Thio-Ligation to Vanadium: The *NSSN* and *S'N'O* Donor Sets (N = Pyridine, N' = Enamine; S = Thioether, S' = Thiolate)☆

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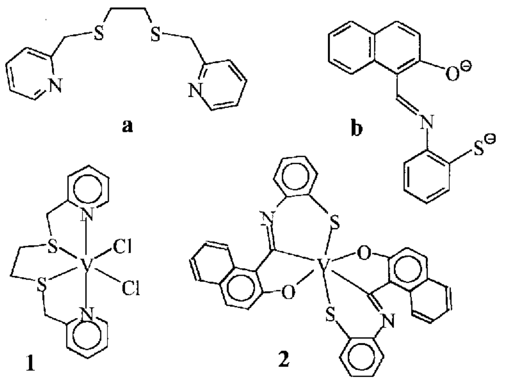
The tetradentate, neutral disulfide [bis(thioether)] ligand 1,6-bis(*o*-pyridyl)-2,4-dithiahexane, *NSSN*, reacts with $[VCl_2(tmeda)_2]$ to form the octahedral (all-*cis*; C_{2v}-symmetric) complex $[VCl_2(NSSN)]$ **1**, the first low-valent vanadium complex in which the thio functions are exclusively organic sulfides. Treatment of $[VOCl_2(thf)_2]$ with *o*-mercaptoaniline, followed by reaction with *o*-hydroxynaphthaldehyde yields the non-oxo V^{IV} complex $[V(S'N'O)_2]$ **2**, derived from the Schiff base H*S'N'O*H, where *O* and *S'* are phenolate and thiophenolate functions, respectively, and *N'* is the Schiff base (enamine) nitrogen. Complex **2**, with the ligands in a distorted trigonal-antiprismatic array, is a rare example of a structurally characterized complex where the Schiff base is preserved at the expense of its thiazoline tautomeric form.

Introduction

Investigations into the thio-ligation of vanadium are of interest for several reasons: Firstly, low-valent vanadium coordinated to, inter alia, sulfide has been discovered in a vanadium nitrogenase, which is expressed in free-living nitrogen-fixing bacteria such as *Azotobacter*[1] alongside the more common molybdenum analogue. Secondly, vanadium plays a role in the redox inhibition of certain enzymes with a thiol group (cysteine) in their active site[2], such as glyceraldehyde 3-phosphate dehydrogenase[3], suggesting coordination of vanadium prior to, or concomitantly with, the oxidation of thiol to disulfide. Thirdly, the presence of vanadyl porphyrins and thiophenogenic compounds in crude oil leads to the formation of vanadium sulfide during processing of the oil (e.g. in the hydrodesulfurization process), possibly via intermediates in which vanadium is linked to thiophene or a related compound[4]. Finally, the potential of vanadium complexes with *ON'O* and *ON'N'O* donor sets (where *O* is a phenolate or alcoholate and *N'* is an enamine) to act as catalysts in the in vitro (enantioselective) peroxide oxidation of organic sulfides to sulfoxides[5] again suggests an active intermediate in which the sulfide (and sulfoxide) coordinate to the vanadium centre[6]. The latter process is of relevance in the context of enantioselective enzymatic oxidation of sulfides (including thiophenes) to sulfoxides[7].

Complexes of vanadium containing thio ligands are still scarce (see refs.[8] and [9] for overviews). In this study, we have investigated the coordination properties of two ligands that have not previously been employed in vanadium chemistry, and indeed, have not been extensively used as ligand systems for other transition metal ions. One of the ligands, the non-cyclic tetradentate 1,6-bis(*o*-pyridyl)-2,4-dithiahexane, *NSSN* (**a** in Scheme 1), is a neutral ligand that contains two central sulfides (thioether functions) and two terminal pyridines. The second ligand, a Schiff base dianion (*S'N'O*, **b** in Scheme 1) derived from *o*-hydroxynaphthaldehyde and *o*-mercaptoaniline becomes stabilized upon coordination to vanadium. Schematic drawings of the complexes $[V(NSSN)Cl_2]$ (**1**) and $[V(S'N'O)_2]$ (**2**) formed with these ligands are also shown in Scheme 1.

Scheme 1



Results and Discussion

Complex **1** was prepared by the reaction of $[VCl_2(tmeda)_2]$ (tmeda = tetramethylethylenediamine) with the ligand **a** in boiling THF. A structure determination of crystals of $\mathbf{1} \cdot CH_2Cl_2$, obtained from a saturated dichloromethane solution, revealed an octahedral arrangement of the ligand sphere with the two chlorines in a *cis* orientation and an overall C_{2v} symmetry; cf. Figure 1. Distortions from ideal octahedral geometry were apparent, attributable to strain resulting from the bite angles of the tetradentate bis-

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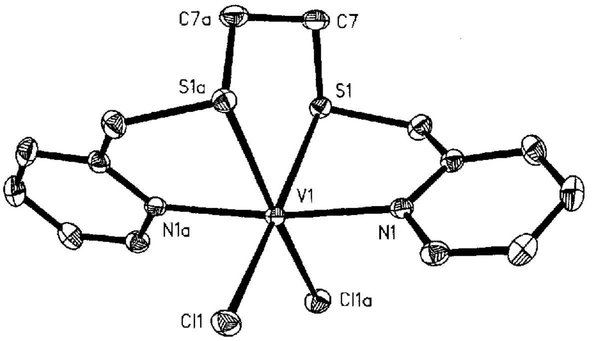
(pyridine)disulfide ligand [N−V−S = 79.86(7), S−V−S = 82.78(4)°]. As a consequence, the N−V−N axis shows a deviation from linearity [172.3(1)°] and the Cl−V−Cl angle is rather wide at 101.33(4)°. A similar situation has been reported for [Ni(*NSSN*)(NCMe)$_2$]$^{2+}$[10] and for [V(*S'SSS'*)(tmeda)][11].

Figure 1. ORTEP drawing, showing the 50% probability ellipsoids, of [VCl$_2$(*NSSN*)] (**1**)[a]



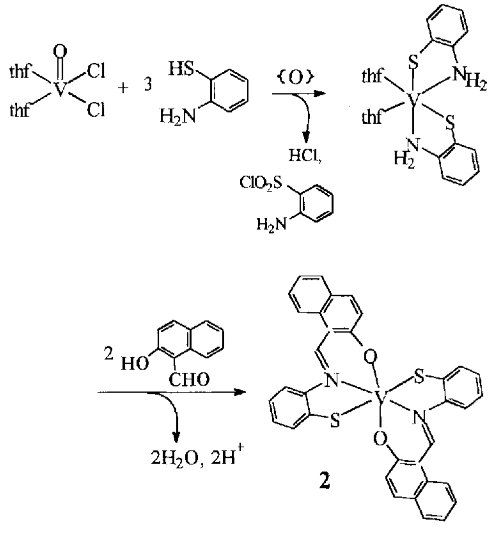
[a] Selected bond lengths [Å] and bond angles[°]: V−Cl 2.4644(8), V−N 2.188(2), V−S 2.5057(8), S−C6 1.804(3), S−C7 1.822(3), C5−C6 1.512(4); N1−V−S1 79.86(7), N1−V−Cl1 96.62(7), S1−V−Cl1 169.90(3), N1−V−N1a 172.35(13), S1−V−S1a 82.78(4), S1−V−Cl1a 88.09(3), Cl1−V−Cl1a 101.33(4).

Schiff base dianions comprising *ON'O* or *ON'N'O* donor sets complex to vanadium(IV) in a direct manner, if a suitable, water-soluble vanadyl precursor compound such as vanadyl sulfate or vanadyl acetyiacetonate (acac) is employed. Alternatively, and in many cases more conventiently, the template effect of the vanadyl ion (VO^{2+}) can be exploited in order to build up the ligand in the coordination sphere of the metal, using the aldehyde and amine components of the Schiff base[6,12]. Similarly, Dutton et al. showed that the reaction mixture between [VO(acac)$_2$] and H*ON'S'*H (the Schiff base formed from *o*-hydroxyaniline and *o*-mercaptobenzaldehyde) leads to the formation of [V(*ON'S'*)$_2$] (structurally not characterized)[13].

For the preparation of **2**, with a Schiff base (**b**H$_2$) composed of *o*-mercaptoaniline and *o*-hydroxynaphthaldehyde units, i.e. with the thio and oxo functions interchanged with respect to Dutton's complex, one has to take into account that the Schiff base is in tautomeric equilibrium with its thiazoline form[14a−c]. The position of this equilibrium strongly favours the latter, which is readily oxidized to thiazole, a process which has been shown to be promoted by oxo-transition metal units[14d]. Nonetheless, the dioxomolybdenum complexes [MoO$_2$(*S'N'O*)dmso][15] and [MoO$_2$(*S'N'O*)*dmso][16] [where (*S'N'O*)* is derived from the Schiff base with salicylaldehyde as the aldehyde component] have been prepared by the direct reaction of an oxomolybdenum precursor with the thiazoline form of the Schiff base, as has the related complex [Ni(*S'N'O*)*(py)] (py = *p-tert*-butylpyridine)[15,17]. In contrast, the complexes [M(*S'N'O*)*L] (M = Zn, L = bipyridine[18]; M = Cd, L = *o*-phenanthroline[19]) have been obtained by generating the ligand via cathodic reduction of the disulfide H*ON'S'*−*S'N'O*H.

Reaction of the (thiazoline form of) **b**H$_2$ with vanadyl ions in aqueous solution did not lead to a defined product. Complex **2** was therefore prepared in THF by reacting *o*-hydroxynaphthaldehyde with a performed intermediate complex obtained from [VOCl$_2$(thf)$_2$] and *o*-mercaptoaniline. The oxo group was removed from the vanadium in the course of the formation of this complex (IR evidence). Although a few non-oxo vanadium(IV) complexes are now known[20], the deoxygenation of oxophilic V^{IV} by a thiofunctional aniline derivative is still rather unexpected. The driving force behind this process is possibly an oxo-transfer to (oxidation of) the thiophenolate. The reversible gain and loss of O^{2-} in phenolatovanadium(+V/+III) complexes[21a], and vanadium-mediated oxo-transfer reactions[21b] have been documented previously, as has the oxidation of thiolates by VO^{2+}, which is accompanied by a partial loss of oxygen[9]. The overall reaction scheme that we propose is illustrated in Scheme 2.

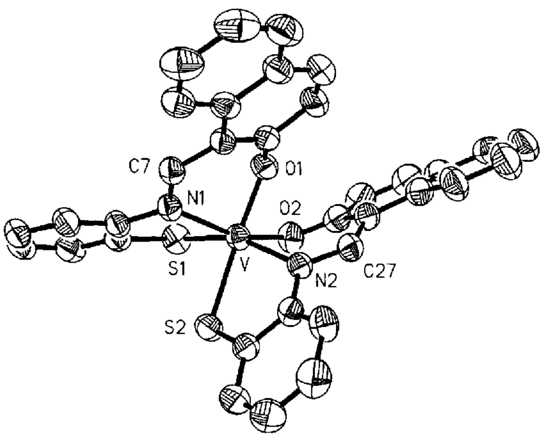
Scheme 2



Complex **2** crystallizes in the monoclinic space group *P*2(1)/*c*. An ORTEP drawing is given in Figure 2. The molecule is highly distorted: The two trigonal planes [O1N1S1 (plane 1) and O2N2S2 (plane 2)] are inclined towards each other by 28.6°. The "twist angle" between plane 1 and the projection of plane 2 onto plane 1 amounts to 69° (cf. also Figure 3). This compares to a regular twist angle (60° for ideally octahedral, 0° for ideally trigonal-prismatic geometries) of 40.3° for [V(*OS'*)$_3$], where H*OS'*H is *o*-mercaptophenol[22a]. An essentially trigonal-prismatic arrangement has been described for [V(*ON'S'*)$_2$] (twist angle not reported), where H*ON'S'*H is the Schiff base built up from thiobenzoylhydrazine and acetylacetone[22b]. Another structural feature of interest in **2** is intra-ligand distortion: While Schiff base ligands are commonly considered as being essentially planar, the angles between the planes defined by the naphthylenamine and the phenylene systems in **2** amount to 23.8 and 31.4°, respesenting a significant deviation from planarity (compare, e.g., [Ni(*S'N'O*)*(py)], where the angle between the two aromatic systems is 1.3°[15]). On the other hand, the distortion in **2** is not as pronounced as it is in [MoO_2(*S'N'O*)(dmso)], where the corresponding angle is 40°[15].

The bond lengths *d*(V–S') in **2** [2.306(2) and 2.351(2) Å] fall at the short end of the range of *d*(V–S') values found in other vanadium complexes with thiophenolate[9,11,13,21,23] and thiolate coordination[22,24]. They are shorter than the *d*(V–S) in the thioether complexes **1** [2.5057(8) Å], [V(NSSN)(tmeda)] [2.478(3) Å][11], [$VOCl_2$(trithiacyclononane)] [2.475(5) and 2.634(5) Å][25], or [V(3-thiapentane-1,5-dithiolate)] [2.507(5) Å][26], and also shorter than in [$VCl_2(S_2CNEt_2)_2$] (2.378 to 2.452 Å)[27]. Other bond lengths in **1** [*d*(V–Cl), *d*(V–N); cf. legend to Figure 1] and **2** [*d*(V–N') and *d*(V–O); legend to Figure 2] are comparable to those of corresponding bonds in similar complexes.

Figure 2. ORTEP drawing, showing the 50% probability ellipsoids, of [V(*S'N'O*)$_2$] (**2**)[a]

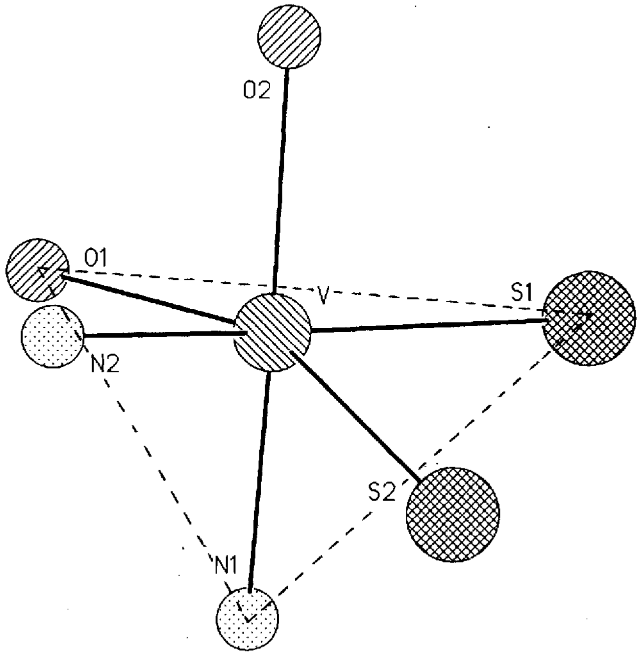


[a] Selected bond lengths [Å] and bond angles [°]: V–S1 2.306(2), V–S2 2.351(2), V–O1 1.897(2), V–O2 1.916(2), V–N1 2.122(3), V–N2 2.115(3), N1–C7 1.306(4), N2–C27 1.303(4); S2–V–O2 110.27(9), N2–V–O2 85.68(11), O1–V–O2 85.74(11), O1–V–S2 154.66(8), S2–V–N2 78.16(8), O2–V–S1 89.71(8), S1–V–S2 84.88(4), N1–V–N2 108.68(10), O1–V–N2 83.85(11), S1–V–N1 81.78(8), O2–V–N1 158.85(11), S1–V–O1 115.64(9), N1–V–S2 88.33(8), N1–V–O1 80.65(10), N2–V–S1 159.61(8).

Conclusion

The thiolate (*S'*) complex **2** and the sulfide (*S*) complex **1** represent rare examples of vanadium in sulfur coordination environments. Complex **2** is only the second example of a vanadium complex with a thio-functional ligand coordinated to a non-oxo V^{IV} centre, while **1** constitutes the first example of a low-valent vanadium complex in which the thio functions are exclusively provided by sulfide. Sulfide coordination to V^{II} has hitherto only been observed in co-coordination with thiolate[9]. While **2** may be considered to mimic the interaction of V^{IV} with cysteinate residues of proteins (cf. Introduction) and biogenic peptides (such as glutathione, an effective intracellular reductant of V^V and perhaps also of V^{IV}[28]), **1** provides a model of some of the structural features of the vanadium co-factor in nitrogenase, in that it demonstrates that combined coordination by sulfide and aromatic amine ligands (the latter mimicking the imidazole-*N*-of histidine) stabilizes V^{II}, which is presumably the oxidation state of the reduced form of the nitrogenase[29]. Further, sulfide cordination to low-valent vanadium is probably of relevance to the formation of thiophenogenic vanadium intermediates during hydrogenation and hydrodesulfurization of crude oil or fractions thereof.

Figure 3. Schematic representation of **2**, with the plane spanned by O1, N1, and S1 (connected by dashed lines; plane 1) put into the plane of the paper. The angles between plane 1 and the projection of the plane spanned by O2, N2, and S2 (plane 2) onto plane 1 are: S2–V–S1 48, N2–V–N1 84, O2–V–O1 78°. Planes 1 and 2 are inclined towards each other by 28.6°.



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Experimental Section

General: All operations were carried out in absolute solvents under an inert gas atmosphere, using standard Schlenk techniques. Starting materials were obtained from commerical sources [2-hydroxynaphthalene-1-carbaldehyde, 2-aminothiophenol (*o*-mercaptoaniline), dithioglycol, 1-methylpyridine] or prepared according to literature procedures ([$VOCl_2(thf)_2$][30], [$VCl_2(tmeda)_2$][31]). Ligand **a** was prepared from 1-chloromethylpyridine, dithioglycol, and sodium ethanolate in ethanol, following a procedure described by Livingstone[23]. In a modification of the published procedure, the viscous oil obtained after removal of the ethanol was chromatographed on silica gel (kieselgel 60; Merck), using ethyl acetate/petroleum ether (1:1) as the eluant. The identity and quality of the product were checked by IR and ^{1}H NMR. – IR: Perkin-Elmer FT-IR 1720 and (FIR) PE 1700 XFT. – Bruker AM 360 with the standard instrument settings. – EPR: Bruker ESP-300 E, 9.75 GHz measuring frequency.

Single-crystal X-ray structure determinations were performed on Hilger & Watts (**1** · CH_2Cl_2) or Syntex $P2_1$ diffractometers (**2** · Me_2CO) in the 2Θ scan mode, using a graphite monochromator and Mo-K_α radiation (λ = 0.71973 Å). The program systems SHELXS-86 and SHELXL-93 were used throughout[33]. Crystal data and details of the data collection and refinement are collated in Table 1. In the case of **2** · Me_2CO, all of the hydrogens of **2** were found. The acetone hydrogens were placed into calculated positions, as were the hydrogens in **1** · CH_2Cl_2, and included in the last cycles of the refinement. There were no disorder problems. Absorption corrections were not made. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100269.

Table 1. Crystal structure and refinement data for [VCl_2(*NSSN*)] (**1** · CH_2Cl_2) and [V($S'N'O$)$_2$] (**2** · Me_2CO)

	1·CH_2Cl_2	**2**·Me_2CO
emperical formula	$C_{15}H_{18}Cl_4N_2S_2V$	$C_{37}H_{28}N_2O_3S_2V$
molecular mass [g mol^{-1}]	483.17	663.67
temperature (K)	173	293
crystal system	orthorhombic	monoclinic
space group	*C*222(1)	*P*2(1)/*c*
a [Å]	12.126(2)	16.514(7)
b [Å]	12.479(2)	11.703(7)
c [Å]	12.726(3)	16.809(10)
β [°]		98.04(4)
Z	4	4
V [Å^3]	1925.7(6)	3217(3)
ρ_{calcd} [g cm^{-3}]	1.667	1.370
μ [mm^{-1}]	1.29	0.48
F(000)	980	1372
crystal dimensions [mm]	0.4, 0.4, 0.2	0.5, 0.5, 0.3
θ range [°]	2.34 – 27.57	2.38 – 27.62
hkl-range	$-2<h<15, -2<k<16, -2<l<16$	$-21<h<21, -15<k<1, -21<l<21$
measured reflections	1985	16375
independent reflections	1658	7455
R_{int}	0.0265	0.0733
refined parameters	110	496
Goodness of fit	1.056	1.093
R for reflections with $I>2\sigma(I_0)$: *R*1 (*wR*2)	0.0288 (0.0665)	0.0619 (0.1386)
R, all data: *R*1 (*wR*2)	0.0333 (0.0685)	0.1081 (0.1634)
ρ_{fin} (max/min) [e Å^{-3}]	0.349/–0.608	0.531/–0.332

Dichloro{1,6-bis(2-pyridyl)-2,5-dithiahexane}vanadium(II), [VCl_2(*NSSN*)] (**1**): [VCl_2(tmeda)$_2$] (610 mg, 1.8 mmol) and the ligand **a** (500 mg, 1.8 mmol) were dissolved in 20 ml of THF and the mixture was refluxed for one hour. A violet precipitate of **1** formed, which was filtered off, washed with 10 ml of cold THF, and dried under high vacuum. Yield: 460 mg (64%). – $C_{14}H_{18}Cl_2N_2S_2V$ (398.27): calcd. C 42.22, H 4.05, N 7.03; found Cl 41.59, H 4.41, N 7.51. – IR (KBr): $\tilde{\nu}$ = 380, 363, and 312 cm^{-1} (V–S and V–Cl); 1436 (CH_2–S–C), 1268 [CH_2–S (wagging)]; all of the characteristic bands for pyridine and the ethylene backbone were present. – CV (MeCN): Irreversible oxidation at −0.15 V, irreversible reduction at −1.63 V (vs. Fc/Fc$^+$). Part of the product was dissolved with slight warming in dichloromethane, and the solution was stored at 4°C. Red crystals of **1** · CH_2Cl_2 suitable for an X-ray analysis were obtained after about a week.

Bis{N-(2-oxido-1-naphthylmethylene)-2'-sulfidobenzimine}vanadium(IV), [V($S'N'O$)$_2$] (**2**): [$VOCl_2$(thf)$_2$] (282 mg, 1 mmol) was dissolved in 20 ml of THF. The blue solution was treated with *o*-mercaptoaniline (220 μl, 2 mmol), whereupon a white solid (anilinium hydrochloride; IR evidence) separated from the still blue solution. The mixture was heated for 1 day at 60°C to generate a wine-red solution. A small sample was removed, filtered, and the filtrate was concentrated to dryness in vacuo. The red-brown oil thus produced was checked by IR to verify the absence of a ν(V=O) band. The bulk of the wine-red suspension was then treated with 2-hydroxynaphthalene-1-carbaldehyde (344 mg, 2 mmol), resulting in the formation of a dense, dark-brown suspension. After 2 days of stirring at 60°C, the suspension was filtered. On storing the filtrate at 4°C, **2** separated in the form of small red-brown crystals. The frit was rinsed once with 10 ml of acetone. The red-brown filtrate thus obtained was stored for 1 week at 4°C to yield red-brown crystals of **2** · Me_2CO suitable for X-ray structure analysis, along with small red crystals of an unidentified V^{IV}-Schiff base (IR, ^{1}H-NMR, and EPR evidence) complex, **2***. Overall yield 240 mg (ca. 40%, calcd. for **2**). – IR (KBr): $\tilde{\nu}$ = 1595 and 1530 cm^{-1} (C=N), 437 and 428 (V–S). **2** · Me_2CO additionally showed a ν(C=O) = 1709 cm^{-1} for acetone of crystallization. – ^{1}H NMR ([D$_8$]THF): δ = 9.74 (s, 1H, HC=N), 8.42 (d, *J* = 8.9 Hz, 1H), 7.94–7.17 (three d and four m, 9H, ArH). – EPR ($CDCl_3$): g_0 = 1.974; A_0 = 108 Hz. **2*** exhibits the same EPR data as **2**, a similar IR pattern [ν(C=N) = 1617 cm^{-1}], and the same ^{1}H-NMR pattern, albeit shifted 0.09 ppm further downfield (to higher frequencies).

☆ Dedicated to Prof. Dr. *G. Huttner* on the occasion of his 60th birthday.

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