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Note

Bis(2-mercaptopyridine-*N*-oxide)oxovanadium(IV): synthesis, structure and its conversion to the dichloro complex

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Abstract

Reaction of $VOCl_2(thf)_2$ with two equivalents of the sodium salt of mercaptopyridine-*N*-oxide yields $[VO(C_5H_4NOS)_2]$ (**1**). **1** crystallizes in the orthorhombic space group *Pbca* with the following cell dimensions: $a = 11.148(2)$, $b = 14.103(2)$, $c = 15.258(3)$ Å, $Z = 8$. The molecule possesses square pyramidal geometry with a V=O double bond length of 1.597(5) Å and average V–S and V–O distances of 2.375 and 1.964 Å, respectively. The vanadium atom is displaced from the best plane spanned by the four ligand donor atoms by 0.644(1) Å. Reaction of **1** with $SOCl_2$ affords the dichloro complex *trans*-$[VCl_2(C_5H_4NOS)_2]$ (**2**).

Key words: Crystal structures; Vanadium complexes; Oxo complexes; Amine *N*-oxide complexes

Introduction

We are interested, in the context of investigations into model systems for biologically relevant vanadium compounds [1], in synthetic strategies aiming at the substitution of chloro ligands in chlorovanadium compounds by other anionic, preferentially biomimetic ligands [2]. We describe here, as a precursor compound for a suitable chloro complex, an improved synthesis and the structure of the title compound, carrying a ligand system with the O,S-donor set.

2-Mercaptopyridine-*N*-oxide (HL) coordinates to metal ions out of its thiolate form [3]. In aqueous solution, it forms complexes with V^{III}, V^{IV} and V^V [4, 5], with the V^{IV} complex being the only stable one under aerobic conditions and in the presence of an excess of the ligand. The proposed stoichiometry for this complex, VOL_2 (**1**) [4–6] has now been confirmed. **1** has been obtained as a violet, crystalline compound from the reaction of $VOCl_2(thf)_2$ with two equivalents of NaL[**]. The reaction between $VCl_3(thf)_3$ and NaL in the molar ratio 1:3 and in the presence of air also yields **1**. Crystals suitable for an X-ray structure analysis[†] have been obtained from a solution of **1** in CH_2Cl_2 layered with hexane. Figure 1 shows the molecular structure of **1**; selected bonding parameters are collated in the legend of Fig. 1, fractional coordinates and thermal factors in Table 1.

1 forms a tetragonal pyramid with the doubly bonded oxygen in the apex. The vanadium atom is displaced from the best plane formed by the mutually *cis* standing two sulfur and oxygen donors by 0.644(1) Å towards the apical O. This compares to a corresponding displacement of 0.608(1) Å in [VO(tsalen)] (tsalen = *N*,*N*′-ethylene-bis(thiosalicylideneiminate(2−))) [7]. The reason for the more pronounced pyramidal geometry of

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[**] *Experimental details.* **1**: A solution of 0.71 g (2.52 mmol) of $VOCl_2(thf)_2$ [18] in 30 ml of thf was treated with 0.75 g (5.04 mmol) of the sodium salt of 2-mercaptopyridine-*N*-oxide and stirred for 24 h. The resulting violet, air-stable precipitate was filtered off, washed consecutively with 50 ml portions of H_2O, H_2O/EtOH (1:1), Et_2O and pentane, and dried *in vacuo*. Yield 0.69 g (85%). Layering a solution of **1** in CH_2Cl_2 with hexane afforded violet crystals within four days. IR (KBr): 1238 (ν(NO)), 984 (ν(V=O)), 826 (δ(NO)), 711 (ν(CS)), 445 (ν(VO)) cm^{-1}. IR (nujol): 397 (ν_{as}(VS)), 342 (ν_s(VS)) cm^{-1}. *Anal.* Calc. for $C_{10}H_8N_2O_3S_2V$ (319.26): C, 37.62; H, 2.53; N, 8.77; V, 15.96. Found: C, 36.98; H, 2.63; N, 8.85; V, 16.28%. **2**: A suspension of 0.38 g (1.19 mmol) of **1** in toluene was treated, by dropwise addition, with 127 μl of $SOCl_2$. The colour of the reaction mixture changed from violet to dark green. After stirring for 4 h, the precipitate was filtered off, washed with 20 ml of toluene and with three 10 ml portions of pentane, and dried under high vacuum. Yield 0.33 g (74%). IR (KBr): 1247 (ν(NO)), 836 (δ(NO)), 715 (ν(CS)), 444 (ν(VO)) cm^{-1}. IR (nujol): 390 (ν_{as}(VS)), 361 (ν(VCl)), 348 (ν_s(VS)) cm^{-1}. *Anal.* Calc. for $C_{10}H_8Cl_2N_2O_2S_2V$ (374.17): C, 32.10; H, 2.16; N, 7.49; V, 13.61. Found: C, 32.79; H, 2.43; N, 7.80; V, 13.99%.

[†] Crystal structure analysis of **1**: crystal dimensions 0.2 × 0.2 × 0.3 mm, orthorhombic, space group *Pbca*; $a = 11.148(2)$, $b = 14.103(2)$, $c = 15.258(3)$ Å, $Z = 8$, $V = 2398.9$ Å^3, ρ(calc.) 1.77 g cm^{-3}; Enraf-Nonius-CAD4 diffractometer (Cu Kα; $\lambda = 1.54178$ Å, graphite monochromator, 2θ-scan mode, $T = 173$ K), 2θ range 4.5–153°; 2932 measured reflections (*hkl* range: $0 < h < 14$, $0 < k < 17$, $0 < l < 19$), 1980 of which were significant ($F_0 > 4\sigma(F_0)$). $R_{int} = 4.78\%$. The structure was solved by direct methods with the SHELXTL PLUS programme system. An absorption correction was not applied. H atoms were calculated into ideal positions and included in the final FMLS refinement. $R = 0.0673$, $R_w = 0.0757$, reflex-to-parameter ratio 12.1; residual electron density max./min. 0.88/−0.68 e Å^{-3}.

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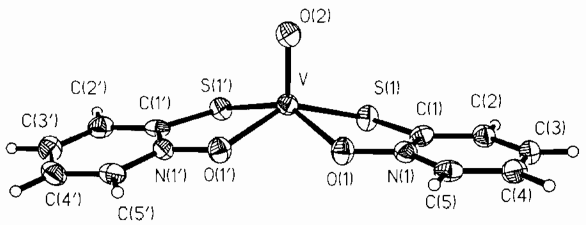

Fig. 1. Molecular structure of $VO(C_6H_4NOS)_2$ (**1**), showing 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): V–S1 2.360(2), V–S1′ 2.390(2), V–O1 1.970(5), V–O1′ 1.958(5), V–O2 1.597(5), S1–C1 1.719(6), S1′–C1′ 1.732(7), O1–N1 1.353(7), O1′–N1′ 1.333(7), N1–C1 1.376(8), N1′–C1′ 1.355(8); S1–V–S1′ 91.2(1), S1–V–O1 82.8(1), S1′–V–O1′ 81.6(1), S1–Vl–O1′ 142.2(1), S1′–V–O1 147.7(1), O1–Vl–O1′ 83.8(2), S1–V–O2 107.0(2), S1′–V–O2 105.6(2), O1–V–O2 106.5(2), O1′–V–O2 110.7(2), V–S1–C1 95.5(2), V–S1′–C1′ 96.0(2), V–O1–N1 118.5(4), V–O1′–N1′ 120.3(4).

TABLE 1. Atomic coordinates and equivalent thermal displacement factors (Å^2) U_{eq} for $VO(C_6H_4NOS)_2$ (**1**)

Atom	x	y	z	U_{eq}
V	0.1630(1)	0.0958(1)	0.0807(1)	0.0233(3)
S1	0.1711(2)	−0.0699(1)	0.0596(1)	0.0280(5)
S1′	0.2445(2)	0.1232(1)	−0.0620(1)	0.0272(4)
O1	0.0216(4)	0.0633(3)	0.1520(3)	0.028(1)
O1′	0.0690(4)	0.2082(3)	0.0499(3)	0.028(1)
O2	0.2676(5)	0.1224(4)	0.1478(3)	0.035(2)
N1	0.0119(5)	−0.0261(4)	0.1835(3)	0.025(2)
N2	0.1045(5)	0.2649(4)	−0.0150(3)	0.023(2)
C1	0.0789(6)	−0.0974(5)	0.1463(4)	0.025(2)
C2	0.0675(6)	−0.1883(5)	0.1831(4)	0.027(2)
C3	−0.0092(7)	−0.2042(5)	0.2518(5)	0.031(2)
C4	−0.0778(6)	−0.1301(5)	0.2848(4)	0.031(2)
C5	−0.0657(6)	−0.0404(5)	0.2495(4)	0.027(2)
C1′	0.1902(5)	0.2377(5)	0.0727(4)	0.024(2)
C2′	0.2255(6)	0.3024(5)	−0.1370(4)	0.030(2)
C3′	0.1696(7)	0.3893(5)	−0.1438(4)	0.032(2)
C4′	0.0792(6)	0.4127(5)	−0.0867(4)	0.031(2)
C5′	0.0467(6)	0.3499(5)	−0.0219(4)	0.028(2)

the $\{VS_2O_2\}$ moiety in **1** may be the greater flexibility of L^- as compared to tsalen. In the anion $[VO(edt)_2]^{2-}$ (edt = ethane-1,2-dithiolate(2 −)), with an even more flexible ligand, the distance of the vanadium ion to the basal plane amounts to 0.668 Å [8]. d(V=O) in **1** (1.597(5) Å) lies within the V=O double bond range observed with complexes containing similar donor sets (e.g. [VO(tsalen)]: d(V=O) = 1.598(6) Å [7, 9]). d(V–O1) and d(V–O1′) are 1.958(5) and 1.970(5) Å and hence about the same as, for example, d(V–O) = 1.97 Å in $[VO(acac)_2]$ [10]. The d(V–S) values in **1** (2.360(2) and 2.390(2) Å) compare to those in [VO(tsalen)] (2.346 Å) and $[VO(edt)_2]^{2-}$ (2.378 Å). The average angle V–S–C in **1** (95.8°) indicates that the bonding orbitals of the sulfur atoms predominantly exhibit p character, while the mean angle V–O–N (119.4) stresses the sp^2 character of the bonding orbitals on the oxygens. The aromatic nature and hence the planarity of L^- remains intact on coordination. All bonding parameters in **1** are very much the same as in $[NiL_2]$ [11] and $[ZnL_2]$ [12]. The closest intermolecular contact in **1**, 4.311 Å, is between V and S, with the sulfur in '*trans*' position to the apical oxygen of the adjacent molecule.

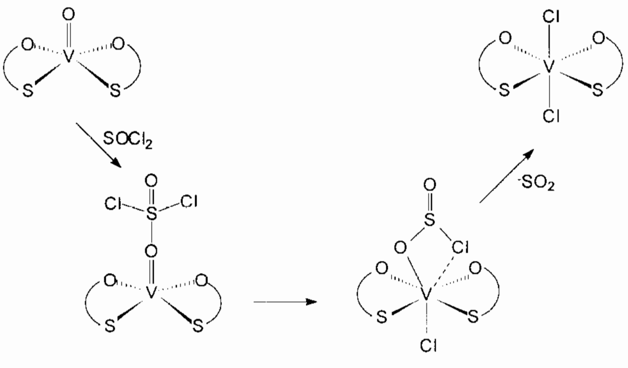

Fig. 2. Mechanism of the substitution of O by two Cl.

The IR spectrum of **1** shows, in addition to the strong ν(V=O) at 984 cm^{-1}, characteristic metal–ligand stretches at 445 (ν(V–O)), 397 ($\nu(V\text{–}S)_{as}$) and 342 ($\nu(V\text{–}S)_s$) cm^{-1}. ν(N–O) = 1238 cm^{-1} is shifted to higher wave numbers by 20 cm^{-1} with respect to NaL; it is in the same range as ν(N–O) in other V^{IV} complexes containing N-oxidic donor functions [13]. ν(C–S) in **1** (711 cm^{-1}) is practically the same as in NaL (708 cm^{-1}). Similar results have been reported for other complexes with L^- [14]. The magnetic susceptibility of **1**, 1.68 BM, is close to the spin-only value of 1.73 BM to be expected for a V^{IV} complex.

When **1**, dissolved in toluene is treated with excess $SOCl_2$, the vanadyl oxygen is substituted by two chlorines to afford $[VCl_2L_2]$ (**2**) (see footnote on p. 213). In the IR spectrum, the ν(V=O) disappears and an additional band at 361 cm^{-1} is observed, attributable to $\nu(V\text{–}Cl)_{as}$ in a complex with *trans* standing Cl ligands [15, 16]. The magnetic moment for **2** is 1.82 BM. For the reaction between thionyl chloride and vanadyl complexes carrying flexible ligands, a mechanism had been proposed (Fig. 2), in which the definite step, the elimination of SO_2 from a seven-coordinated intermediate, in fact leads to a *trans* configuration [17].

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References

1 (a) D. Rehder, *Angew. Chem., 103* (1991) 152–172; *Angew. Chem., Int. Ed. Engl., 30* (1991), 148–167; (b) A. Butler and C.J. Carrano, *Coord. Chem. Rev., 109* (1991) 61–105; (c) R. Wever and K. Kustin, *Adv. Inorg. Chem., 35* (1990) 81–115.

2 (a) R. Seangprasertkij and T. Riechel, *Inorg. Chem., 25* (1986) 3121–3124; (b) A. Hills, D.L. Hughes, G.J. Leigh and J.R. Sanders, *J. Chem. Soc., Dalton Trans.,* (1991) 325–329; (c) J.G. Reynolds, S.C. Sendlinger, A.M. Murray, J.C. Huffman and G. Christou, *Angew. Chem., 104* (1992) 1275–1277; *Angew. Chem., Int. Ed. Engl., 31* (1992) 1253–1255; (d) G. Henkel, B. Krebs and W. Schmidt, *Angew. Chem., 104* (1992) 1380–1382; *Angew. Chem., Ind. Ed. Engl., 31* (1992) 1366–1368.

3 M.A. Robinson, *J. Inorg. Nucl. Chem., 26* (1964) 1277–1281.

4 H.J. Friese and F. Umland, *Fresenius'Z. Anal. Chem., 287* (1977) 298–303.

5 B. Steinbrech and K.H. König, *Fresenius'Z. Anal. Chem., 316* (1983) 465–471.

6 F.J. Higes-Rolando, A. Perez-Florindo and C. Valenzuela-Calahorro, *Thermochim. Acta, 186* (1991) 43–52.

7 J.C. Dutton, G.D. Fallon and K.S. Murray, *Inorg. Chem., 27* (1988) 34–38.

8 (a) R.W. Wiggins, J.C. Huffman and G. Christou, *J. Chem. Soc., Chem. Commun.,* (1983) 1313; (b) J.K. Money, J.C. Huffman and G. Christou, *Inorg. Chem., 24* (1985) 3297.

9 N.V. Gerbelen, V.B. Arion, Y.A. Simonov, P.N. Bourosh, A.A. Dvorkin and K.M. Indrichan, *Russ. J. Inorg. Chem. (Engl. Transl.), 35* (1990) 515–519.

10 R.P. Dodge, D.H. Templeton and A. Zalkin, *J. Chem. Phys., 35* (1961) 55–67.

11 X. Chen, Y. Hu, D. Xu, L. Weng and B. Kang, *Polyhedron, 23* (1991) 2651–2657.

12 B.L. Barnett, H.C. Kretschmar and F.A. Hartman, *Inorg. Chem., 16* (1977) 1834–1838.

13 S.N. Choi, Y.I. Kim, Y.B. Shim, H.S. Choo and Y.J. Kim, *Bull. Korean Chem. Soc., 10* (1989) 138–142.

14 D.X. West and C.A. Frank, *J. Inorg. Nucl. Chem., 41* (1979) 49–53.

15 R.B. Von Dreele and R.C. Fay, *J. Am. Chem. Soc., 94* (1972) 7935–7936.

16 J.G. Reynolds, E.L. Jones, J.C. Huffman and G. Christou, *Polyhedron, 12* (1993) 407–414.

17 M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem., 18* (1979) 2401–2404.

18 H. Tietz, K. Schwetlick and G. Kreisel, *Z. Chem., 25* (1985) 290–291.