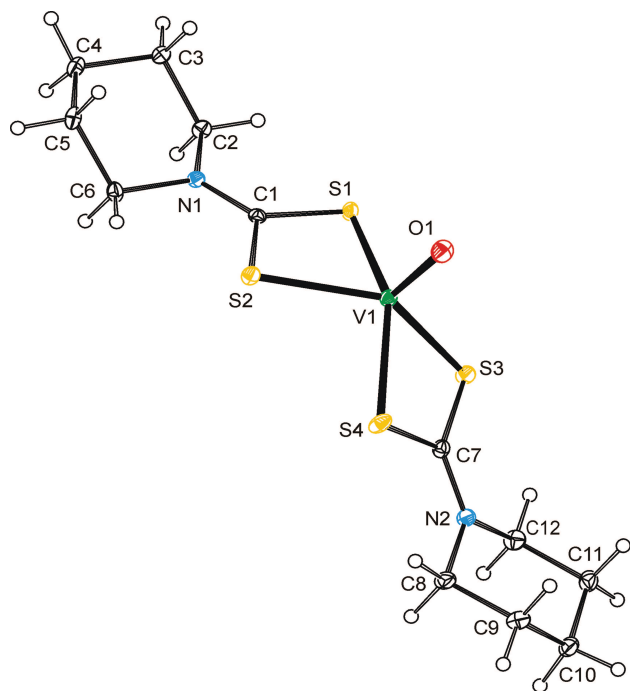


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Crystal structure of oxidobis(piperidine-1-carbodithioato- $\kappa^2 S, S'$)vanadium(IV), $C_{12}H_{20}N_2OS_4V$



Abstract

$C_{12}H_{20}N_2OS_4V$, triclinic, $P\bar{1}$ (no. 2), $a = 7.0892(2)$ Å, $b = 8.8797(2)$ Å, $c = 13.8486(3)$ Å, $\alpha = 87.1010(10)^\circ$, $\beta = 82.3160(10)^\circ$, $\gamma = 71.4110(10)^\circ$, $V = 818.84(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0249$, $wR_{ref}(F^2) = 0.0707$, $T = 150(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters, respectively.

Table 1: Data collection and handling.

Crystal:	Green prism
Size:	0.30 × 0.27 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.11 mm ⁻¹
Diffractometer, scan mode:	Kappa Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	17432, 3755, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3414
$N(param)_{refined}$:	182
Programs:	Bruker [1], PLATON [2], SHELX [3]

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Source of material

The vanadyl dithiocarbamate complex was prepared according to literature procedure [4]. Under a nitrogen atmosphere, oxidovanadium(IV) sulfate (1.5 g, 6.9 mmol) was dissolved in deionized water (10 mL) and treated by sodium piperidine-1-carbodithioate (2.53 g, 13.8 mmol) in a 1:1 mixture of deionized water-ethanol (20 mL). The reaction mixture was stirred for 60 min while fine green precipitate was obtained. All solvents were filtered off and the remaining powder was purified using a Soxhlet extractor (2 cycles – diethylether to remove other impurities, dichloromethane for recrystallization). The resulting product was vacuum dried to give grey-green powder (1.11 g; yield 41.6%).

The single crystal was obtained by slow diffusion of hexane into a saturated solution of title complex in

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.2290(3)	0.4588(2)	0.16031(12)	0.0136(3)
C2	0.3778(3)	0.2406(2)	0.04422(13)	0.0167(4)
H2A	0.439807	0.135674	0.074027	0.020*
H2B	0.482136	0.293318	0.028912	0.020*
C3	0.2993(3)	0.2179(2)	-0.04903(14)	0.0188(4)
H3A	0.409628	0.147035	-0.093244	0.023*
H3B	0.250277	0.321801	-0.082363	0.023*
C4	0.1292(3)	0.1461(2)	-0.02727(15)	0.0218(4)
H4A	0.076247	0.136277	-0.088477	0.026*
H4B	0.180111	0.038559	0.001403	0.026*
C5	-0.0379(3)	0.2519(2)	0.04369(15)	0.0208(4)
H5A	-0.097162	0.355873	0.012231	0.025*
H5B	-0.144755	0.202010	0.060365	0.025*
C6	0.0409(3)	0.2774(2)	0.13628(14)	0.0183(4)
H6A	-0.067455	0.354145	0.178302	0.022*
H6B	0.082610	0.175593	0.172544	0.022*
C7	0.3656(3)	0.7371(2)	0.45494(13)	0.0157(4)
C8	0.2620(3)	0.7993(3)	0.62803(14)	0.0227(4)
H8A	0.272599	0.709082	0.674268	0.027*
H8B	0.125969	0.832947	0.607555	0.027*
C9	0.2928(3)	0.9358(2)	0.67804(15)	0.0228(4)
H9A	0.195490	0.964245	0.737718	0.027*
H9B	0.267610	1.029794	0.634146	0.027*
C10	0.5052(3)	0.8920(2)	0.70500(14)	0.0222(4)
H10A	0.524606	0.985406	0.733312	0.027*
H10B	0.525708	0.806007	0.754635	0.027*
C11	0.6575(3)	0.8374(2)	0.61538(15)	0.0226(4)
H11A	0.794238	0.800834	0.634988	0.027*
H11B	0.648512	0.928064	0.569658	0.027*
C12	0.6222(3)	0.7032(2)	0.56407(15)	0.0205(4)
H12A	0.714844	0.677803	0.502713	0.025*
H12B	0.650772	0.606990	0.606072	0.025*
N1	0.2133(2)	0.33817(18)	0.11385(11)	0.0143(3)
N2	0.4131(2)	0.74806(19)	0.54210(11)	0.0172(3)
O1	0.2133(2)	0.88143(15)	0.20516(11)	0.0251(3)
S1	0.44321(7)	0.51475(5)	0.14671(3)	0.01716(11)
S2	0.03816(7)	0.57162(5)	0.24339(3)	0.01768(11)
S3	0.54246(7)	0.67672(6)	0.35371(3)	0.01816(11)
S4	0.12117(7)	0.77960(6)	0.43065(4)	0.02207(12)
V1	0.26244(5)	0.71744(3)	0.26431(2)	0.01483(8)

dichloromethane. Complex [VO(S₂CN(CH₂)₅)₂] characterization data: **Anal. Calcd.** for (C₁₂H₂₀N₂OS₄V): C, 37.21%; H, 5.21%; N, 7.24%; S, 33.05%. Found: C, 37.05%; H, 5.32%; N, 7.19%; S, 33.00%. **EPR spectrum** (solution, CH₂Cl₂): $A_{iso} = 89.1$ G; $g_{iso} = 1.979$. **FT-IR spectrum** (ATR-C): 3356w, 3078w, 2996w, 2938m, 2852w, 1669m, 1639w, 1614w, 1479m, 1431m, 1406m, 1359w, 1350w, 1278w, 1240s, 1227m, 1202s, 1116s, 1106s, 973vs, 888m, 852m, 818m, 664m, 646s, 624s, 603s, 585s, 548s, 513s, 476m, 456m, 432m.

Experimental details

Crystal appeared to be two-component non-merohedral twin, with refined volume ratio of 0.507:0.492. Twin law: $-1\ 0\ 0$; $-0.469\ 0.465\ -0.538$; $0.459\ -1.430\ -0.473$. Hydrogen atoms of piperidine were included in their calculated positions (HFIX 23) and further refined as riding atoms (SHELX [3]) with the U_{iso} values set to $1.2U_{eq}$ of their bonding carbon atoms. The structural drawing and all numerical parameters discussed below were obtained with a recent version of the PLATON program [2].

Comment

In general, dithiocarbamates are widely studied due to their interesting chemical and physical properties. For more than 80 years, they are used in agriculture as pesticides and fungicides [5, 6]. Their strong chelating effect toward metal ions predetermines them as suitable radical precursors in organic chemistry [7]. The dithiocarbamate ligands are further investigated for their antibacterial and antifungal properties [5].

Oxidovanadium(IV) compounds are known as catalysts of various oxygen-transfer reactions. Simple bis(pentane-2, 4-dionato- κ^2O, O')-oxidovanadium(IV) works as potent catalyst for the oxidation of hydrocarbons, alcohols and sulfides [8–10]. Its crystal structure is well known for long time [11] and the number of its derivatives, characterized with X-ray crystal structure analysis, is still increasing [12, 13]. Due to the stable redox system V(IV)/V(V), oxidovanadium compounds are promising catalysts of autoxidation reactions, which have found the application in paint-producing industry as the ecologically sustainable alternative to toxic cobalt-based alkyd driers [14–16].

So far, only few oxidovanadium dithiocarbamate complexes have been structurally characterized by X-ray crystallography, namely diethyldithiocarbamate compounds [V^{IV}O(S₂CNEt₂)₂] [4, 17] and [V^VO(S₂CNEt₂)₃] [18].

Here, we report the first crystal structure for oxidovanadium(IV) compound bearing cyclic dithiocarbamate ligands, [VO(S₂CN(CH₂)₅)₂], which was determined by single crystal X-ray diffraction analysis. The coordination polyhedron of the title compound forms a square-pyramid with oxygen atom in apical position while the basal plane is occupied with sulfur atoms of two κ^2 -coordinated cyclic dithiocarbamates (figure). The basal plane of the square pyramid is slightly twisted as documented by S1-S2-S3-S4 dihedral angle of 168.19(2)°. The vanadium-oxygen bond, with a length typical for oxidovanadium(IV) complexes [1.5954(12) Å], is nearly perpendicular to the basal plane [$\alpha = 89.40(5)^\circ$] and exceeds it for 0.794(1) Å. Both dithiocarbamate ligands are symmetrically coordinated to vanadium as evident from narrow range of the vanadium-sulfur bond distances [V1–S1 = 2.4086(6) Å, V1–S2 2.4005(6) Å, V1–S3 2.3997(6) Å,

V1–S4 2.4027(6) Å]. The bond distances are similar to the values previously reported for the diethyl derivative [V^{IV}O(S₂CNET₂)₂], [2.3945(14)–2.4138(14) Å] [17]. We note that core of the dithiocarbamate ligand is planar with the vanadium located in this plane [V1–P1(S1,S2,C1,N1) = 0.002(1) Å, V1–P1(S3,S4,C7,N2) = 0.054(1) Å]. Piperidine rings of the ligands take the usual chair conformation.

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References

- BRUKER. SAINT. Version 8.23B., Bruker AXS Inc., Madison, WI, USA (2013).
- Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7–13.
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
- Henrick, K.; Raston, C. L.; White, A. H.: Crystal structure of bis(diethylthiocarbamato)oxovanadium(IV). *J. Chem. Soc., Dalton Trans.* (1976) 26–28.
- Kanchi, S.; Singh, P.; Bisetty, K.: Dithiocarbamates as hazardous remediation agent: a critical review on progress in environmental chemistry for inorganic species studies of 20th century. *Arab. J. Chem.* **7** (2014) 11–25.
- Carta, F.; Aggarwal, M.; Maresca, A.; Scozzafava, A.; McKenna, R.; Masini, E.; Supuran, C. T.: Dithiocarbamates strongly inhibit carbonic anhydrases and show antiglaucoma action in vivo. *J. Med. Chem.* **55** (2012) 1721–1730.
- Shahvelayati, A. S.; Yavari, I.; Adhami, F.; Sanaei shora, T.: An efficient synthesis of dithiocarbamates from primary amines, CS₂ and maleic anhydride. *Iran. J. Org. Chem.* **4** (2009) 244–247.
- Pokutsa, A.; Kubaj, Y.; Zaborovskiy, A.; Maksym, D.; Muzart, J.; Sobkowiak, A.: The effect of oxalic acid and glyoxal on the VO(*acac*)₂-catalyzed cyclohexane oxidation with H₂O₂. *Appl. Catal. A* **390** (2010) 190–194.
- Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Kawamura, T.; Uemura, S.: Oxovanadium complex-catalyzed aerobic oxidation of propargylic alcohols. *J. Org. Chem.* **67** (2002) 6718–6724.
- Cogan, D. A.; Liu, G.; Kim, K.; Backes, B. J.; Ellman, J. A.: Catalytic asymmetric oxidation of *tert*-butyl disulfide. Synthesis of *tert*-butanesulfinamides, *tert*-butyl sulfoxides, and *tert*-butanesulfinimines. *J. Am. Chem. Soc.* **120** (1998) 8011–8019.
- Mahmoudkhani, A. H.; Casari, B.; Langer, V.: Refinement of the crystal structure of bis(2,4-pentanedionato-*O,O'*)-oxovanadium(IV) at 183 K, VO(C₅H₇O₂)₂. *Z. Kristallogr. NCS* **216** (2001) 205–206.
- Yin, N.; Wu, Q.; Zhang, H.-Q.; Zhang, Q.-Y.: Crystal structure of (acetylacetonato-κ²O,*O'*)-(2-amino-6-chlorobenzoato-κO)-oxido(1,10-phenanthroline-κ²N,*N'*)vanadium(IV)-trichloromethane (1/1). *Z. Kristallogr. NCS* **232** (2017) 1045–1047.
- Preininger, O.; Charamzová, I.; Vinklársek, J.; Císařová, I.; Honzík, J.: Oxovanadium(IV) complexes bearing substituted pentane-2,4-dionate ligands: synthesis, structure and drying activity in solvent-borne alkyd paints. *Inorg. Chim. Acta* **462** (2017) 16–22.
- Charamzová, I.; Vinklársek, J.; Kalenda, P.; Honzík, J.: Application of oxovanadium complex stabilized by *N,N,N*-chelating ligand in air-drying paints. *Coatings* **8** (2018) 204.
- Preininger, O.; Vinklársek, J.; Honzík, J.; Mikysek, T.; Erben, M.: A promising drying activity of environmentally friendly oxovanadium(IV) complexes in air-drying paints. *Prog. Org. Coat.* **88** (2015) 191–198.
- Preininger, O.; Honzík, J.; Kalenda, P.; Vinklársek, J.: Drying activity of oxovanadium(IV) 2-ethylhexanoate in solvent borne alkyd paints. *J. Coat. Technol. Res.* **13** (2016) 479–487.
- Atzori, M.; Tesi, L.; Benci, S.; Lunghi, A.; Righini, R.; Taschin, A.; Torre, R.; Sorace, L.; Sessoli, R.: Spin dynamics and low energy vibrations: insights from vanadyl-based potential molecular qubits. *J. Am. Chem. Soc.* **139** (2017) 4338–4341.
- Dewan, J. C.; Kepert, D. L.; Raston, C. L.; Taylor, D.; White, A. H.; Maslen, E. N.: Crystal structures of tris(*NN*-diethylthiocarbamato)oxo-niobium(v) and -vanadium(v). *J. Chem. Soc., Dalton Trans.* (1973) 2082–2086.