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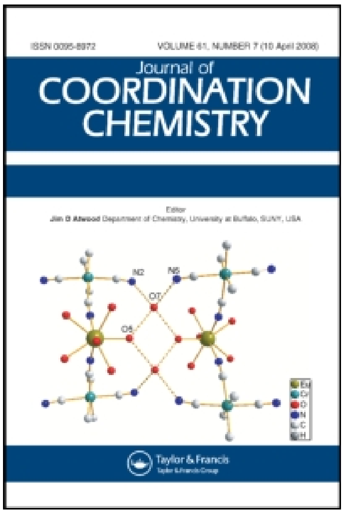

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Synthesis and structural characterization of 3,4-diphenylcyclopenta-2,4-diene-1 thione and its reactivity with V(V)

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Synthesis and structural characterization of 3,4-diphenylcyclopenta-2,4-diene-1 thione and its reactivity with V(V)

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In the first part of this work, we have studied the reactivity of an ethanolic solution of diphenylthiocarbazone ($C_{13}H_{12}N_4S$) with an aqueous solution of vanadium(V), leading to a new compound $C_{17}H_{12}S$ (**L**). This compound was crystallographically characterized and identified by XRD. This technique reveals no metal in the structure. Then, we reacted **L** with the same metal, producing a dimeric complex $V_2O_4(L)_2(H_2O)_2(OH)_2$ (**C1**), characterized by elemental analysis, IR, UV–Visible, ^1H NMR, ^{13}C NMR, and ^{51}V NMR spectra. A probable structure has been proposed.

Keywords: V(V); Ethanolic solution; Diphenylthiocarbazone vanadium(V)

1. Introduction

The chemistry of vanadium has been the subject of extensive study since its biological and industrial significance has been recognized. Vanadium is an inhibitor of Na^+, K^+-ATPases, and nucleases [1] and involved in enzymes such as bromoperoxidases [2] and nitrogenases [3], revealing the importance of its redox chemistry. Recently, interest has focused on the vanadium insulin-mimicking ability [4]. Vanadium is also an important catalyst for reactions such as oxidation, epoxidation, and hydroxylation [5]. The presence of mixed valence vanadium compounds in biological and chemical catalysis provides great interest and stimulus to this area of research.

Coordination chemistry of vanadium in ligand environments containing sulfur are gaining momentum in view of the use of this metal center as catalysts and in the

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oxidation of organic sulfides into sulfoxides [6]. A number of vanadium complexes in complete and partial sulfur environments covering a wide nuclearity and oxidation state range have been reported [6].

We report the reactivity of diphenylthiocarbazone, a chelating and extracting agent, with vanadium(V) in which vanadium reveals its catalytic character, transforming the ligand to another organic compound $C_{17}H_{12}S$ (**L**) which has been identified by X-ray diffraction (XRD).

Reaction of **L** with the same metal under other experimental conditions results in a dioxovanadium(V) complex, characterized by different spectroscopic methods (IR, UV–Visible, ^{1}H, ^{13}C, and ^{51}V NMR).

In this article, the synthesis of 3,4-diphenylcyclopenta-2,4-diene-1 thione and $V_2O_4(L)_2(H_2O)_2(OH)_2$ (**C1**) are described.

2. Experimental

2.1. *Reagents*

All reagents and solvents used in this study were Fluka products and were used without purification.

2.2. *Apparatus*

Elemental analyses were carried out at the Central Service of Analysis CNRS, Solaize, France. Melting points were measured using a Büchi 512 digital melting point apparatus. Conductometric measurements were carried out on a CD 810 Tacussel apparatus employing a calibrated dip-type cell at 25°C. UV–Visible and near-infrared spectra were recorded on a Lambda 9 Perkin–Elmer spectrometer using special cells. The IR spectra were recorded on a FTS-7 Biorad Fourier transform infrared spectrometer using KBr pellets. ^{1}H NMR spectra were recorded at room temperature on a Bruker AM 300 spectrometer with TMS as internal reference in DMSO-d6. The ^{51}V NMR spectra were measured using a Bruker AM 300 spectrometer in D_2O or in DMSO-d6 using $VOCl_3$ as internal reference.

2.3. *Single-crystal data collection*

Suitable crystals were mounted on a Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) equipped with a CCD area detector. Intensities were collected at 293 K by the program COLLECT [7] with a step rotation angle of 1° for the w angle. Reflection indexing, Lorentz-polarization correction, peak integration, and background determination were carried out with the DENZO [8] program. Frame scaling and unit-cell parameter refinement were made through the program SCALEPACK [8]. The resulting set of hkl was used for structure solution and refinement. Crystallographic data details on data collection and structure refinement are listed in table 1. Atomic coordinates and equivalent displacement ellipsoids are gathered in Supplementary Material. Structure drawings were carried out with diamond [9].

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Table 1. Crystal data, collection data, and structure refinement.

Formula	$C_{17}H_{12}S$
Formula weight	248.34
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$C12/c1$
Unit cell dimensions (Å, °)	
a	14.762(5)
b	12.199(5)
c	6.974(4)
α	90.00
β	97.249(5)
γ	90.00
V	1245.9(11) Å^3
Z	4
Density (calculated) (mg m^{-3})	1.32
$F(000)$	520.000
Diffractometer/scan	Nonius $2\theta/\omega$ scans
Absorption coefficient (mm^{-1})	0.236
θ range for data collection (°)	0–0°
Reflections measured	2859
Independent observed reflections	1476
R_{int}	0.0003
$\theta_{\max}$	27.8331
h	$-19 \rightarrow +19$
k	$-15 \rightarrow +15$
l	$-9 \rightarrow +9$
Reflections used	909
Cutoff	$I \geq 2\sigma(I)$
Parameters refined	107
S	1.06
R-factor	0.073
Weighted R-factor	0.081
Largest difference peak and hole (e · Å^{-3})	0.61/–0.54

Notes: Refinement on F; $w = w' \times [1 - (\Delta F_{\text{obs}}/6 \times \Delta F_{\text{est}})^2]^2$; $w' = [P_0T'_0(x) + P_1T'_1(x) + \cdots P_{n-1}T'_{n-1}(x)]^{-1}$, where P_i are the coefficients of a Chebychev series in $t_i(x)$, and $x = F_{\text{Calcd}}/F_{\text{calcdmax}}P_0 - P_{n-1} = 0.852$, 0.400, 0.372, -0.616^{E}, –01.

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The structure was solved by direct methods with SIR97 [10]. The remaining nonhydrogen atoms were located by successive difference Fourier map analyses. The hydrogen atoms were located in a difference map and then refined using soft restraints on bond lengths and angles to regularize their geometry (C–H in the range 0.87–93) and isotropic atomic displacement parameters (U_{iso}(H) in the range 1.2–1.5 times U_{equiv} of the adjacent atom). The structure refinement was carried out with crystals [11].

2.4. *Preparation of 3,4-diphenylcyclopenta-2,4-diene-1 thione: (L)*

To 10 mmol (2.56 g) of diphenylthiocarbazone dissolved in 50 mL of ethanol, was added a solution of $NaVO_3 \cdot H_2O$ (10 mmol, 1.4 g) dissolved in 20 mL of water.

The pH of this solution was adjusted to 2 with a few drops of concentrated H_2SO_4. Purple crystals are formed after 5 h at 50°C.

The obtained compound with a melting point of 145°C is insoluble in water and soluble in most organic solvents. Elemental analyses, ^{1}H NMR and XRD suggest the empirical formula $C_{17}H_{12}S$. Anal. found: C, 82.59; H, 4.25; S, 12.78%. Calcd for: C, 82.25; H, 4.83; S, 12.90%.

2.5. *Preparation of C1*

On mixing 3,4-diphenylcyclopenta-2,4-diene-1 thione (**L**) (20 mmol, 4.96 g) dissolved in 50 mL of ethanol and an equivalent amount of an aqueous solution (20 mL) of $NaVO_3 \cdot H_2O$ (20 mmol, 2.8 g) at room temperature, a green precipitate formed immediately. The pH of the aqueous solution was adjusted to 4 with a few drops of concentrated H_2SO_4. The compound is insoluble in water and soluble in most organic solvents. It is an electrolyte, diamagnetic and has a melting point higher than 400°C. The elemental analyses and physical characterization suggest $V_2O_8C_{34}H_{30}S_2$. Anal. found: C, 55.22; H, 3.99; S, 8.71; V, 13.68%. Calcd for: C, 55.73; H, 4.09; S, 8.74; V, 13.96%.

The reactions were conducted with constant stirring until complete precipitation. The product was filtered and washed with a mixture of water–ethanol (50–50 vol.%) and dried at 50°C in an oven.

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3. Results and discussion

According to the related experimental conditions (pH = 2 and ligand/metal ratio = 1), the transformation of diphenylthiocarbazone into 3,4-diphenylcyclopenta-2,4-diene-1 thione by vanadium(V) occurs following the reaction path. To well understand the ligand transformations, we propose the mechanism given in Supplementary Material.

The structure of H_2L was confirmed by XRD, chemical analyses, ^1H NMR, and ^{13}C NMR.

3.1. *^1H NMR of L*

The ^1H NMR of H_2L in DMSO shows two principal signals. The resonance of phenyl protons as three separate signals are at 7.71 ppm (4H), 7.6 ppm (4H), and 7.5 ppm (2H) and the signal at 4.2 ppm, corresponding to 2 protons, assigned to the resonance of C–H group.

3.2. *13C NMR of L*

The ^{13}C spectrum of **L** in DMSO shows seven signals, of which one signal at 229.05 ppm is due to the $C_1 = S$ carbon. The chemical shifts for the ring carbons are (δ, ppm): C_2 (2) = 109.1 ppm, C_3 (2) = 150 ppm, C_4 (2) = 133.81 ppm, C_5 (4) = 126.70 ppm, C_6 (4) = 130.10 ppm and C_7 (2) = 132.79 ppm.

3.3. *Crystal structure*

$SC_{17}H_{12}$ (figure 1) crystallizes in monoclinic space group *C*2/*c*. The mean C–C distance of 1.381(7) Å and the C–C bond of 1.438(4) Å between the phenyl and pentyl rings

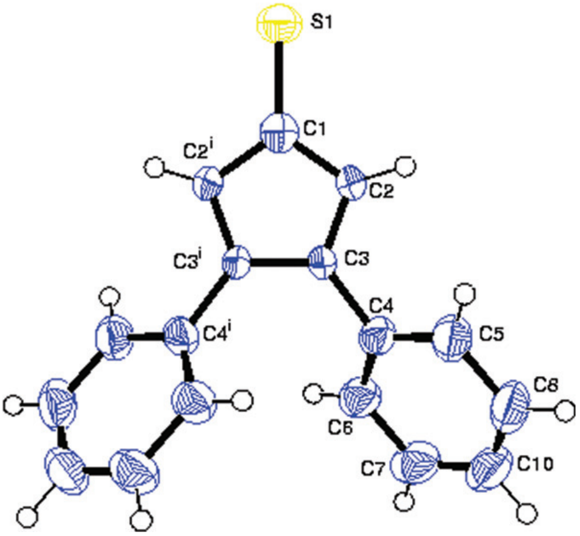

Figure 1. Molecular structure of **L**.

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are expected. The 1.690(5) Å S–C bond is close to previously reported values for carbon–sulfur double bond [12]. The mean plane of the pentyl ring is 45.1(1)° to phenyl. The angle between the two mean planes of the phenyl ring is 61.8(1)°. The distances and angles are given in Supplementary Material.

The crystal structure of $SC_{17}H_{12}$ is constituted by discrete entities, which stack along the *c* axis of the unit cell in a see-saw manner (Supplementary Material). The cohesion of the crystal structure is achieved through inter-molecular short-contacts (distance less than the sum of van der Waals radii) between sulfur and hydrogen [2.93(2) Å] and between two hydrogens [2.52(2)–2.82(3) Å range].

3.4. *Characterization of* C1

The resulting ligand **L** (Supplementary Material) can chelate VO_2^+ leading to $V_2O_4(H_2L)_2(H_2O)_2(OH)_2$ by changing the experimental conditions (pH = 4 and ligand/metal ratio = 1).

3.5. *IR spectrum*

Complex **C1** is green when freshly prepared and diamagnetic, indicating vanadium(V). The elemental analyses and mass spectrum, 730.9 *m*/*z*, suggest a dimeric complex of vanadium with a calculated molar mass of 732 from the proposed formula $V_2O_4(L)_2(H_2O)_2(OH)_2$.

The IR spectrum of **C1** shows the presence of coordinated ligand from the C=S stretch at 1380 cm^{-1} [13]. The spectrum exhibits an intense absorption at 3450 cm^{-1}, corresponding to the bound water and OH of **C1**. Also observed were a strong absorption at 960 cm^{-1}, due to terminally bound V=O [14], and absorptions at 889 and 500 cm^{-1} from the asymmetric and symmetric V–O–V stretching vibration [15].

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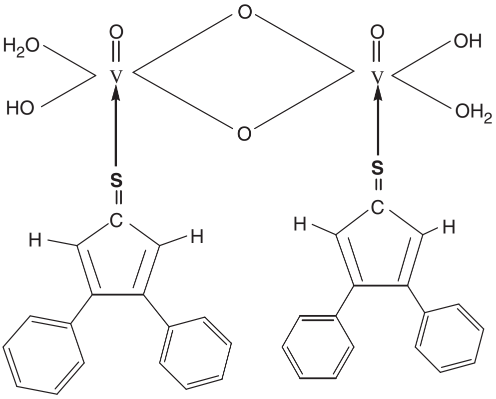

Figure 2. Proposed structure of **C1**.

3.6. *UV–visible*

The electronic absorption spectrum of the pentavalent d° complex in ethanol exhibits intense transitions, the one at lowest energy lying around $\lambda = 420\,\mathrm{nm}$ ($\varepsilon = 1.7610^{+2}\,\mathrm{cm}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{L}$) assigned to LMCT excitation, a shoulder at $\lambda = 325\,\mathrm{nm}$ ($\varepsilon = 265.48\,\mathrm{cm}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{L}$) assigned to oxygen–metal charge transfer $\mathrm{O} \rightarrow \mathrm{V}$ characteristic of the $3d^0$ configuration of vanadium(V) [16] and a band at 266 nm ($\varepsilon = 663.71\,\mathrm{cm}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{L}$) due to intraligand $\pi \rightarrow \pi^*$ transition.

3.7. ^{51}V, ^{1}H, and ^{13}C NMR

The ^{51}V NMR spectrum of **C1** presents an intense line at −369.745 ppm suggesting equivalent vanadiums, in agreement with those reported in the literature for vanadium(V) complexes of the coordination number six [17–19].

The ^{1}H NMR of **C1** in DMSO exhibits upfield shifts compared to the free ligand and indicating coordination. The spectrum displays a range of proton resonances of the phenyl between 7 and 7.8 ppm and a singlet around 5 ppm due to the resonance of C–H proton. The signal at 12.13 ppm was assigned to OH.

Similarity between the ^{13}C NMR of H_2L and **C1** in DMSO confirms coordination of ligand to the metal. Literature suggests coordination causes the chemical shift of thione carbon to be larger than other carbons because this atom is bonded to sulfur. The carbon of C=S in the free ligand is at 229.05 ppm, while the corresponding peak of the coordinated ligand is at 219.21 ppm.

Gravimetric analyses of **C1** show that water is lost at 120°C (Found: 4.83%, Calcd: 4.91%), indicating that water is coordinated to vanadium.

On the basis of physical chemical studies and the foregoing discussion, the proposed structure of **C1** is shown in figure 2.

Supplementary material

Full tables of bond lengths and angles, tables of nonhydrogen atomic coordinates, anisotropic thermal parameters for nonhydrogen atoms as well as hydrogen atom parameters are available as supplementary material from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, on request (CCDC deposition number 602396).

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