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Vanadium(III) Dithiophosphate Complex $[V(S_2P(O\text{-}iso\text{-}Pr)_2)_3]$: Synthesis and Structure

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Abstract—The reaction of $[VO(OPr)_3]$ with $(iso\text{-}PrO)_2P(S)SH$ (Pr is *n*-propyl, and *iso*-Pr is isopropyl) followed by the treatment with hexamethyldisilthiane ($Me_3SiSSiMe_3$) affords the vanadium(III) dithiophosphate complex $[V(S_2P(O\text{-}iso\text{-}Pr)_2)_3]$. The structure of the complex is determined by X-ray diffraction analysis (CIF file CCDC 986354).

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INTRODUCTION

As compared to the well developed chemistry of chalcogenide clusters of molybdenum, the chemistry of chalcogenide clusters of its diagonal analog vanadium was studied to a lower extent [1, 2]. The relatively easily accessible clusters with the $\{V_2(\mu\text{-}S_2)_2\}^{4+}$ core were studied fairly well, and the cluster core $\{V_2(\mu\text{-}S_2)_2\}^{4+}$ was coordinated only by bidentate sulfur-containing ligands (dithiocarbamates, dithiocarboxylates, xanthates, and thioxanthates) in all known cases [3–9]. In this work, we studied the possibility of the synthesis of dithiophosphate complexes $[V_2S_4(S_2P(OR)_2)_4]$ from $[VO(OPr)_3]$, prepared in situ dialkyl dithiophosphoric acid, and hexamethyldisilthiane (HMDST) as a sulfidizing agent. It turned out that no sulfide clusters were formed and the reaction resulted in the reduction of vanadium(V) to vanadium(III) to form the dithiophosphate complex $[V(S_2P(O\text{-}iso\text{-}Pr)_2)_3]$.

EXPERIMENTAL

All experiments were carried out in an argon atmosphere using the standard Schlenk techniques. The solvents were purified using standard procedures. The starting reagents from commercial sources (Sigma-Aldrich) were used as received. IR spectra were recorded on a Scimitar FSC-2000 spectrophotometer in KBr pellets. Elemental analysis was carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

Synthesis of $[V(S_2P(O\text{-}iso\text{-}Pr)_2)_3]$ (I). Diphosphorus pentasulfide P_2S_5 (730 mg, 3.3 mmol) was dissolved in isopropanol (5 mL), and $VO(OPr)_3$ (270 μL, 1.1 mmol) was added with stirring. The obtained red solution was treated with HMDST (600 μL, 2.7 mmol), and a crystalline product isolated in several hours was filtered off.

For $C_{18}H_{42}O_6P_3S_6V$

anal. calcd., %:	C, 31.3;	H, 6.1;	S, 27.8.
Found, %:	C, 31.5;	H, 5.7;	S, 27.8.

IR, (ν, cm^{-1}): 2980 s, 2930 m, 1751 w, 1658 w, 1465 m, 1452 m, 1374 s, 1352 m, 1179 m, 1143 m, 1103 m, 1018 s, 968 s, 890 s, 804 m, 786 s, 766 s, 731 m, 638 s, 552 m, 540 m, 499 m, 453 m, 403 w.

X-Ray diffraction analysis. All measurements were carried out using a standard procedure on a Bruker-Nonius X8Apex automated four-circle diffractometer (two-coordinate CCD detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Reflection intensities were measured in the φ and ω scan modes using narrow (0.5°) frames. An absorption correction was applied empirically using the SADABS program [10]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation using the SHELXTL program package [11]. Hydrogen atoms were refined in the rigid body approximation.

The crystallographic characteristics and details of diffraction experiments are given in Table 1. Selected interatomic distances are listed in Table 2. The full information on the studied structure was deposited with the Cambridge Crystallographic Data Centre (CCDC 986354; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

As mentioned above, in the vanadium chemistry, the sulfide cluster groups are stabilized by the coordi-

Table 1. Crystallographic data and details of diffraction experiments for compound **I**

Parameter	Value
FW	690.73
Crystal system	Monoclinic
Space group; Z	$C2/c$; 4
Temperature, K	100
a, Å	10.9169(3)
b, Å	26.5739(9)
c, Å	11.4823(4)
β, deg	92.1330(10)
V, Å^3	3328.76(19)
F(000)	1448
ρ_{calcd}, g/cm^3	1.378
$\mu(MoK_\alpha)$, mm^{-1}	0.847
Crystal size, mm	0.12 × 0.15 × 0.40
T_{min}, T_{max}	0.728, 0.905
Measured reflections	7435
Independent reflections (R_{int})	3236 (0.0157)
Reflections with $I > 2\sigma(I)$	2853
Refinement variables	161
θ_{max}, deg	28.88
R_1 ($I > 2\sigma(I)$)	0.0229
$wR(F^2)$ for all reflections	0.0570
GOOF	1.042
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.302/–0.251

nation of the sulfur-containing ligands, first of all, dithiocarbamates, which are most abundant representatives of ligands, derivatives of dithiocarboxylic acids. It should be noted that complexes of vanadium sulfide clusters with dithiophosphate ligands $(RO)_2PS_2^-$ (Dtp) are nearly absent. We attempted to fill this gap using the reaction of $VO(Dtp)_3$ with sulfidizing agents (H_2S, HMDST). It is known that the reactions of dithiocarbamates $VO(S_2CNEt_2)_3$ and xanthates $VO(S_2COR)_3$ with hydrogen sulfide afford $[V_2S_4(S_2CNEt_2)_4]$ and $[V_2S_4(S_2COEt)_4]$ in high yields [9]. Since compounds $VO(Dtp)_3$ are not mentioned in literature, we attempted to synthesize the initial complex $VO(S_2P(O\text{-}iso\text{-}Pr)_2)_3$ by the reaction of sodium vanadate with $NaS_2P(O\text{-}iso\text{-}Pr)_2$ in the presence of acetic acid using a procedure developed for the synthesis of similar xanthates and dithiocarbamates [9]. However, under these conditions, vanadium(V) is rapidly reduced to vanadium(IV) and, hence, the desired product was not isolated. Then we decided to generate $VO(S_2P(O\text{-}iso\text{-}Pr)_2)_3$ in situ via the reaction

$$\begin{aligned}&VO(OPr)_3 + 3(iso\text{-}PrO)_2P(S)SH\\&= VO(S_2P(O\text{-}iso\text{-}Pr)_2)_3 + 3PrOH,\end{aligned}$$

using the well known fact that phosphorus dithio acids are strong acids. The starting acid $(iso\text{-}PrO)_2P(S)SH$ was obtained from P_4S_{10} and isopropanol and used without isolation. After the addition of $(iso\text{-}PrO)_2P(S)SH$ to $VO(OPr)_3$, HMDST was rapidly added and the solution was left to crystallize. The color of the solution changed to dark brown, and in several hours crystals precipitated that turned out, according to the elemental and X-ray diffraction analyses data, to be the vanadium(III) dithiophosphate complex $[V(S_2P(O\text{-}iso\text{-}C_3H_7)_2)_3]$ (**I**). Thus, in this reaction vanadium(V) was reduced to vanadium(III) without sulfidization, probably, via the scheme

$$\begin{aligned}&VO(S_2P(O\text{-}iso\text{-}Pr)_2)_3 + (Me_3Si)_2S\\&= [V(S_2P(O\text{-}iso\text{-}C_3H_7)_2)_3] + (Me_3Si)_2O + S.\end{aligned}$$

The method described [12] for the synthesis of the diethyl dithiophosphate analog $[V(S_2P(OC_2H_5)_2)_3]$ assumes the use of VCl_3 as a reagent or reflux of $VOSO_4$ with an excess of a solution of the ligand: under such drastic conditions, vanadium(IV) oxidizes sulfur in the dithio acid. HMDST is a stronger reducing and deoxygenating agent due to the formation of strong Si–O bonds.

Most likely, reasons for different behaviors of dithiophosphate, on the one hand, and dithiocarbamates and xanthates, on the other hand, are related to high steric hindrances of dithiophosphate ligands (the phosphorus atom has four substituents, and the carbon atom has three substituents). According to the X-ray diffraction data (figure), the synthesized vanadium(III) diisopropyl dithiophosphate (complex **I**) crystallizes in the same monoclinic crystal system as the known vanadium(III) diethyl dithiophosphate (**II**) (space group $C2/c$, $Z = 4$) [12]. The comparative geometric parameters of two dithiophosphate complexes are given below.

Compound	V–S, Å	P–S, Å	SVS, grad	SPS, grad	θ	Bite
$[V\{S_2P(OC_2H_5)_2\}_3]$ (II)	2.43–2.48	1.97–1.99	81.0–82.4	106.4–108.0	20.8	1.31
$[V\{S_2P(O^iC_3H_7)_2\}_3]$ (I)	2.43–2.50	1.98–2.00	81.0–81.6	105.2–107.6	18.8	1.31

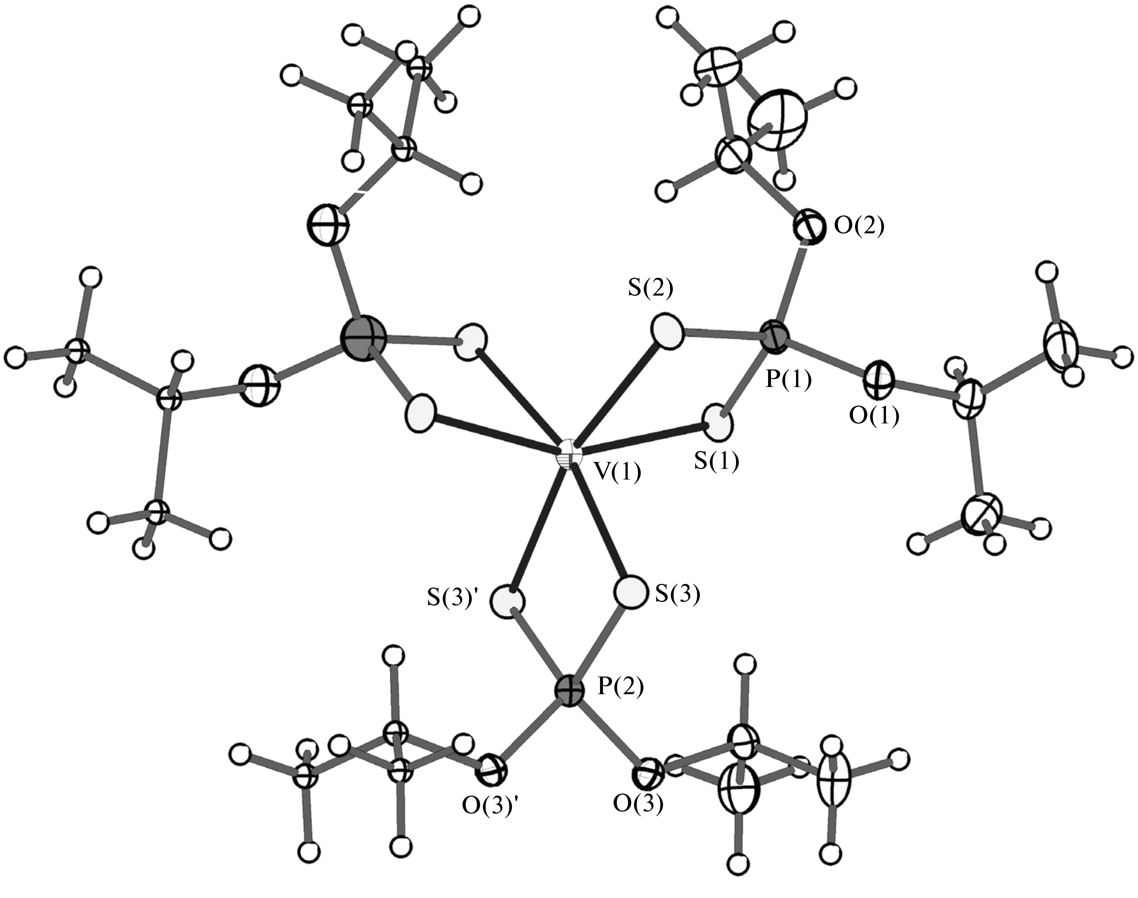
However, the mutual molecular packings in crystals **I** and **II** differ noticeably. In ethyl derivative **II**, the distances between the centers of the molecules range from 8.6 to 10.2 Å, which makes it possible to distin-

Table 2. Selected interatomic distances (Å) in structure **I**

V(1)–S(1)	2.4490(4)	S(3)–P(2)	1.9991(5)
V(1)–S(2)	2.5020(4)	P(1)–O(1)	1.5704(11)
V(1)–S(3)	2.4332(5)	P(1)–O(2)	1.5779(11)
S(1)–P(1)	2.0092(6)	P(2)–O(3)	1.5738(11)
S(2)–P(1)	1.9789(5)		

guish corrugated layers in the arrangement of the centers of the molecules. In isopropyl complex **I**, these distances are averaged from 9.5 to 9.7 Å, which transforms the packing in an almost isotropic one over all three dimensions. The topological analysis results obtained by the TOPOS program [13] show that the mutual arrangement of the centers of gravity in compound **II** corresponds to the hexagonal close packing, whereas in compound **I** the packing is distorted and exhibits the topological type chb/CrB according to the O'Keeffe classification (http://rcsr.anu.edu.au/).

As can be seen from the data presented above, the V–S, P–S, and S–P–S distances in both complexes are nearly identical. The SPS angle in complex **I** is slightly more acute that that in complex **II**, which is due to higher steric requirements of the isopropyl substituents compared to the ethyl substituents. The θ angle determines the degree of deviation of the geometry of an octahedron (which is considered as a trigonal antiprism) to the trigonal prismatic geometry. For a trigonal prism, the θ angle (half an angle between two opposite triangular faces) is zero, whereas this angle is 30° for an ideal octahedron. The presence of chelate ligands, as a rule, decreases the θ angle by 5°–15°. The degree of distortion depends on another parameter *b* designated by the term "bite" of ligand. The "bite" is measured by the parameter that is calculated as a ratio of the distance between two donor atoms of the chelating ligand to the M–L distance. The higher *b*, the larger θ; i.e., the smaller the distortion of the octahedron [14]. The parameters of both dithiophosphate complexes obey the observed correlation and are close to those for [Cr($S_2P(OEt)_2)_3$] [15]. Interestingly, the value of *b* for the dithiophosphate ligands exceeds that for dithiocarbamates (1.27–1.12) and approaches that



Molecular structure in compound **I** (ellipsoids of atomic shifts with 50% probability).

for the complexes with five-membered chelates: En, Phen, and Bipy (1.27–1.33), which additionally emphasizes the difference in steric requirements between dithiocarbamates and dithiophosphates.

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