenylacetohydroxamato)vanadium(V), $ClOV(N\text{-}PhAH)_2$ (**2**); chloro-oxo-bis(*N*-methylbenzohydroxamato)-vanadium(V), $ClOV(N\text{-}MBH)_2$ (**3**); chloro-oxo-bis(*N*-methyldecanohydroxamato)vanadium(V), $ClOV(N\text{-}MDH)_2$ (**4**); chloro-oxo-bis(*N*-methylacetohydroxamato)vanadium(V), $ClOV(N\text{-}MAH)_2$ (**5**). In addition, the previously described [4] chloro-oxo-bis(*N*-phenylbenzohydroxamato)vanadium(V), $ClOV(N\text{-}PhBH)_2$ (**1**) was also synthesized by our methods (Scheme 1).

2. Experimental

2.1. Materials

Acetonitrile, about 2–10 mm granular calcium chloride (drying agent), chloroform, hexane, molecular sieves (0.3 and 0.4 nm), toluene and triethylamine were obtained from MERCK. *N*-phenyl-

* Corresponding author.
E-mail address: l_koval@ionc.kiev.ua (L.I. Koval).

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benzohydroxamic acid was obtained from ALDRICH. Fluorinated grease Krytox 240AC was obtained from DUPONT. All the chemicals used were of reagent grade. The solvents were purified by distillation. Acetonitrile and chloroform were dried over 0.3 and 0.4 nm molecular sieves, respectively.

Vanadium(V) oxytrichloride, $VOCl_3$, was prepared by substantially modifying a published method [15]. 20.0 g (0.11 mol) of vanadium pentoxide was boiled under reflux (cold finger condenser in a Claisen head) in 22.0 ml (0.30 mol) of thionyl chloride, protected from moisture in the air by granulated calcium chloride, for two hours at 80 °C until the formation of the condensate stopped; then the temperature of the reaction mass was adjusted to 128 °C, and it was boiled for another hour. Water was removed from the finger condenser and the required amount of the product was distilled off at 126–127 °C through a descending Liebig condenser. The ground glass joints were lubricated with fluorinated grease.

The proligands were prepared by published methods: *N*-methyldecanohydroxamic acid (*N*-MDHA) [16]; *N*-methylacetohydroxamic acid (*N*-MAHA), *N*-methylbenzohydroxamic acid (*N*-MBHA) and *N*-phenylacetohydroxamic acid (*N*-PhAHA) [17].

2.2. Synthesis of the copper complexes

The initial copper complexes were obtained by known procedures: bis(N-phenylbenzohydroxamato)copper(II), Cu(*N*-PhBH)$_2$ [18]; bis(N-phenylacetohydroxamato)copper(II), Cu(*N*-PhAH)$_2$, bis(N-methylbenzohydroxamato)copper(II), Cu(*N*-MBH)$_2$ [19].

Bis(*N*-methyldecanohydroxamato)copper(II), Cu(*N*-MDH)$_2$, was prepared by the following procedure. To a solution of 6.0 g (0.03 M) of *N*-methyldecanohydroxamic acid in 100 ml of ethanol, was added dropwise a solution of 3.0 g (0.015 M) of copper acetate monohydrate in 50 ml of water under vigorous stirring. The blue-green reaction mixture was further stirred for 3 h. The precipitated mass was filtered and then washed in the filter with three 10 ml portions of a cooled ethanol–water mixture, taken in a 1/1 ratio, and dried under 12 Pa vacuum at 50 °C to remove the traces of the solvent. The solid precipitate was purified by recrystallization from hexane to obtain blue-grey crystals, which were dried in air to a constant mass. Yield of Cu(N-MDH)$_2$: 6.7 g, 95%. M.p. 84–86 °C. Anal. Found: C, 56.42; H, 9.29; N, 6.01. Calcd for $C_{22}H_{44}N_2O_4$-Cu (MW 464.15): C, 56.93; H, 9.56; N, 6.03%. IR (KBr) ν_{max}/cm^{-1}: 2930 (m), 2849 (m), 1592 (vs, br), 1468 (vs), 1441 (vs), 1222 (m), 1148 (s), 1103 (m), 1062 (w), 1001 (m), 972 (s), 891 (w, br), 817 (m), 804 (s), 729 (w), 712 (m), 680 (s), 594 (s), 532 (m), 503 (w), 485 (m), 471 (m), 453 (w), 402 (m).

2.3. Synthesis of the vanadium complexes

Method 1 (in organic aprotic solvents). To a solution of the proligand (10 mmol) and triethylamine (10 mmol, 1.01 g, 1.4 ml) in dry solvent (100 ml), was added dropwise vanadium(V) oxytrichloride (5 mmol, 0.867 g, 0.47 ml) with vigorous stirring. After the addition, the deep violet colored reaction mixture was stirred for another 3 h. The starting substances were fed and the reaction was carried out with the complete isolation from atmospheric moisture by granular $CaCl_2$. After the termination of the stirring, the $(C_2H_5)_3N{\cdot}HCl$ precipitate that formed was filtered off and washed on a filter with three 10 ml portions of the solvent; the solvent was then evaporated under reduced pressure. The solid deep violet precipitate thus obtained was dried under 12 Pa vacuum at 40 °C to remove any traces of the solvent; the pure complexes were isolated by crystallization and then vacuum drying.

Method 2 (extractive (metal exchange) route). To a suspension of 1.76 g (15 mmol) of ammonium metavanadate in 25 ml of water was added 5 ml of concentrated hydrochloric acid with vigorous stirring, and a homogeneous solution was obtained. This solution was divided into three equal parts. In a 100 ml separatory funnel was put 20 ml of a 2.5 mmol solution of a copper complex in chloroform. To this, the three above portions were added successively to extract the copper completely into the aqueous solution. A violet complex was extracted into the organic phase and this was treated three times with 10 ml portions of water and dried over sodium sulfate. The solvent was then evaporated under reduced pressure. The solid deep violet precipitate was dried under 12 Pa vacuum at 40 °C to remove any traces of the solvent and the pure complexes were isolated by crystallization and then vacuum drying.

Method 3 (in aqueous media). To a suspension of 0.66 g (5.6 mmol) of ammonium metavanadate in 8 ml of water was added 3 ml of concentrated hydrochloric acid with vigorous stirring, and a homogeneous solution was obtained. A solution of 1.0 g (11.2 mmol) of N-MAHA in 5 ml of water was added dropwise the above solution. After the addition, the deep violet colored reaction mixture was stirred for another 3 h and frozen by rotating the flask around its axis over liquid nitrogen; water was removed by freeze drying under 12 Pa vacuum. The pure complexes were isolated by crystallization and then vacuum drying.

2.3.1. Chloro-oxo-bis(N-phenylbenzohydroxamato)vanadium(V) (**1**)

Complex **1** was prepared by method 1, taking *N*-phenylbenzohydroxamic acid (10 mmol, 2.13 g) in dry chloroform as a basis, and purified by crystallization from a chloroform/hexane mixture (1/5) at 5 °C. Yield: 1.95 g, 74%. Anal. Found: C, 59.03; H, 3.91; N, 5.25. Calc. for $C_{26}H_{20}N_2O_5ClV$ (MW 526.85): C, 59.28; H, 3.83; N, 5.32%. UV/Vis $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 530 (4327). IR (KBr) ν_{max}/cm^{-1}: 3073 (w), 1600 (m), 1585 (m), 1549 (s), 1530 (vs), 1490 (vs), 1457 (s), 1442 (s), 1430 (vs), 1380 (vs), 1310 (w), 1285 (w), 1270 (m), 1180 (m), 1160 (m), 1142 (m), 1101 (w), 1070 (m), 1040 (m), 1015 (m), 1000 (w), 970 (vs), 937 (s), 840 (w), 770 (vs), 720 (m), 690 (vs), 665 (s), 642 (s), 612 (m), 580 (s), 558 (s), 495 (m), 455 (m), 422 (m), 400 (w). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 7.52 (m, 5H, N-C_6H_5), 7.42 (m, 5H, C_6H_5). ^{51}V NMR (105.2 MHz, $CDCl_3$, 25 °C, $VOCl_3$), δ, ppm: −285.0, −295.5; (−283.4, −292.0, CH_3CN).

Complex **1** was also prepared by method 2 using Cu(*N*-PhBH)$_2$ (2.5 mmol, 1.22 g) and was purified by crystallization. Yield: 1.00 g, 76%. The compound was identified by comparing the IR spectra of samples prepared by methods 1 and 2, and also to literature data [4].

2.3.2. Chloro-oxo-bis(N-phenylacetohydroxamato)vanadium(V) (2)

Complex **2** was prepared by method 1, taking *N*-phenylacetohydroxamic acid (10 mmol, 1.51 g) in dry chloroform as a basis, and purified by crystallization from a chloroform/hexane mixture (1/5) at 5 °C. Yield: 1.39 g, 69%. Anal. Found: C, 47.23; H, 4.32; N, 6.67. Calc. for $C_{16}H_{16}N_2O_5ClV$ (MW 402.71): C, 47.72; H, 4.01; N, 6.96%. UV/Vis $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 514 (3175). IR (KBr) ν_{max}/cm^{-1}: 3056 (w, br), 2935 (w), 1560 (vs, br), 1458 (vs, br), 1420 (s), 1373 (s), 1312 (w), 1291 (w), 1251 (s), 1166 (w, br), 1086 (m), 1067 (m), 1034 (w), 1005 (vs), 970 (vs), 920 (w), 835 (w, br), 770 (vs), 730 (s), 691 (vs), 644 (s), 596 (m), 551 (s), 526 (vs), 481 (w, br), 449 (m), 416 (w). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 7.47 (m, 5H, N-C_6H_5), 2.33 (s, 3H, CH_3). ^{51}V NMR (105.2 MHz, $CDCl_3$, 25 °C, $VOCl_3$), δ, ppm: −285.7, −303.7; (−280.3, −295.6, CH_3CN).

Complex **2** was also prepared by method 2 using Cu(*N*-PhAH)$_2$ (2.5 mmol, 0.91 g) and was purified by crystallization. Yield: 0.64 g, 64%. The compound was identified by comparing IR spectra of samples prepared by methods 1 and 2.

2.3.3. Chloro-oxo-bis(N-methylbenzohydroxamato)vanadium(V) (3)

Complex **3** was prepared by method 1, taking *N*-methylbenzohydroxamic acid (10 mmol, 1.51 g) in dry chloroform as a basis, and purified by crystallization from a chloroform/hexane mixture (1/8) at 5 °C. Yield: 1.57 g, 78%. Anal. Found: C, 47.31; H, 3.92; N, 6.76. Calc. for $C_{16}H_{16}N_2O_5ClV$ (MW 402.71): C, 47.72; H, 4.01; N, 6.96%. UV/Vis: $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 514 (4072). IR (KBr) ν_{max}/cm^{-1}: 3064 (w), 3030 (w), 2930 (w, br), 1590 (s), 1570 (m), 1540 (m), 1496 (s), 1455 (vs), 1425 (vs), 1380 (s), 1313 (w), 1281 (w), 1229 (s), 1185 (s), 1066 (s), 1023 (m), 1000 (w), 965 (vs), 830 (w, br), 777 (s), 735 (s), 692 (s), 655 (s), 620 (m), 577 (s), 550 (m), 512 (w), 494 (w), 446 (s), 417 (w), 404 (w). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 7.59 (m, 5H, C_6H_5), 3.77 (s, 3H, N-CH_3). ^{51}V NMR (105.2 MHz, $CDCl_3$, 25 °C, $VOCl_3$), δ, ppm: −283.7, −297.3; (−274.7, −288.0, CH_3CN).

Complex **3** was also prepared by method 2 using Cu(*N*-MBH)$_2$ (2.5 mmol, 0.91 g) and was purified by crystallization. Yield: 0.71 g, 71%. The compound was identified by comparing IR spectra of samples prepared by methods 1 and 2.

*2.3.4. Chloro-oxo-bis(N-methyldecanohydroxamato)vanadium(V) (**4**)*

Complex **4** was prepared by method 1, taking *N*-methyldecanohydroxamic acid (10 mmol, 2.01 g) in dry toluene as a basis, and purified by crystallization from a toluene/hexane mixture (1/5) at −12 °C. Yield: 1.81 g, 72%. Anal. Found: C, 52.31; H, 9.02; N, 5.76. Calc. for $C_{22}H_{44}N_2O_5ClV$ (MW 502.99): C, 52.53; H, 8.82; N, 5.57%. UV/Vis $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 514 (3955). IR (KBr) ν_{max}/cm^{-1}: 2935 (m), 2860 (m), 1594 (s), 1560 (m), 1457 (s, br), 1392 (m), 1373 (w), 1330 (w, br), 1212 (m, br), 1144 (m), 1103 (m, br), 1060 (w), 1044 (w), 970 (vs), 810 (m), 772 (w, br), 730 (m br), 685 (w, br), 655 (m), 625 (m), 588 (m), 540 (w), 530 (w), 497 (m), 484 (w), 475 (w), 464 (w), 455 (w), 420 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 3.64 (s, 3H, N-CH_3) 2.42 (m, 2H, b-CH_2), 1.67 (m, 2H, c-CH_2), 1.26 (m, 12H, $(CH2)_6$), 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3). ^{51}V NMR (105.2 MHz, $CDCl_3$, 25 °C, $VOCl_3$), δ, ppm: −282.5, −297.0; (−270.5, −285.5, CH_3CN).

Complex **4** was also prepared by method 2 using Cu(N–MDH)$_2$ (2.5 mmol, 1.16 g) and was purified by crystallization. Yield: 1.02 g, 81%. The compound was identified by comparing IR spectra of samples prepared by methods 1 and 2.

*2.3.5. Chloro-oxo-bis(N-methylacetohydroxamato)vanadium(V) (**5**)*

Complex **5** was prepared by method 1, taking *N*-methylacetohydroxamic acid (10 mmol, 0.89 g) in dry chloroform as a basis, and purified by crystallization from a chloroform/hexane mixture (1/1) at 5 °C. Yield: 0.89 g, 64%. Anal. Found: C, 25.16; H, 4.84; N, 10.65. Calc. for $C_6H_{12}N_2O_5ClV$ (MW 278.55): C, 25.87; H, 4.34; N, 10.05%. UV/Vis $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}): 514 (2075). IR (KBr) ν_{max}/cm^{-1}: 3029 (m), 3010 (m), 2947 (w), 1619 (s), 1556 (s), 1458 (vs), 1444 (vs), 1397 (vs), 1366 (m), 1225 (s), 1208 (s), 1168 (s), 1030 (m), 1009 (m), 994 (m), 965 (vs), 755 (vs), 669 (m), 633 (s), 592 (s), 545 (w), 524 (m), 501 (m), 465 (w), 420 (s). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 3.77 (s, 3H, N-CH_3), 2.43 (s, 3H, CH_3). ^{51}V NMR (105.2 MHz, $CDCl_3$, 25 °C, $VOCl_3$), δ, ppm: − 280.8, − 297.6; (−270.6, −286.8, CH_3CN).

Complex **5** was also prepared by method 3. Yield: 1.01 g, 65%. The compound was identified by comparing IR spectra of samples prepared by methods 1 and 3.

2.4. Physical measurements

The IR spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} on a Specord M80 spectrophotometer and electronic spectra on a Specord M40 spectrophotometer, both of which were equipped with an IBM-compatible operating computing system. The elemental analysis was carried out on a Carlo Erba 1106 analyzer. The ^{1}H and ^{51}V NMR spectra were recorded on a BRUKER AVANCE 400 spectrometer in $CDCl_3$ and CH_3CN solutions with internal TMS and external $VOCl_3$ standards.

2.5. X-ray crystallography

The structure of compound **5** was determined by X-ray crystallography. Suitable deep violet single crystals were formed by crystallization from a chloroform/ hexane mixture, obtained by interdiffusion of solvents through the gaseous state in a closed space. The single crystal X-ray diffraction data collection for the complex was performed on a BRUKER SMART APEX-II CCD diffractometer, using Mo Kα radiation with a graphite monochromator (λ = 0.71073 Å) at 205 K. Reflection intensities were integrated using SAINT software [20] and corrected for absorption by multi-scan absorption corrections using SADABS [21]. The structure was solved by the direct method and refined against F^2 by the full-matrix least-squares method using the SHELXTL package [22]. Positions of the hydrogen atoms were located from electron density difference maps and refined by the "riding" model with U_{iso} = nU_{eq} of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). Crystal data for $C_8H_{14}Cl_7N_2O_5V$ (M = 517.30 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 8.2670 (2) Å, b = 13.8107(4) Å, c = 8.6884(2) Å, α = 90.00°, β = 98.3290 (10)°, γ = 90.00°. V = 981.52(4) Å^3, Z = 2, T = 205 K, μ (MoKα) = 1.477 mm^{-1}, D_{calc} = 1.750 g/cm^3, 23,128 reflections measured (4.74° ≤ 2Θ ≤ 62.76°), 6393 unique (R_{int} = 0.0302, R_{sigma} = 0.0274) which were used in all calculations. The final R_1 value was 0.0332 (>2sigma(I)) and wR_2 was 0.0859 (all data).

3. Results and discussion

3.1. Synthesis

The overwhelming majority of publications dealing with metal and metalloid hydroxamato complexes relate to chemical biology and medicinal chemistry [23]. The pharmaceutical industry remains completely dependent on the development of synthetic chemistry methods for the preparation of compounds for new medicaments [24,25]. One of the key indicators of the possible implementation of synthesis methods in industry is the availability of affordable and high-quality raw materials. Multi-megawatt all-vanadium redox flow battery (VRFB) systems for large-scale energy storage have been demonstrated worldwide. The electrolyte of these huge batteries is an aqueous sulfate solution of high-purity vanadium pentoxide, the intermediate product of which is vanadium oxytrichloride, of appropriate purity [26]. This low-cost, large-tonnage, high-purity product as a precursor opens up broad prospects for the applied chemistry of chloro-oxo-bis(hydroxamato)vanadium(V) complexes. On the other hand, the preparative method for the synthesis of vanadium oxytrichloride from vanadium pentoxide and thionyl chloride [15] turned out to be acceptable after minor modifications. A small stoichiometric excess of V_2O_5 allows the separation of $VOCl_3$ from the reaction mass by simple distillation, without first distilling off the excess $SOCl_2$. The application of fluorinated grease on the ground glass joints allows the reuse of the same reactor. It should be noted that $VOCl_3$ is extremely easily hydrolyzed and, for example, all syntheses with bidentate dicarbonyl proligands were carried out in rigorously dried glassware using freshly dried proligands and solvents [27]. An attempt to adapt the method used to obtain bis(hydroxamato)-dioxo-molybdenum(VI) complexes from MoO_2Cl_2 [16] for the synthesis of chloro-oxo-bis(hydroxamato)vanadium(V) complexes involved considerable difficulties. Vanadium oxytrichloride

exhibits, despite the relatively high boiling point (127 °C), extremely high volatility and it fills the space of the reaction vessels with a gaseous product, even in a weak argon flow; on the contrary, air moisture protection with granulated $CaCl_2$ allows one to carry out all the necessary procedures. The liquid aggregate state of $VOCl_3$ provides its quantitative dropwise addition, without the use of solvents, to the reaction mass by means of a conventional graduated glass pipette connected to a syringe with a heat-shrink tube. All the vanadium complexes presented in this article (**1**–**5**) were synthesized in this way (Eq. (1)).

$$VOCl_3 + 2\,HL \xrightarrow[\text{[dry solvent]}]{+\,2\,NEt_3} VOL_2Cl + 2\,NEt_3 \cdot HCl \quad (1)$$

Another, preparatively convenient method turned out to be an "extraction" method – the synthesis of complexes at a liquid phase boundary [28]. Hydroxamic acids are relatively unstable compounds, so their copper complexes are used for purification and storage [29]. Since complexes **1**–**4** are stable in a strongly acidic medium, they were synthesized from their corresponding copper complexes due to a shift in the reaction equilibrium towards the formation of the VOL_2Cl complexes (Eq. (2)), which are stable in an acidic medium unlike the original CuL_2. By adding concentrated HCl to an NH_4VO_3 suspension in water, a homogeneous, relatively temporally stable, sufficiently concentrated precursor for the above synthesis was obtained. Complexes **2**–**4**, obtained by us using both methods, were identical; additionally, complex **1** is identical to that previously reported [4].

$$NH_4VO_3 + CuL_2 \xrightarrow[\text{[}H_2O/CHCl_3\text{]}]{+4HCl} VOL_2Cl + NH_4Cl + CuCl_2 + 2\,H_2O \quad (2)$$

However, the above technique does not pertain to the chloro-oxo-bis(*N*-methyl-acetohydroxamato)vanadium(V) complex (**5**), since like the original proligand, it is soluble in water, so the synthesis as per Eq. (3) was carried out. Complex **5**, in a two-phase water-chloroform system, is distributed in the aqueous phase and therefore was separated from the frozen aqueous solution by freeze drying.

$$NH_4VO_3 + 2\,HL \xrightarrow[\text{[}H_2O\text{]}]{+2\,HCl} VOL_2Cl + NH_4Cl + 2H_2O \quad (3)$$

It turned out to be identical to complex **5** obtained from $VOCl_3$ by the earlier method.

3.2. Spectral analysis

The IR spectral data of the compounds under investigation corroborate the complex formation. The vibrations of the C—O groups bonded to the metal manifest themselves in the lower-frequency spectral region in comparison to the stretching vibration frequencies of the C=O groups of free hydroxamic acid (1660–1600 cm^{-1}). Additionally, intense characteristic vibrational bands of the ν (V=O) group in the range of 980–950 cm^{-1} are observed in the spectra of the complexes, like those of complex **1** [4]. The preparation of identical compounds by two alternative synthesis methods is one of the proofs of their chemical structure.

Complexes **2**–**5** have an intense dark purple color. The UV–Vis spectra of their solutions in chloroform have λ max, as well as values of the molar extinction ε, similar to those of complex **1** [4].

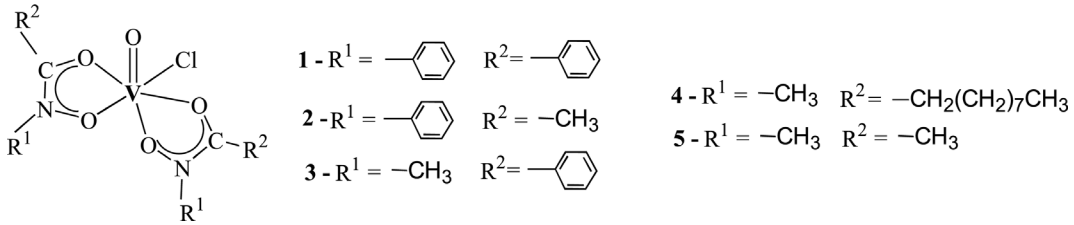
The chemical shifts and integral intensities of the signals in the ^1H NMR spectra of complexes **1**–**5** corroborate the above chemical structure (Scheme 1). The absence of broadening of the NMR signals indicates the valence of the central atom –V(V), as well as the absence of any paramagnetic impurity from copper(II) complexes in the desired reaction products from the "extraction" method. The presence of an additional signal (in the form of a shoulder or a neighboring peak (Δ δ < 18 ppm)) in the ^{51}V NMR spectra of complexes **1**–**5** can be explained by the presence of two different forms: with near and distant arrangements of identical fragments of chelate rings in the molecules. The presence of the aforementioned shoulder was shown earlier for complex **1** [30]. The rise (not above 325 K) of the temperature of solutions leads to a rapid, on the timescale of NMR, exchange process and with the merging of the signals of these species (Fig. 1).

The presence of aryl substituents on the hydroxamate fragment of a molecule of the complex noticeably shifts the ^{51}V NMR signal to the strong field region, especially for the complexes with aryl substituents at the nitrogen atom, which indicates a noticeable flow of electron density from the ligand to the central atom with the participation of the free electron pair of the nitrogen atom. The shape of the ^{51}V NMR spectra of complexes **1**–**5** in acetonitrile (a much more polar solvent than chloroform) remains similar to that for solutions in chloroform. At a tenfold dilution of the acetonitrile solutions, the shape of the ^{51}V NMR spectra do not change. This excludes the interpretation of several closely spaced ^{51}V NMR signals as a manifestation of different degrees of association of the complexes in solution.

3.3. Structure of chloro-oxo-bis(*N*-methylacetohydroxamato)vanadium(V) (*5*)

According to the data of the X-ray structural analysis, each metal complex molecule in the crystal co-crystallizes with two chloroform molecules. The coordination polyhedron of the central vanadium atom has the geometry of a distorted octahedron. The vanadium atom is surrounded by four oxygen atoms of chelating hydroxamate ligands, an oxygen atom of the oxo group and a chlorine atom (Fig. 2). A disordering of the ClVO fragment at two positions, A and B with occupancies of 34 and 66%, respectively, is observed. At both positions, solely the carbonyl oxygen atoms of ligands, O2 and O4, are *trans* disposed to the oxo group and chlorine atom (Fig. 3).

The lengths of the V=O bonds in the coordination polyhedron vary over the ranges 1.885(2)–2.239(2) Å (for the chelate oxygen atom) and 1.575(4)–1.581(5) Å (for the oxo group) and those of V-Cl bonds over the range 2.287(3)–2.293(2) Å. The values of the valence angles O-V-Cl and O-V-O in the coordination polyhedron vary over the range 71.76(10)–100.48(9)° (Table 1).



Scheme 1. Chemical structure of the studied complexes.

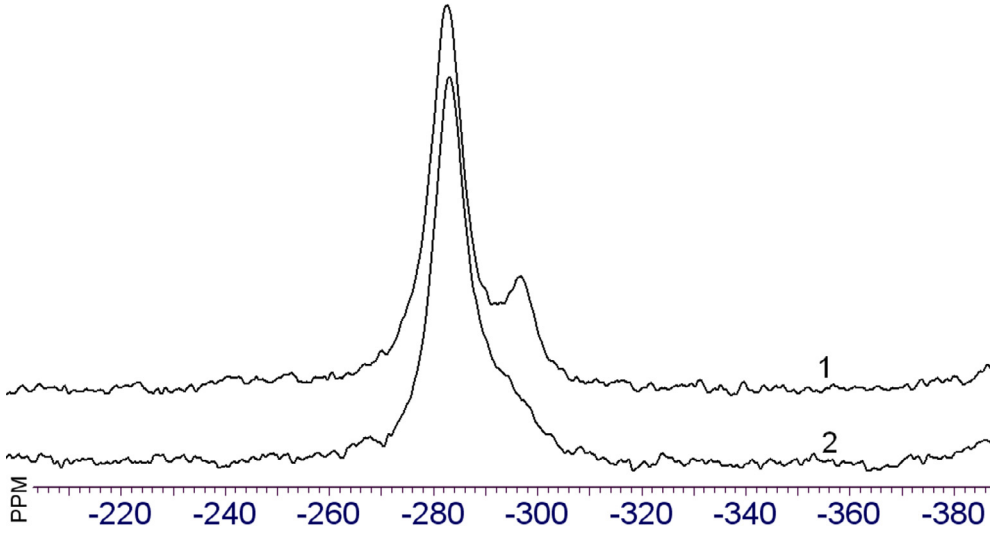


Fig. 1. ^{51}V NMR spectra of complex **4** at 298 and 318 K.

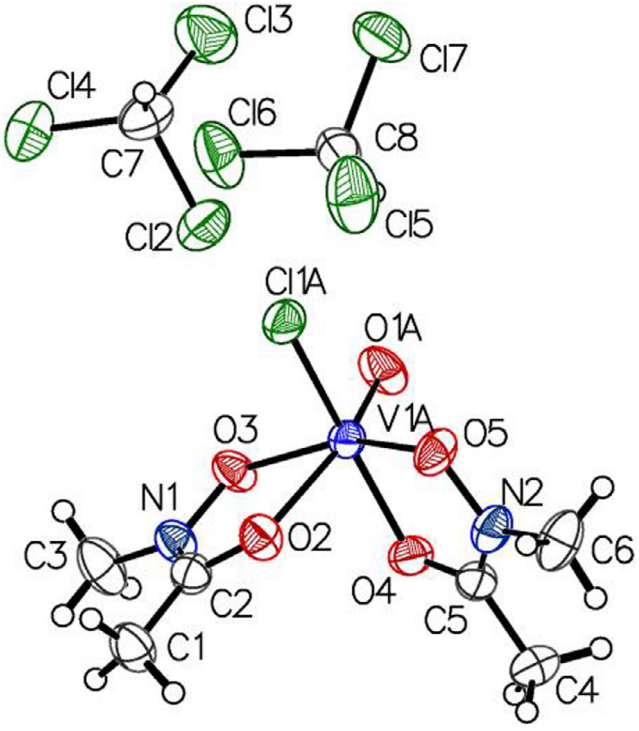


Fig. 2. Molecular structure of complex **5**.

Table 1
Selected bond lengths (Å) and angles (deg) for **5**.

	Position A	Position B
V1-O1	1.581(5)	1.575(4)
V1-Cl1	2.287(3)	2.2928(19)
V1-O2	2.239(2)	1.9346(17)
V1-O3	1.917(3)	1.925(2)
V1-O4	1.949(2)	2.2022(17)
V1-O5	1.923(3)	1.885(2)
O1-V1-Cl1	94.4(6)	97.1(2)
O1-V1-O2	164.7(5)	98.7(2)
O1-V1-O3	93.1(5)	109.3(2)
O1-V1-O4	100.8(5)	165.2(2)
O1-V1-O5	112.6(5)	91.5(2)
O2-V1-Cl1	85.84(13)	159.32(10)
O3-V1-Cl1	97.66(14)	83.41(8)
O3-V1-O2	71.76(10)	78.79(8)
O3-V1-O4	93.23(13)	85.53(8)
O3-V1-O5	154.04(13)	158.31(9)
O4-V1-Cl1	160.74(18)	84.35(7)
O4-V1-O2	82.55(10)	83.87(8)
O5-V1-Cl1	84.25(14)	100.48(9)
O5-V1-O2	82.62(10)	92.44(9)
O5-V1-O4	79.07(12)	73.74(7)

Table 2
Halogen bonds for **5**.

R-Hal. . .A	d(R-Hal), Å	d(Hal-A), Å	<(R-Hal-A), deg
C7-Cl2. . .O2#1	1.746(2)	2.973	172.43
C8-Cl7. . .O4#2	1.743(2)	3.062	163.83

#1 2 − x, 1/2 + y, 2 − z #2 −1 + x, y, −1 + z.

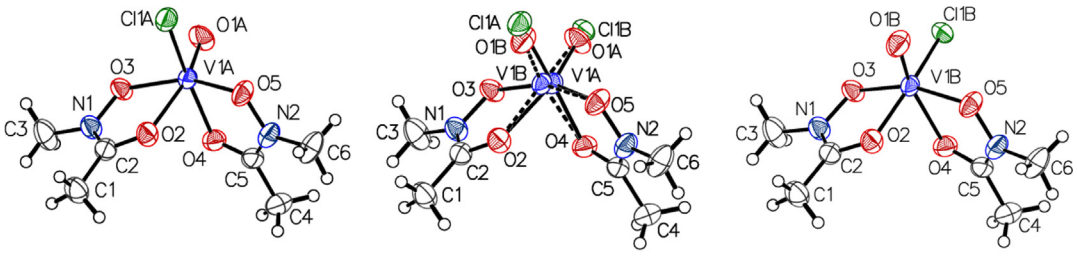


Fig. 3. Model of the disorder in the crystal structure of **5** (chloroform molecules are omited for clarity).

Table 3
Selected short contacts for **5**.

Atom1	Atom2	Symm. op. Atom2	Length, Å	Sum. of VdW, Å [31]	Length-VdW, Å
O1A	H7	x, −1 + y, z	2.643	2.72	−0.077
O4	H7	x, −1 + y, z	2.580	2.72	−0.140
Cl1A	Cl3	1 − x, −1/2 + y, 1 − z	3.291	3.50	−0.209
Cl1A	Cl4	1 − x, −1/2 + y, 2 − z	3.194	3.50	−0.306
C2	Cl4	1 − x, −1/2 + y, 2 − z	3.344	3.45	−0.106
H1A	Cl2	2 − x, −1/2 + y, 2 − z	2.896	2.95	−0.054
H4C	Cl5	1 + x, y, z	2.904	2.95	−0.046
C2	Cl7	1 + x, y, 1 + z	3.411	3.45	−0.039
Cl1A	H8	1 − x, 1/2 + y, 1 − z	2.675	2.95	−0.275
O5	H8	1 − x, 1/2 + y, 1 − z	2.336	2.72	−0.384

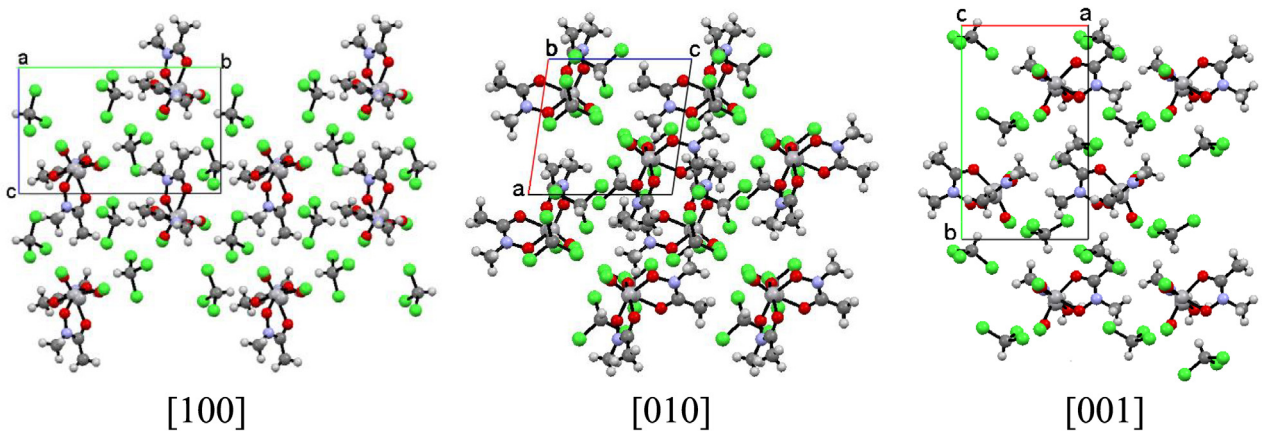


Fig. 4. Crystal structure of complex **5**.

In the crystal, the metal complex molecules are bonded to the chloroform molecules through intermolecular halogen bonds (Table 2), and the formation of a large number of short contacts is observed (Table 3). In this case, a three-dimensional molecular network is formed in the crystal (Fig. 4).

4. Conclusion

In this work, new methods for the synthesis of complexes of vanadium(V) with hydrophobic alkyl- and aryl-substituted hydroxamic acids as well as hydrophilic ones have been developed. Four novel coordination compounds of the general formula VOL_2Cl (where HL is *N*-phenylaceto-, *N*-methylbenzo-, *N*-methyldecano- and *N*-methylacetohydroxamic acids) have been successfully synthesized. The counter synthesis of the above compounds confirmed the declared chemical structure. Chloro-oxo-bis(*N*-methylacetohydroxamato)vanadium(V) has been characterized by X-ray crystallography, which also confirmed the chemical structure presented in this article. Complexes of this type with alkyl substituents on the ligands have been obtained for the first time. Using the ^{51}V NMR method, the presence of two forms of the complexes in solution, which coalesce with increasing temperature, has been shown.

Vanadium oxytrichloride, as a precursor, has a certain universality: it is suitable for the synthesis of both lipophilic and hydrophilic VOL_2Cl complexes with a high yield of the target products. Large-tonnage production of high-purity $VOCl_3$ opens prospects for the reproduction of the developed method on an industrial scale.

Conflicts of interest

There are no conflicts of interest to declare.

CRediT authorship contribution statement

Valeriy I. Dzyuba: Conceptualization, Methodology, Investigation, Writing - original draft. **Lyudmila I. Koval:** Conceptualization, Methodology, Investigation, Data curation, Writing - review & editing, Visualization. **Olherd O. Shtokvysh:** Methodology, Investigation, Visualization, Software. **Volodymyr V. Trachevskii:** Methodology, Investigation. **Vasyl I. Pekhnyo:** Supervision, Validation.

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Appendix A. Supplementary data

CCDC 1920450 contains the supplementary crystallographic data for complex **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114421.

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