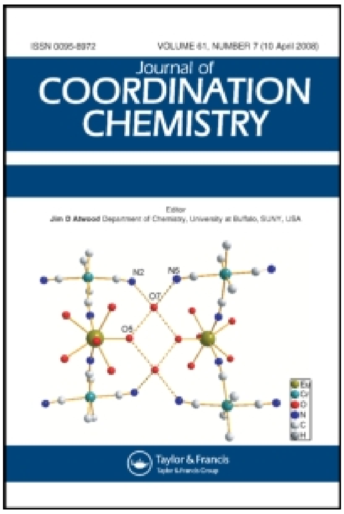

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A binuclear oxovanadium(V) complex containing a tetrasulphido bridging ligand: synthesis, characterization, mechanism, TG-DTA analysis and UV-Vis spectra

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A binuclear oxovanadium(V) complex containing a tetrasulphido bridging ligand: synthesis, characterization, mechanism, TG-DTA analysis and UV–Vis spectra

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A binuclear vanadium(V) complex $\{[VO(OCH_3)C_9H_7ON_3S_2]_2\}$ was synthesized by reaction of VCl_3 with 2-hydroxyacetophenone thiosemicarbazone (ONS ligand). The tridentate thiosemicarbazone did not utilize the thiolate or thione sulfur for coordination to vanadium, but rather employed the $-NH_2$ moiety; a binuclear vanadium complex containing a tetrasulphido bridging ligand was formed. The title complex is monoclinic, space group $P2_1/n$.

Keywords: Vanadium; Tetrasulphido; Structural characterization; Mechanism; TG-DTA; UV–Vis

1. Introduction

Vanadium coordination chemistry receives added attention due to the discovery of two vanadoenzymes (bromoperoxidase from marine algae [1, 2] and nitrogenase from Azotobacter vinelandii [3, 4]). Vanadium nitrogenase has an active center called VFe cofactor, which is generally considered as the nitrogen-fixing part [5], with vanadium coordinated with three bridging sulfurs in a rich vanadium-sulfur coordination environment. Consequently, this kind of model complex of vanadium nitrogenase has been synthesized and characterized [6, 7]. The conversion of sulfides (thioethers) RR′S to sulfoxides RR′S=O *in vivo* is catalyzed by vanadium haloperoxidases [8, 9], while *in vitro* by vanadium complexes containing ONO donor sets; enantioselectivity of these reactions suggests an intermediate coordination of the sulfide to the vanadium center [10]. Vanadium complexes having sulfur functionality have been found to be orally active insulin-mimetic agents in treatment of diabetes [11–13], and much effort has been devoted for studying vanadium-sulfur coordination chemistry. Some vanadium complexes containing ONS ligands exhibit novel structures [14, 15] as well as potential antiamoebic activities [16, 17].

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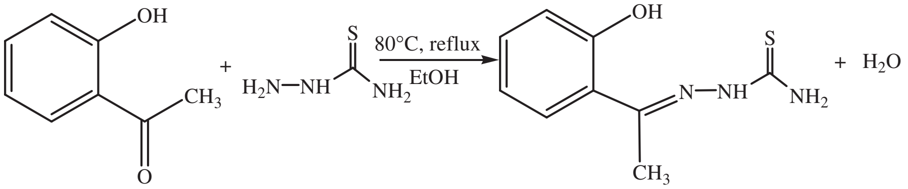
In this work, we used VCl_3 to react with an ONS ligand (e.g. 2-hydroxyacetophenone thiosemicarbazone) in methanol; to our surprise, each sulfur in the ligand was not coordinated with vanadium as expected, but was connected by a disulphido bond, giving a novel binuclear vanadium complex.

2. Experimental

All reagents and materials were obtained from commercial sources [2-hydroxyl acetophenone, VCl_3, thiosemicarbazide, sodium acetate, methanol]. All reagents were of A.R. grade and used without purification. IR spectra were obtained as KBr pellets on a Nicolet-460 spectrophotometer from 4000–400 cm^{-1}. Elemental analyses were performed by an Eager 300 Elementar model. TG-DTA analysis of the complex was carried out on a WCT-1A analyzer. UV–Vis spectra were recorded in a 10 mm quartz cell on a Shimadzu UV-265 instrument.

2.1. *Preparation of 2-hydroxyacetophenone thiosemicarbazone*

The Schiff base used in this article was prepared by reaction of aldehyde with amine in ethanol and water similar to the literature method [18]. Thiosemicarbazide (3.64 g, 40 mmol) was dissolved in a mixed solvent of ethanol (25 mL) and water (10 mL) and then refluxed at 80°C with stirring; the resulting solution was transparent and colorless. To this solution, 2-hydroxyl acetophenone (5 mL) was added dropwise within 30 min. The solution turned yellow and gave yellow precipitate gradually. After 8 h, the solution was allowed to cool to ambient temperature, filtered, the precipitate washed with absolute ethanol and dried *in vacuo*. Yield 6.02 g (72%). $C_9H_{11}ON_3S$ (209): Anal. Calcd C, 51.65; H, 5.30; N, 20.08; S, 15.32. Found: C, 51.83; H, 5.13; N, 20.61; S, 15.44. IR (KBr disk) (cm^{-1}): 3410 ($\upsilon_{N\text{–}H}$, m), 1630 (δ_{NH2}, s), 1617 ($\upsilon_{C=N}$, s), 1501, 748 (benzene ring, s), 1237 ($\upsilon_{C=S}$, s). The ligand was synthesized as described by the following procedure:



2.2. *Preparation of the binuclear vanadium complex, {[VO(OCH$_3$)C$_9$H$_7$ON$_3$S$_2$]$_2$}*

2-Hydroxyacetophenone thiosemicarbazone (0.42 g, 2 mmol) was dissolved in absolute methanol (10 mL) and anhydrous sodium acetate (0.30 g) was added with vigorous stirring to partly dissolve the ligand. To the yellow solution, VCl_3 (0.32 g, 1.5 mmol) was added; the resulting solution turned brown. Ten hours later, the mixture was filtered. The filtrate was covered with absolute diethyl ether (10 mL)

Table 1. Crystal data and structure refinement for the vanadium complex.

Empirical formula	$C_{20}H_{22}N_6O_6S_4V_2$
Formula weight	672.56
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	8.6066(14)
b	14.322(2)
c	22.162(4)
α	90
β	90.402(3)
γ	90
V (Å^3)	2731.8(8)
Z	4
D_{Calcd} (Mg m^{-3})	1.635
Absorption coefficient (mm^{-1})	1.037
F(000)	1368
Crystal size (mm^3)	0.24 × 0.20 × 0.18
θ range for data collection (°)	1.69 to 25.02.
Limiting indices	$-9 \leq h \leq 10$, $-17 \leq k \leq 16$, $-26 \leq l \leq 13$
Reflections collected/unique	13898/4816 [R(int) = 0.0553]
Completeness to $\theta = 25.02$ (%)	99.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8353 and 0.7889
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4816/6/345
Goodness-of-fit on F^2	1.000
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0413$, $wR_2 = 0.0888$
Indices (all data)	$R_1 = 0.0866$, $wR_2 = 0.1088$
Largest differential peak and hole (e Å^{-3})	0.311 and −0.319

Values in parentheses for reflections with $I > 2\sigma(I)$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$.

and maintained at ambient temperature. After three days, black block crystals formed on the inner wall of the tube, were filtered off, washed with absolute diethyl ether thoroughly and dried in air. Yield 0.176 g (35%). $C_{20}H_{22}N_6O_6S_4V_2$ (672.56): Anal. Calcd C, 35.67; H, 3.59; N, 12.46; S, 19.01. Found: C, 35.77; H, 3.95; N, 12.07; S, 18.46. IR (KBr disk) (cm^{-1}): 1597 ($\upsilon_{C=N}$, s), 1537, 1510, 748 (benzene ring, s), 992 ($\upsilon_{V=O}$, s), 653 ($\upsilon_{C\text{–}S}$, m).

2.3. *X-ray crystallography*

X-ray diffraction data were collected on a Bruker–Smart-1000 CCD diffractometer. A single crystal with approximate dimensions 0.24 × 0.20 × 0.18 mm^3 was placed on the diffractometer with monochromated (graphite monochromator) Mo-Kα irradiation ($\lambda = 0.71073$ Å) at 294(2) K. X-ray structure analyses were carried out in the ψ/ω scan mode. The structure was solved by direct methods using SHELX-97 and refined on F^2 by full-matrix least-squares using SHELXL-97. Crystal data and data for the structure solution and refinements are listed in table 1.

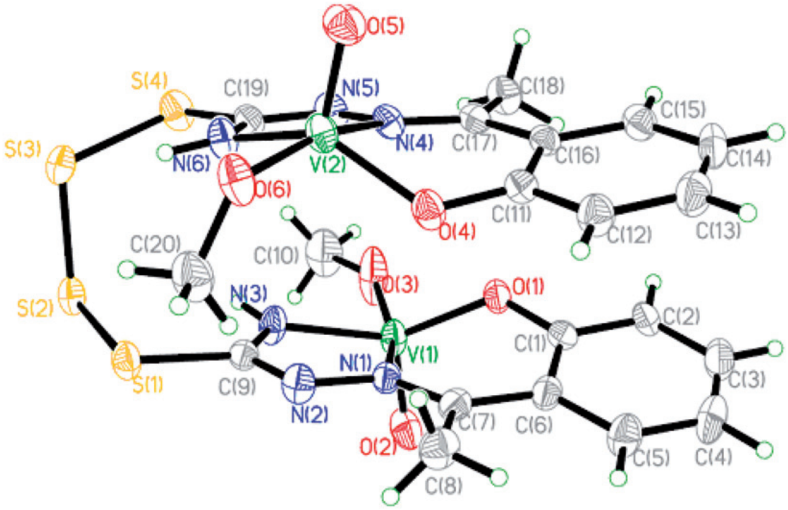


Figure 1. The molecular structure of the complex with thermal ellipsoids at 30% probability.

3. Results and discussion

3.1. *IR spectra of the ligand and vanadium complex*

IR spectra of the ligand exhibited N–H stretches at 3410 cm^{-1}, and a band at 1630 cm^{-1} belonged to the NH_2 bend vibration of the ligand. C=N stretch occurred at 1617 cm^{-1}; a broad band in the free ligand at 1237 cm^{-1} could be assigned to C=S stretch. In the vanadium complex, C=N stretch, 1617 cm^{-1}, underwent a shift to lower wave number by 20 cm^{-1} compared to the ligand, suggesting that N of C=N coordinated with vanadium. In addition, N–H and C=S stretches are not observed, and a new weak band appeared at 653 cm^{-1}, attributable to C–S stretch, consistent with the existence of thiolate rather than thione form. The vanadium complex exhibited a sharp band at 992 cm^{-1}, typical for V=O stretch.

3.2. *Structure descriptions*

The molecular structure of the complex is shown in figure 1 and selected bond distances and angles listed in table 2. The binuclear vanadium complex contains a tetrasulphido bridging ligand. The oxidation state of vanadium was +5, calculated according to the following equation:

$$s = \exp[(r_0 - r)/B]$$

where $B = 0.37$ and r_0 is obtained either from published tables or standard equations and r is the experimental bond distance [19].

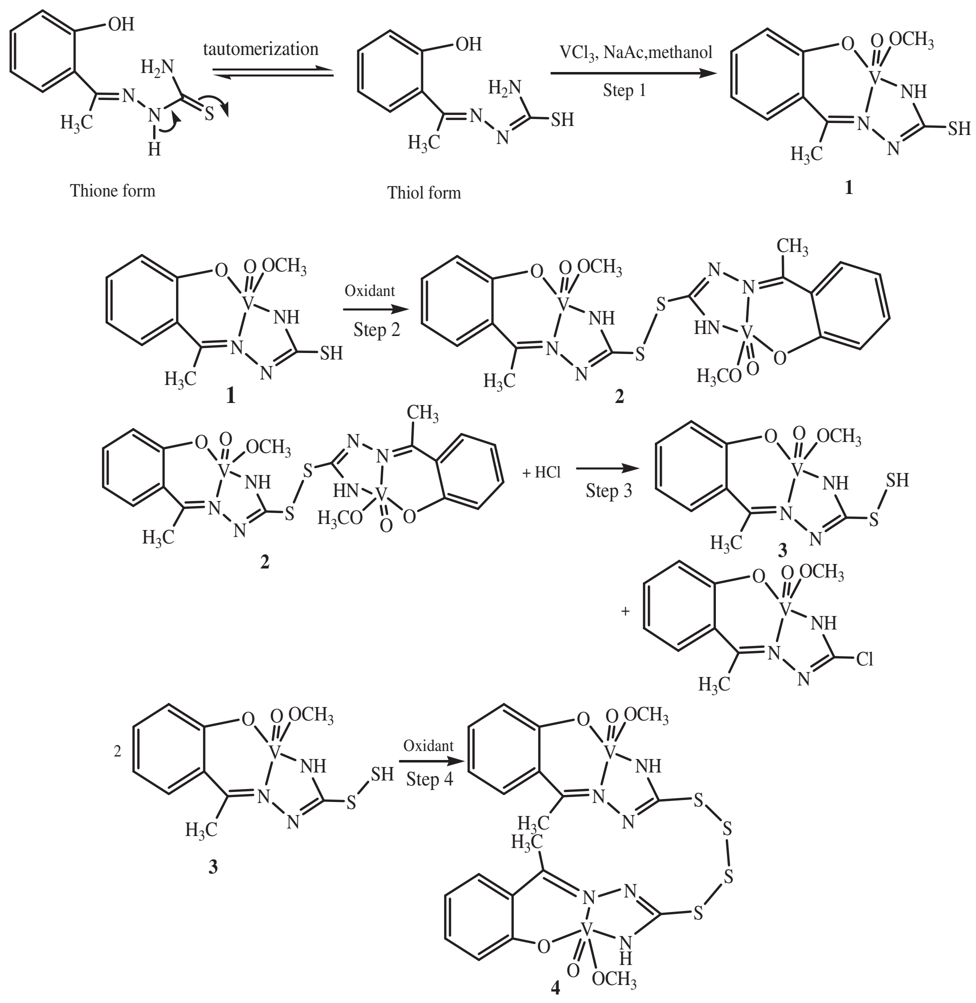
Vanadium started as a non-oxo trivalent state, but the product contained VO^{3+} with vanadium(III) oxidized to vanadium(V).

Table 2. Bond lengths (Å) and angles (°) for the vanadium complex.

V(1)–O(2)	1.584(3)	S(2)–S(3)	2.0800(17)
V(1)–O(3)	1.751(3)	S(3)–S(4)	2.0436(17)
V(1)–O(1)	1.820(3)	S(4)–C(19)	1.800(4)
V(1)–N(3)	1.965(3)	N(1)–N(2)	1.404(4)
V(1)–N(1)	2.137(3)	N(1)–C(7)	1.316(4)
V(2)–O(5)	1.584(3)	N(2)–C(9)	1.306(4)
V(2)–O(6)	1.770(3)	N(3)–C(9)	1.329(5)
V(2)–O(4)	1.836(3)	N(4)–N(5)	1.407(4)
V(2)–N(6)	1.972(3)	N(4)–C(17)	1.308(5)
V(2)–N(4)	2.130(3)	N(5)–C(19)	1.305(5)
S(1)–C(9)	1.791(4)	N(6)–C(19)	1.325(5)
S(1)–S(2)	2.0485(15)		
O(2)–V(1)–O(3)	106.92(18)	O(5)–V(2)–O(6)	105.06(15)
O(2)–V(1)–O(1)	108.78(14)	O(5)–V(2)–O(4)	108.75(14)
O(3)–V(1)–O(1)	101.16(14)	O(6)–V(2)–O(4)	99.21(13)
O(2)–V(1)–N(3)	107.93(15)	O(5)–V(2)–N(6)	112.08(14)
O(3)–V(1)–N(3)	88.29(13)	O(6)–V(2)–N(6)	90.17(12)
O(1)–V(1)–N(3)	137.27(14)	O(4)–V(2)–N(6)	133.89(13)
O(2)–V(1)–N(1)	94.73(14)	O(5)–V(2)–N(4)	94.94(14)
O(3)–V(1)–N(1)	155.39(16)	O(6)–V(2)–N(4)	158.12(13)
O(1)–V(1)–N(1)	82.17(12)	O(4)–V(2)–N(4)	82.29(12)
N(3)–V(1)–N(1)	73.73(12)	N(6)–V(2)–N(4)	73.86(12)
C(9)–S(1)–S(2)	103.24(14)	C(19)–S(4)–S(3)	103.71(14)
S(1)–S(2)–S(3)	105.91(6)	S(4)–S(3)–S(2)	106.98(7)

The geometry of the vanadium was square pyramidal. The two vanadium centers were similar but not identical. For V(1), $\tau = 0.30$ [$\tau = (\theta_1 - \theta_2)/60^\circ$, where θ_1 is the largest angle and θ_2 is the second largest angle in the coordination sphere, $\tau = 0$ for ideal square pyramids, $\tau = 1$ for ideal trigonal pyramids] [20]. For V(2), $\tau = 0.40$, both values indicated severely distorted square pyramidal structures. V(1) had the oxo group O(2) in the apical position, nitrogen N(1) of the imine, nitrogen N(3) of the amino group, oxygen atom O(1) of the phenolate from the ligand and O(3) of deprotoned methanol in the plane. Each vanadium center had the same coordination environment, but was not symmetric, for the corresponding bond distances and angles had a few differences. The 2-hydroxyacetophenone thiosemicarbazone can be described as hexadentate and tridentate to each vanadium, but not utilizing thiolate or thione sulfur for coordination [21–23].

V(1)–O(2) and V(2)–O(5) were typical V=O double bonds with a distance of 1.584(3) Å [24]. Each vanadium center had ONN donor sets from the ligand forming a six-membered ring and a five-membered ring. For V(1), the mean deviation from the plane of six-membered ring and the plane of five-membered ring was 0.2845 and 0.0415 Å, respectively. V(1) was shifted from the pentagonal plane, upward by 0.1759 Å. The bite angles in the two rings formed by the tridentate ligand were 82.1° (V1–N1–O1) and 73.8° (V1–N3–N1), while the angle O2–V1–N1 was 107.93(15)°, completely deviating from 180°, indicative of a square pyramidal structure instead of a trigonal bipyramidal structure. Bond distances of C(9)–N(2) and C(19)–N(5) were close to the C=N double bond and C(9)–S(1) was 1.802 Å in accord with usual values, showing that enolimine form existed. S(3)–S(2) and S(3)–S(4) bonds were 2.080 and 2.044 Å, respectively, consistent with S–S bond distances reported earlier [25].



Scheme 1. The possible formation mechanism of the title complex.

3.3. *Mechanism discussions*

The title complex is very unusual, and the possible formation mechanism is shown in scheme 1. Compounds containing mercapto can be oxidized to form disulfides. In the ligand, C=S underwent a tautomerization, e.g. enolimine and thione (Step 1, scheme 1). During or after coordination between vanadium and the ligand, enolimine was oxidized by oxygen so that a bisulfide formed (Step 2, scheme 1). The next step may be one of the C–S bonds in the resulting product was cleaved by hydrochloric acid so as to produce **3** (Step 3, scheme 1). Complex **3** was oxidized by oxygen again and **4** (Step 4, scheme 1) was obtained; **4** was stable to oxidant and acid.

3.4. *TG-DTA studies*

The binuclear vanadium complex was stable up to 170°C. The first step started at 260°C and ended at 280°C, with weight loss of 31.4%, corresponding to loss of

[–N=C(NH)–S–S–$]_2$ (Anal. Calcd mass loss: 31.2%). The second weight loss of 51.8% appeared in the temperature range 445–474°C, corresponding to loss of the remaining organic components (Anal. Calcd mass loss: 51.1%), e.g. Ph(O)–C(CH_3)=N, OCH_3, bridging oxygen. When the temperature rose to 900°C, the remaining residue of 16.9% agreed with formation of V_2O_5 as final product. Both of the two steps were exothermic with DTA peak at 274°C and 460°C.

3.5. *UV–Vis spectra*

The UV–Vis spectra of ligand and vanadium complex in *Tris*-NaCl/HCl buffer solution are shown in Supplementary material. Both exhibited an absorption at 300 nm, assigned to $\pi \rightarrow \pi^*$ transition of the ligand; the ligand-to-metal charge transfer (LMCT) absorption band of the vanadium complex was not observed.

4. Conclusions

Vanadium complexes containing ONS ligands have been reported with sulfur coordination. However, we obtained a binuclear vanadium complex containing a tetrasulphido bridging ligand, tridentate utilizing the terminal amino group for coordination rather than thione or thiolate sulfur, very unusual coordination for thiosemicarbazone. The binuclear vanadium complex was characterized by IR and X-ray single diffraction analysis. Five-coordinated vanadium(V) exhibited a distorted square pyramidal geometry. The ONS ligand existed in the enthione form, while enolimine in its vanadium complex. The possible formation mechanism of the title complex involved tautomerization with subsequent deprotonation and oxidation of the ligand concomitant with oxidation and oxygenation of the vanadium(III) ion, but the exact mechanism is still under research.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC No. 679459 for the title complex. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: 044-1223-336-033 or Email: deposit@ccdc.cam.ac.uk).

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