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A dimeric oxidovanadium(V) complex derived from a hydrazonate ligand with an unusual asymmetrically bridged μ-(oxido)μ-(H2O){oxidovanadium(V)}2 core

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KEYWORDS

ABSTRACT

The binuclear oxidovanadium(V) complex [{VO(L)}$_2$(μ-O)(μ-H$_2$O)]·2CH$_3$CN (1), where L^{2-} is the dianion of the Schiff base 2-salicylaldehyde-2-hydroxybenzoylhydrazone, were prepared and characterized by elemental analysis, FTIR, ^{1}H, ^{13}C and ^{51}V NMR. Furthermore, the crystal structure of the compound 1 was determined by single crystal X-ray diffractometry revealing a distorted octahedral O$_5$N-coordination geometry around the V(V) acceptor centers. The vanadium ions are connected by the μ-O^{2-} and the μ-H$_2$O asymmetric bridges located in the edge between the two octahedrons which keeps a distance of 3.194 Å between the two vanadium centers. Crystal data for C$_{32}$H$_{28}$N$_6$O$_{10}$V$_2$ (*M* =758.48 g/mol): orthorhombic, space group *P*2$_1$2$_1$2$_1$ (no. 19), *a* = 12.9655(8) Å, *b* = 14.1902(9) Å, *c* = 18.4379(10) Å, *V* = 3392.3(4) Å^3, *Z* = 4, *T* = 293(2) K, μ(MoKα) = 0.616 mm^{-1}, *Dcalc* = 1.485 g/cm^3, 18803 reflections measured (3.622° ≤ 2Θ ≤ 56.704°), 8263 unique (R_{int} = 0.0473, R$_{sigma}$ = 0.1020) which were used in all calculations. The final R_1 was 0.0509 (I > 2σ(I)) and wR_2 was 0.1531 (all data). The (VO)$_2$(μ-O)(μ-H$_2$O) core in compound 1 represents a rare case and few examples of similar type have been structurally characterized.

1. Introduction

The coordination chemistry of vanadium with has received special attention recently due to its catalytic [1-8] and medicinal importance [9-16]. Further, vanadium(V) complexes with a mixed *ON* coordination sphere is of high interest because of the potential of these complexes as structural and/or functional models for vanadate-dependent halo-peroxidases [8,9,17,18]. On the other hand, hydrazones are one of the most important pharmacophoric cores of several antitumor [9], anti-inflammatory [19] and antibacterial [21,22] agents.

Few oxidovanadium(V) complexes of the type μ-(oxido)*bis*{oxidovanadium(V)} with dianionic hydrazonate ligands had their structure determined by X-ray diffraction methods [8,23-26]. In addition, much less is known about complexes of the type μ-*bis*(oxido)*bis*{oxidovanadium(V)}, which are generally acetylpyridine derivatives with V=O units in *trans* configurations [19,27]. For the μ-(oxido)*bis*{oxidovanadium(V)}

complexes the angle V–O–V were found to be in the range 101-112°, while for the μ-*bis*(oxido)*bis*{oxidovanadium(V)} complexes this angle is of 101.78 ° and 102.41 ° for the hydrazones derived from of 2-acetylpyridine and nicotinic acid hydrazide [19] and 2-furoic acid hydrazide [27], respectively.

Mononuclear oxidoalkoxidovanadium(V) complexes and monoanionic dioxidovanadium(V) complexes derived from H$_2$L are already known, as well as 4,4'-bipyridine-bridged binuclear oxidovanadium(V) complexes [17]. We now report the syntheses and structural characterization of a neutral complex with an asymmetrically bridged μ-(oxido)μ-(H$_2$O){oxidovanadium(V)}$_2$ core, where different characteristics from those observed for similar structures reported in the literature.

2. Experimental

2.1. Materials and physical methods

Table 1. X-ray structure data collection and refinement parameters for the complex [{VO(L)}$_2$(µ-O)(µ-H$_2$O)]·2CH$_3$CN (**1**).

Parameters	Compound 1
Empirical formula	$C_{32}H_{28}N_6O_{10}V_2$
Formula weight	758.48
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, (Å)	12.9655(8)
b, (Å)	14.1902(9)
c, (Å)	18.4379(10)
Volume (Å^3)	3392.3(4)
Z	4
ρ_{calc} (Mg·m^{-3})	1.476
µ (mm^{-1})	0.613
θ Range for data collection (°)	1.81 to 28.35
Index ranges	$-17 \le h \le 16$
	$-18 \le k \le 17$
	$-16 \le l \le 24$
Reflections collected	18803
Reflections unique/ R$_{int}$	8263 / 0.0473
Data/restraints/param.	8263 / 0 / 453
Absorption correction	Semi-empirical from equivalents
Max/min. transmission	1.000 and 0.557
R$_1$ [$I > 2\sigma(I)$]	0.0509
wR$_2$ [$I > 2\sigma(I)$]	0.1168
GOF on F^2, S	0.935

[VO(acac)$_2$] and analytical reagents grade chemicals and solvents were obtained commercially and used without further purification. IR spectra were recorded as KBr pellets on a Shimadzu FTIR-spectrometer in the 4000-400 cm^{-1} region. Melting points were measured on a Melt-Temp II apparatus. ^{1}H, ^{13}C and ^{51}V NMR spectra were acquired on a Varian MERCURY plus spectrometer operating at 300.07, 75.46 and 78.92 MHz for ^{1}H and ^{51}V, respectively. The ^{1}H spectra were internally referenced to TMS. The ^{51}V spectra was externally referenced to VOCl$_3$ (δ = 0), checked against an aqueous (NH$_4$)VO$_3$ solution containing capillary (δ = -541.2 for VO$_4^{3-}$). Elemental analyses (CHNS) were determined with FISONS EA-1108 analyzer.

2.2. Synthesis

2.2.1. Synthesis of the ligand H$_2$L

The Schiff base compound was prepared by an adaption of the method previously described [28]. 5 mmol (0.76 g) of 2-hydroxydebenzoylhydrazide and 5 mmol of salicylaldehyde (0.68 g) were refluxed methanol (15 mL) for 2 hours.

2-Hydroxy-N'-(2-hydroxybenzylidene)benzohydrazide (H$_2$L): Color: White. Yield: 80 % (1.02 g). M.p.: 170-172 °C. FT-IR (KBr, ν, cm^{-1}): 3200 ν(OH); 3075 ν(NH); 1661 ν(C=O); 1637, 1618, 1560 ν(C=C + C=N); 1231 ν(C–O); 1034 ν(N–N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 6.94-7.01 (m, 4H, C$_6$H$_4$), 7.33 (ddd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.46 (ddd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.58 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.90 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 8.69 (s, 1H, -CH=N), 11.22 (s, 1H, NH), 11.76 (s, 1H, OH), 12.02 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 115.6, 116.4, 117.2, 118.5, 119.0, 119.3, 128.5, 129.4, 131.6, 133.9, 148.9, 157.4, 158.9, 164.4.

2.2.2. Preparation of [{VO(L)}$_2$(µ-O)(µ-H$_2$O)]·2CH$_3$CN (1)

To a hot solution of H$_2$L (0.064 g, 0.25 mmol) in acetonitrile (10 mL) was added a solution of [VO(acac)$_2$] (0.066 g, 0.25 mmol) in acetonitrile (10 mL). A dark solution was immediately formed. The reaction mixture was kept under constant stirring for 2 hours and then deposited at –15 °C for one day for obtaining dark crystals of compound **1**. The dark crystals were filtered off and dried in air. Some crystals, suitable for diffraction analysis, were kept in the solution.

µ-Oxido-µ-aqua-bis(((1Z, N'E)-2-hydroxy-N'-(2-oxidobenzylidene)benzohydrazonate)oxidovanadium(V)) diacetonitrile solvate (**1**): Yield: 55 % (0.104 g). The substance suffers a continuous darkening without melting up to 300 °C. FT-IR (KBr, ν, cm^{-1}): 1621, 1597, 1550, 1523 ν(C=C + C=N), 1270, 1250 ν(C–O, phenolate and enolate), 997 ν(V=O), 909 ν(V–O–V). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 6.60-7.40 (m, 8H, C$_6$H$_4$), 7.75-7.82 (m, 8H, C$_6$H$_4$), 9.19 (s, 1H, CH), 9.07 (s, 1H, CH), 11.35 (s, 2H, OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 113.7; 115.5; 116.7; 119.1; 119.9; 120.6; 129.2; 133.0; 133.6; 134.6; 152.1; 158.3; 163.3; 170.3. ^{51}V NMR (79 MHz, DMSO-d_6, δ, ppm): -542.9 (25.7 %), -575.1 (74.3 %). Anal. calcd. for C$_{32}$H$_{28}$N$_6$O$_{10}$V$_2$: C, 50.67; H, 3.72; N, 11.08. Found: C, 50.66; H, 3.49; N, 10.86%.
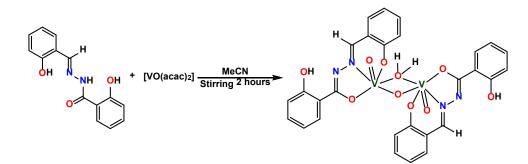
2.3. Crystal structure determination

Dark crystals of the complex **1** were obtained as described above. The data collections were performed with Mo-Kα radiation (λ = 71.073 pm) on a Bruker KAPPA APEX II CCD diffractometer. The structure was solved by direct methods using SHELXS-97 [29] and refined by full-matrix least-squares methods against F^2 (SHELXL2016) [30]. All non-hydrogen atoms were refined with anisotropic displacement parameters with SHELXL2016 [30]. The hydrogen atoms positions were found in Fourier map or calculated in the idealized positions. Crystallographic data and experimental details for structural analysis are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The complex **1** was obtained in satisfactory yield from 1:1 reaction mixtures of [VO(acac)$_2$] and the free H$_2$L hydrazone ligand (Scheme 1) by a similar procedure to that described in reference [17]. Microanalyses and spectroscopic results are consistent with the formation of the complex **1**.

The FTIR spectroscopy provides some information about the coordination modes of the H$_2$L to the vanadium central atoms. The spectrum of the complex **1** does not present the bands at 3200 cm^{-1} [ν(NH)] and 1661 cm^{-1} [ν(C=O)], observed in the spectrum of the free ligand. The absence of these bands in the spectrum of the complex is consistent with the enolisation of the amide functional group and subsequent proton replacement by the metal ion. A new band appearing at 1251 cm^{-1} is assigned to the ν(C–O)(enolic) mode [19, 23, 31].
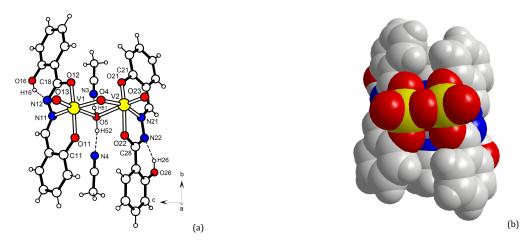
Scheme 1. Synthesis of the complex **1**.

Figure 1. Crystal and molecular structure of [{VO(L)}$_2$(μ-O)(μ-H$_2$O)]·2CH$_3$CN (**1**) with labeling scheme (a). Space filling of the dinuclear oxidovanadium(V) hydrazonate complex (b).

The bands related to the ν(C=N) and ν(C=C) stretching modes are found shifted in comparison to the spectrum of the free ligand. One strong band observed at 997 cm^{-1} is attributed to the terminal ν(V=O) stretching. Another band moderately strong observed at 909 cm^{-1}, asymmetric bridge ν(V–O–V) vibrations.

The coordination modes of the ligand were further confirmed by recording ^{1}H and ^{13}C NMR spectra of the ligand and complex in DMSO-d_6 solutions. The free H$_2$L ligand exhibit a signal at δ 11.22 ppm due to the NH proton of the hydrazone moiety. The absence of this signal in the spectrum of complex **1** suggests the deprotonation of the ligand upon coordination, enolisation of the of the amide functional group as observed in the FTIR spectrum. Similarly, the absence of the signal for the phenolic OH (*ca.* δ 12.02 ppm in the ligand) indicates coordination of phenolate oxygen. The signals due to the azomethine protons (–CH=N), are downfield shifted to the δ 9.01-9.25 ppm region with respect to the signal of the free ligand, observed at δ 8.69 ppm, which confirms the coordination of the azomethine nitrogen. The aromatic protons of the ligand as well as complex appear within the expected range, but in the spectrum of the complex the signals are overloaded by each other, making attributions difficult.

The ^{13}C NMR spectra of both ligand and complex present all expected signals. There are both downfield and upfield shifts by comparing the spectrum of the complex in relation to the spectrum of the free ligand. Assignments of the peaks are based on the chemical shift and intensity patterns. Large displacements observed for carbon atoms in the vicinity of the phenolate (δ$_{ligand/complex}$ = 148.9/152.1), azomethine (δ$_{ligand/complex}$ = 158.9/163.3) and enolate (δ$_{ligand/complex}$ = 164.4/170.3) groups suggest their involvement in coordination.

The appearance of two signals at δ -542.9 and -575.1 ppm for complex **1** in the spectrum of ^{51}V NMR, approximately in the ratio of 3:1, indicates the presence of two species. The major signal (δ -575.1 ppm) is assigned to complex **1**. The nature of the minor, down-field signal is proposed to be from the corresponding square pyramidal dimeric complex without the water and acetonitrile molecules.

3.2. Structure description

A single crystal of complex **1**, obtained from a CH$_3$CN solution, was analyzed by X-ray diffraction methods. The structure of the dimeric oxidovanadium complex with atomic labels as well as a space filling model representation are depicted in Figure 1. Selected bond lengths and angles for complex **1** are shown in Table 2.

The L^{2-} ligand coordinates in *O,N,O*-tridentate mode forming one five- and one six-membered chelate ring around each V(V) center. The two vanadium centers are not equivalent in relation to the V–O–V bridges, which are slightly asymmetric in relation to the μ-O^{2-} bridge, but considerably asymmetric for the μ-H$_2$O bridge (see Figure 2) and there are significant metric differences for the bonding parameters in the two parts of the molecule (see the caption to Figure 1). The interatomic distances for the terminal vanadyl groups, V(1)–O(13) and V(2)–O(23), correspond to double bonds, being in the normal bond length range [19,23-25,27]. It is to note that the V–O bond involving the phenolate oxygen, V(1)–O(11)/V(2)–O(21) 1.818(3)/1.824(3) Å, is shorter than the corresponding bond involving the enolate oxygen atom, V(1)–O(12)/V(2)–O(22) 1.934(3)/1.922(3) Å, showing the greater ability of the first to act as donor to the vanadium center.

Table 2. Selected bond lengths (Å) and angles (°) refined from X-ray data and calculated for [{VO(L)}$_2$(μ-O)(μ-H$_2$O)]·2CH$_3$CN (**1**).

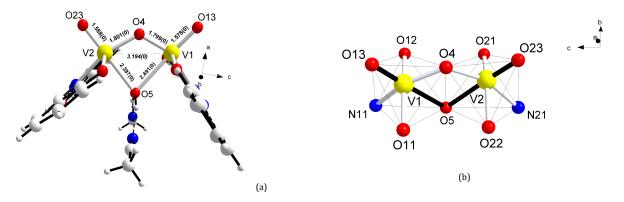|			
V(1)-O(10)	1.578(3)	V(2)-O(20)	1.588(3)
V(1)-O(30)	1.799(3)	V(2)-O(30)	1.801(3)
V(1)-O(1)	1.818(3)	V(2)-O(4)	1.824(3)
V(1)-O(2)	1.934(3)	V(2)-O(40)	2.397(3)
V(1)-O(40)	2.491(3)	V(2)-O(5)	1.922(3)
V(1)-N(1)	2.095(4)	V(2)-N(3)	2.104(3)
O(30)-V(1)-O(40)	75.33(11)	O(20)-V(2)-O(4)	101.68(16)
O(30)-V(1)-O(10)	106.74(14)	O(20)-V(2)-O(30)	103.35(14)
O(10)-V(1)-O(40)	174.40(15)	O(20)-V(2)-O(40)	177.93(14)
O(30)-V(1)-O(2)	92.42(14)	O(5)-V(2)-N(3)	74.25(13)
O(10)-V(1)-O(2)	96.76(16)	O(40)-V(2)-N(3)	82.91(11)
O(40)-V(1)-N(1)	78.07(12)	O(20)-V(2)-N(3)	95.64(14)
O(10)-V(1)-N(1)	99.09(14)	O(4)-V(2)-O(5)	150.52(13)
O(2)-V(1)-N(1)	74.61(14)	O(20)-V(2)-O(5)	99.52(15)
V(1)-O(40)-V(2)	81.59(9)	V(1)-O(30)-V(2)	125.09(15)

Figure 2. Perspective view from the direction [010] with the principal bond distances (Å) on left and of the environment around the two vanadium centers forming the coordination polyhedrons connected by one edge on the right.

The distances from the vanadium centers to the oxygen of the μ-O bridge, V(1)–O(12) and V(2)–O(22), are considerably shorter than the distances to the oxygen of the μ-H$_2$O bridge, V(1)–O(13) and V(2)–O(23), indicating a *trans* effect caused by the vanadyl groups (see Figure 2). The angles between the two vanadium atoms (*i.e.* the angles formed by the vanadium atoms and the bridges), V(1)–O(4)–V(2) and V(1)–O(5)–V(2), differ significantly, with values of 125.09(15) and 81.59(9)°, respectively. The value of 125.09(15)° for the V–(μ-O)–V is intermediate among the observed for similar compounds, 112.06° [19], 151.5° [20], 102.41(4)° [22] and 101.78° [27]. Each vanadium center is six-coordinated, with the axial angles O(13)–V(1)–O(5)/O(23)–V(2)–O(5), forming the almost linear axis, with values of 174.40(15)° and 177.93(14)°, respectively. The vanadium centers are almost in the same plane spanned by the *O,N,O*-tridentate ligands and the μ-O bridging oxygen, 0.301 Å and 0.272 Å toward de oxido ligands for V(1) and V(2), respectively. The V–V distance [3.194(0) Å] is higher than those of other reported complexes [23,32]. The environments around the two vanadium atoms may be considered as two octahedrons attached by one edge, formed by the μ-O^{2-} and the μ-H$_2$O bridges (see Figure 2).

The compound is stabilized by two molecules of aceto-nitrile. The acetonitrile molecules are in H-bonding contact with the hydrogen atoms from the μ-(H$_2$O) bridge: O(5)–H(52)···N(4) [O(5)···N(4) = 280.3(6) pm, O(5)–H(52)···N(4) = 171.4°] and O(5)–H(51)···N(3) [O(5)···N(3) = 281.7(6) pm, O(5)–H(51)···N(3) = 171.5 °]. Intramolecular hydrogen bonds of the type O–H···N, formed by the hydroxide groups with the nitrogen atoms N(12) and N(21) are also found: O(16)–H(16)···N(12) [O(16)···N(12) = 261.9(5) pm, O(16)–H(16)···N(12) = 147.0°] and O(26)–H(26)···N(22) [O(26)···N(22) = 261.6(5) pm, O(26)–H(26)···N(22) = 146.7°]. These hydrogen bonds can be observed in Figure 1.

4. Conclusion

A dimeric oxidovanadium(V) complex with a hydrazonate ligand has been synthesized and its structure was elucidated with various modalities. The ligand is able to coordinate in a dianionic *NOO*-tridentate mode. The metal centers are connected by asymmetric oxido and aqua bridges, forming an octahedral geometry with the V=O units in a *syn* configuration. Further studies regarding the biological applications of the complex are now ongoing.

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Supporting information Ⓢ

CCDC-1972103 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement ⒟ⓢ

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