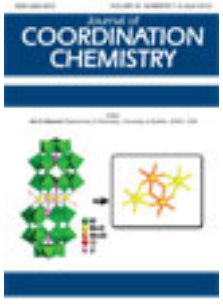

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Formation of an asymmetrical ligand (H_3L_{cyclic}) via a metal-induced cyclization of symmetrical thiocarbohydrazone (H_4L) in synthesizing an oxovanadium(IV) complex $VO(HL_{cyclic})(EtOH)_2$

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Formation of an asymmetrical ligand (H_3L_{cyclic}) *via* a metal-induced cyclization of symmetrical thiocarbohydrazone (H_4L) in synthesizing an oxovanadium(IV) complex $VO(HL_{cyclic})(EtOH)_2$

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A symmetrical tetraprotic pentadentate (ONS) ligand, 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone (H_4L), undergoes metal-induced cyclization to form an asymmetrical triprotic tetradentate ligand (H_3L_{cyclic}) containing a thiadiazole ring when it reacts with $[VO(acac)_2]$ under an aerobic environment in ethanol. The final isolated product is an oxovanadium(IV) complex, $VO(HL_{cyclic})(EtOH)_2$ (**1**), which contains HL^{2-}_{cyclic} derived from H_4L. Complex **1** has been characterized by X-ray single-crystal structure analysis, ^1H NMR, and EPR. EPR spectrum demonstrates that the oxidation state of vanadium is +4. In **1**, O–H···N/O–H···S hydrogen bond between the free phenolic hydroxyl and N/S of the thiadiazole ring are both possible, probed by density functional theory computation, showing that the hydrogen-bond energy of O–H···N is lower than that of O–H···S by 8.3 kcal mol^{-1} and is preferred.

Keywords: Thiocarbohydrazone; Vanadium complex; Crystal structure; Cyclization

1. Introduction

Vanadium has applications with vanadium-dependent enzymes, like nitrogenase [1], haloperoxidases [2, 3], and phosphomutases, which have been used as effective catalysts for selective oxidation reactions [4], bromination reactions [5], and coupling reactions [6]. Oxovanadium (IV/V) motifs have medical properties, like insulin-mimetic [7] or anticancer [8]. Researchers have become interested in studying the metabolic mechanism of vanadate in life, which will give insight into the relationship of vanadium transportation with genes [9]. Asymmetrical thiosemicarbazones are commonly used as bidentate ligands to prepare vanadium complexes, which have applications in biology [10], clinic [11], and analysis [12], and also have important roles in organic synthesis [13]. However, reports on symmetrical thiocarbohydrazone associated metal complexes are especially rare [14–17], with none involving vanadium. In this work, a symmetrical thiocarbohydrazone, 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone (H_4L) from

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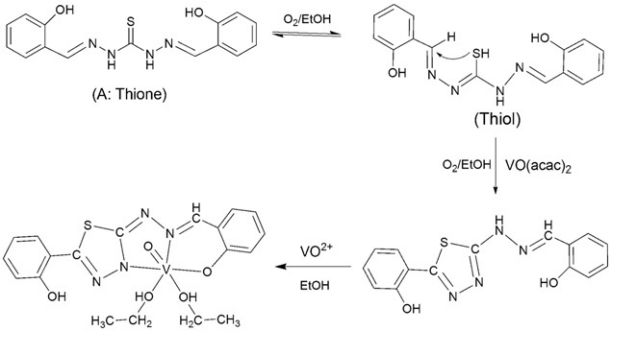
thiocarbonohydrazide and salicylaldehyde has been employed as a multidentate ligand to synthesize a vanadium complex. An unexpected vanadium complex with an unusual ligand (HL^{2-}_{cyclic}) with a thiadiazole ring was obtained from the reaction system, different from the past literature [16]. The thiadiazole ring is derived from oxidative cyclization of the parent thiocarbohydrazone H_4L induced by the vanadyl ion. Oxidative cyclizations of thiosemicarbazone [18] or dithiocarbazate induced by transition metal have rarely been reported [19]. Herein, we report synthesis, spectroscopic characterization, and crystal structure of $VO(HL_{cyclic})(EtOH)_2$ (**1**) containing one HL^{2-}_{cyclic} bearing a thiadiazole ring, which resulted from a metal-induced cyclization of the parent H_4L (scheme 1). The parent thiocarbohydrazone ligand H_4L has two possible tautomeric forms in solvent, thione form A and thiol form B, which are in equilibrium [16, 20]. X-ray diffraction studies showed that the metal-free compound crystallized in thione form A [21] and the metal complexes in thiol form B [22]. The thiol tautomer can adopt different configurations as a consequence of the double-bond character of the central N–C linkage. According to the previous report [19], the oxidative cyclization of the parent ligand H_4L and its subsequent complexation behavior is not straightforward and demands further investigation.

2. Experimental

2.1. *Materials and measurements*

Chemicals except 1,5-bis(2-hydroxybenzaldehyde)thiocarbonohydrazide (H_4L) were readily available from commercial sources and used without purification: vanadyl acetylacetonate ($VO(acac)_2$, AR, J&K), salicylaldehyde ($C_7H_6O_2$, AR, J&K), thiocarbonohydrazide (CH_6N_4S, AR, J&K). H_4L was prepared according to the literature [22]. Anal. Calcd for H_4L ($C_{15}H_{14}N_4O_2S$) (%): C, 57.32; H, 4.46; N, 17.83; S, 10.19. Found (%): C, 57.33; H, 4.44; N, 17.81; S, 10.20. IR(KBr, cm^{-1}): 3453(m), 2979(m), 1618(s), 1561(s), 1485(s), 1282(s), 955(s), 796(m), 746(s). ^1H NMR (500 MHz, DMSO-d_6) [ppm] δ: 6.80–6.95(4H, aromatic ring protons), 7.25–7.40(3H, aromatic ring protons), 8.09(1H, aromatic ring proton), 8.50(1H, CH=), 8.78(1H, CH=), 10.08(1H, OH), 11.64(1H, OH), 11.90(1H, NH), 12.11(1H, NH). The C, H, and N elemental analyzes



Scheme 1. The possible cyclization process of **1**.

were performed on the Elemental Vario EL-3 elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Equinox55 FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1}. The proton NMR spectrum was determined on a Bruker-Am 500 spectrometer with TMS as standard. The EPR spectrum of **1** was recorded on a Bruker E500 spectrometer by using a standard resonance (ST4102) at room temperature (EPR conditions for the spectrum: microwave power, 10 mW; modulation amplitude, 10 G; modulation frequency, 100 kHz).

2.2. *Synthesis of $VO(HL_{cyclic})(EtOH)_2$ (1)*

Complex **1** was synthesized from a mixture containing $VO(acac)_2$ (0.5 mmol, 0.1326 g) and H_4L (0.5 mmol, 0.155 g) in 40 mL ethanol solution. The mixture was stirred at 80°C for 6 h, resulting in a dark brown solution. After filtering at room temperature, the filtrate was held at ambient temperature for several days until brown solid crystallized in good yield 0.094 g (40%). IR(KBr, cm^{-1}): 3442(m), 2987(w), 1604(s), 1484(s), 1276(m), 1042(s), 963(s), 785(s). Anal. Calcd for $C_{19}H_{22}N_4O_5SV$ (%): C, 48.62; H, 4.72; N, 11.94; S, 6.83. Found (%): C, 48.57; H, 4.69; N, 12.13; S, 6.65.

2.3. *Single-crystal structure determination*

Reflection data were collected using a Bruker Smart Apex II X-ray single-crystal diffractometer (Mo-Kα, $\lambda = 0.71073$ Å, $T = 293$ K) for $VO(HL_{cyclic})(EtOH)_2$ (**1**). The data were corrected for empirical absorption with SADABS. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. For the two coordination ethanol molecules, H(3) on O(3) of one ethanol was located by the difference Fourier electron density maps; the hydrogen on O(2) of the other ethanol was not found by residual electron density peaks. The not-found hydrogen atom on O(2) may be neglected because it has no significance to the structural discussion on the complex. The remaining hydrogen atoms including on all carbon atoms, O(6), and O(6′) were added as the riding model. The free phenolic hydroxyl O(6) was treated as disordered owing to rotation of the single bond C(9)–C(10), and the occupancy at the two positions are 0.313(3) and 0.687(3), respectively. The whole methyl group ($-C(19)H_3$) and the hydrogen atoms on the methylene ($-C(18)H_2-$) of the ethoxy group were also treated as disordered. The crystallographic data of **1** are shown in table 1. Selected bond distances and angles for **1** are listed in table 2.

2.4. *DFT calculation*

The initial model was built based on the X-ray crystal structure. Two possible configurations with two types of hydrogen bond, O–H···S or O–H···N, have been constructed and full geometric optimizations were performed on all models by using the MPWB1K with 6–31 + G** basis set with the Gaussian03 program.

Table 1. Crystallographic data and structure refinement parameters for **1**.

Empirical formula	$C_{19}H_{22}N_4O_5SV$
Formula weight	469.41
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.9247(2)
b	10.1728(2)
c	10.9697(2)
α	77.3160(10)
β	85.0490(10)
γ	78.7750(10)
Volume (Å^3), Z	1058.73(4), 2
Calculated density (Mg m^{-3})	1.472
Absorption coefficient (mm^{-1})	0.605
F(000)	486
Crystal size (mm^3)	$0.3 \times 0.26 \times 0.22$
θ range for data collection (°)	1.90–26.07
Index ranges	$-12 \le h \le 12$; $-12 \le k \le 12$; $-13 \le l \le 13$
Reflections collected	15,955
Independent reflections	4181 [R(int) = 0.034]
Data/restraints/parameters	4181/3/278
Goodness-of-fit on F^2	1.107
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1421$
Final R indexes (all data)	$R_1 = 0.0653$, $wR_2 = 0.1522$
Largest difference peak and hole (e Å^{-3})	0.67 and −0.52

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

V(1)–O(1)	1.580(2)	N(3)–C(8)	1.344(4)
V(1)–O(2)	1.752(2)	N(3)–N(4)	1.378(3)
V(1)–O(4)	1.854(2)	N(4)–C(9)	1.297(4)
V(1)–N(3)	2.050(2)	N(1)–N(2)	1.402(3)
V(1)–N(1)	2.154(2)	N(1)–C(7)	1.292(4)
V(1)–O(3)	2.390(2)	O(1)–V(1)–O(3)	174.73(10)
N(2)–C(8)	1.315(3)	O(4)–V(1)–N(3)	150.98(10)
S(1)–C(8)	1.736(3)	O(2)–V(1)–N(1)	159.97(10)
S(1)–C(9)	1.757(3)		

3. Results and discussion

3.1. *Crystal structure of VO(HL_{cyclic})(EtOH)$_2$ (1)*

The crystal structure determination confirms the presence of a new ligand (HL^{2-}_{cyclic}) containing a thiadiazole ring in **1**. The vanadyl VO^{2+} is coordinated with four oxygen atoms and two nitrogen atoms, existing in a distorted octahedral geometry (figure 1). The axial position is taken up by a terminal oxo O(1) and an O(3) of coordinated ethanol; the O(1)–V(1)–O(3) angle is 174.73(10)°. The square plane around vanadium is not strictly planar with average deviation of N(1), O(2), N(3), and O(4) from the weighted least-squares plane 0.0315 Å, and the central vanadium is shifted slightly out of the basal plane by 0.8123 Å toward the apical oxo. The V(1)–O(2) and V(1)–O(3) lengths are disparate with V(1)–O(3) (2.390(2) Å) significantly elongated compared to

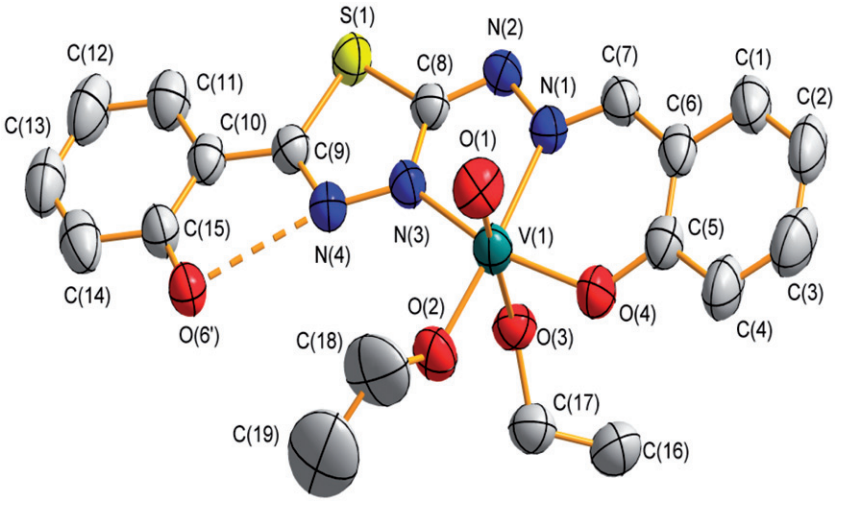


Figure 1. Molecular structure of **1** with 50% thermal ellipsoids, showing the atom-numbering scheme (hydrogen atoms omitted for clarity).

V(1)–O(2) (1.752(2) Å), due to the strong *trans*-influence of the terminal oxo [19]. The bond length of V(1)–O(1) (1.580(2) Å) is much shorter than other V–O bonds, indicating that it has double bond character while others are single bonds.

The most striking structural feature of **1** is that it contains an asymmetrical tetradentate ligand with a heterocyclic thiadiazole ring formed by an oxidative cyclization. Similar phenomenon has been reported previously [19]. The parent H_4L is divided into two parts. One part coordinates bidentate in the customary fashion and the other undergoes metal-induced intramolecular cyclization, leaving a nitrogen of the thiadiazole ring to coordinate with vanadium, and retaining a free phenolic hydroxyl. In the thiadiazole ring, the bond lengths of S(1)–C(8) and S(1)–C(9) are 1.736(3) Å and 1.757(3) Å, respectively, similar to the usual S–C length. The N(3)–C(8) (1.344(4) Å) and N(4)–C(9) (1.297(4) Å) lengths are close to normal double bond and the N(3)–N(4) (1.378(3) Å) bond is closer to the normal single bond. The corresponding bond distances in the thiadiazole ring show the heterocyclic ring has delocalization. The distances of N(2)–C(8) (1.315(3) Å), N(1)–N(2) (1.402(3) Å), and N(1)–C(7) (1.292(4) Å) adjacent to the thiadiazole ring have differences with normal bonds, showing a certain extent of delocalization.

3.2. *Intra- and inter-molecular interactions*

In the free phenolic ring, the O(6)–S(1) and O(6′)–N(4) distances are 2.936(6) Å and 2.652(4) Å, respectively, showing possible O–H···N and O–H···S hydrogen bonds between the free phenolic hydroxyl and N and S of the thiadiazole ring. The rotation of C(9)–C(10) provides the possibility that the O(6) has a disorder distribution on the phenolic ring. Probed by density functional theory (DFT) computation, the bond energy of O(6′)–H···N(4) is lower than that of O(6)–H···S(1) by 8.3 kcal·mol^{-1},

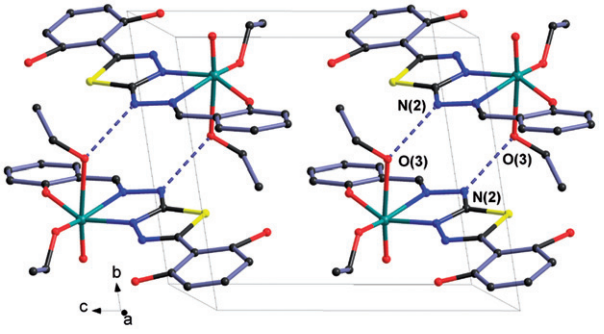


Figure 2. The packing diagram of **1** with intermolecular hydrogen bonds shown as dotted lines.

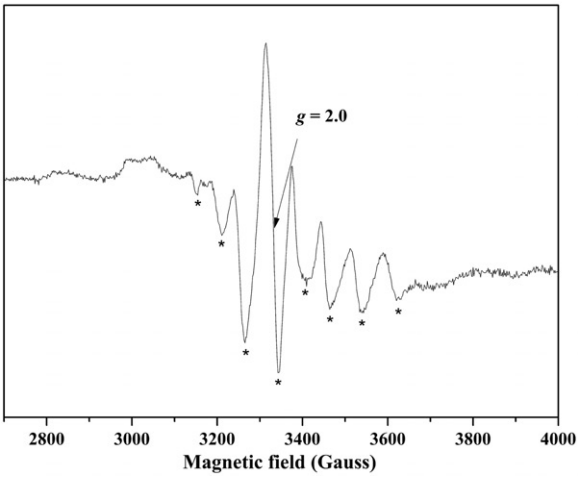


Figure 3. The EPR signal of **1**.

showing that the O–H $\cdots$ N hydrogen bond is preferred in **1**. Meanwhile, occupancy of O(6) at the two position is 0.313(3) and 0.687(3) in the crystal structure, exhibiting that O(6)′–H $\cdots$ N(4) is favored, consistent with the DFT calculation. An obvious intermolecular hydrogen bond benefits packing of the complex (figure 2). Every two molecules form a dimer linked by O(3) in one molecule with N(2) in the adjacent molecule $(-x, -y+1, -z)$. The distance of donor and acceptor atoms O(3)–N(2) is 2.779(3) Å and the angle of O(3)–H(3) $\cdots$ N(2) is 169(8)°.

3.3. *Analysis of EPR*

The crystalline sample of **1** gives the typical eight-line EPR signal with an average spacing of 67 G at $g = 2.0$ range (figure 3), which clearly support the presence of paramagnetic V^{4+} in the sample.

4. Conclusion

The reaction of symmetrical pentadentate ligand 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone (H_4L) with $VO(acac)_2$ resulted in an asymmetrical ligand (H_3L_{cyclic}) containing a thiadiazole ring and sequentially led to an oxovanadium complex, **1**. Except for a metal-induced effect [19], we are unable to comment further on the mechanism of this interesting ligand-based cyclization reaction. The oxidation state of vanadium is +4 which has been confirmed by EPR. The resulting H_3L_{cyclic} from the parent ligand H_4L is triprotic in neutral form and plays a role of dianionic HL^{2-}_{cyclic} by removal of the protons from the phenolic hydroxyl and the imine. Ambient hydrogen bonds between the free phenolic hydroxyl and the N or S atoms in the resulted thiadiazole result in a disorder distribution of the free phenolic hydroxyl.

Supplementary material

Crystallographic data of **1** for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center and allocated under the deposition number CCDC ID: 820001. Copies of available data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments

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