



Synthesis and characterization of low valent vanadium thiolate complexes

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ABSTRACT

The reaction of the bulky lithium terphenyl thiolate LiSAr^* ($\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-Pr}_2^i)_2$) with $\text{Vl}_2(\text{THF})_2$ in THF resulted in the formation of two new V(II) and V(III) thiolate complexes. The addition of one equivalent of LiSAr^* to $\text{Vl}_2(\text{THF})_4$ led to the isolation of the dimeric V(II) species $\{\text{V}(\mu\text{-SAr}^*)\}_2$ (**2**); a rare example of a structurally characterized V(II) thiolate. The thiolate ligands bridge the two vanadium centers, which are also bonded to a terminal iodide. In addition, there is an η^6 -interaction between a flanking aryl ring from a terphenyl substituent with each metal. The attempted preparation of the vanadium dithiolate $\text{V}(\text{SAr}^*)_2$ by reaction of $\text{Vl}_2(\text{THF})_2$ with two equivalents of LiSAr^* led to disproportionation which resulted in the isolation of the V(III) product $\text{V}(\text{SAr}^*)_2\text{I}$ (**3**) in which the vanadium center is coordinated by two sulfurs, an iodine, and a weaker interaction to a flanking aryl ring of the terphenyl group.

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1. Introduction

Transition metal thiolate and related derivatives [1–4] have been extensively studied because of their relevance for biological systems [5,6]. In many instances, they can serve as structural models for active sites in numerous metal–sulfur proteins such as ferredoxins [7,8] or nitrogenases [9–11], which feature cysteine residues as ligands [6]. However, the preparation of the simplest neutral homoleptic transition metal thiolates has often been difficult because of extensive M-(μ -SR)-M thiolate bridging which results in the formation of intractable oligomers or polymers. The use of sufficiently bulky ligands [12,13] such as $-\text{SC}_6\text{H}_2\text{-2,4,6-Bu}_3^t$ ($-\text{SMes}^+$) [14,15] and $-\text{SC}_6\text{H}_2\text{-2,4,6-Ph}_3$ [16] mitigates extensive bridging interactions so that low coordinate species, exemplified by the dimeric transition metal complexes $\{[\text{M}(\text{SMes}^*)_2]\}$ (M = Mn, Fe, Co) [15] and $\{[\text{Fe}(\text{SC}_6\text{H}_2\text{-2,4,6-Ph}_3)_2]\}$ [16], can be obtained. In a more recent development, the use of the very hindered thiolate derivative, $-\text{SAr}^*$ ($\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,4,6-Pr}_3^i)_2$) has led to the isolation of a series of soluble, monomeric first row transition metal(II) dithiolates $\text{M}(\text{SAr}^*)_2$ (M = Cr, Mn, Fe, Co, Ni and Zn) in which the metals are nominally two-coordinate [17]. These complexes exhibit linear (or nearly linear) S–M–S units with varying degrees of weak interaction between the metal center and the flanking aryl rings of the terphenyl ligands. We wished to extend these results to vanadium via the synthesis and characterization of low valent vanadium thiolates of formula $\text{V}(\text{SAr}^*)_2$ (Ar = bulky terphenyl). Vanadium thiolates have been studied because of their potential relevance to the function of vanadium nitrogenase enzymes [18–20]. Vanadium

nitrogenases, although less well understood than their molybdenum analogues [6–10,21], are believed to have a similar coordination environment to Mo in Mo-based nitrogenases, with low oxidation state (II–IV) oxidation states [11,18–20] wherein the metal is coordinated to several sulfur atoms. We now report on our initial investigations which have resulted in the synthesis of two low coordinate V(II) and V(III) thiolate complexes.

2. Experimental

2.1. General procedures

All manipulations were carried out with use of modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried by the method of Grubbs and degassed three times (freeze–thaw) prior to use. $\text{Vl}_2(\text{THF})_4$ was synthesized according to the literature procedure [22]. ^1H NMR spectra were recorded on a Varian 300 MHz instrument and referenced to the residual protio benzene in the C_6D_6 solvent. Melting points were recorded in glass capillaries sealed under N_2 or Ar and are uncorrected. UV–Vis data were recorded on a Hitachi-1200 spectrometer. Solution magnetic moment measurements were carried out by the method of Evans as a solution in C_6D_6 [23].

2.2. Ar^*SH (**1**)

The terphenyl thiol Ar^*SH was synthesized in an analogous manner to that described for the related thiol $\text{HSC}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Pr}_3^i)_2$ [24]. Yield: 72%, m.p. 165–168 °C. ^1H NMR (C_6D_6 , 400 MHz, 25 °C): δ 1.11 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12 H, $o\text{-CH}(\text{CH}_3)_2$), 1.32 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $o\text{-CH}(\text{CH}_3)_2$), 2.83 (sept,

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$^3J_{\text{HH}} = 6.9$ Hz, 4H, *o*-CH(CH₃)₂), 3.08 (S, 1H, –SH), 6.96 (1H *p*-C₆H₃), 7.21 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, *m*-C₆H₃-2, 6-Pr₂^{*i*}), 7.31 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, *p*-C₆H₃-2, 6-Pr₂^{*i*}). ¹³C{¹H} NMR (C₆D₆, 100.59 MHz): δ 24.00, δ 24.92 (*o*-CH(CH₃)₂), 31.14 (*o*-CH(CH₃)₂), 123.67 (*m*-C₆H₃-2, 6-Pr₂^{*i*}), 124.36 (*i*-C₆H₃), 129.20 (*p*-C₆H₃-2, 6-Pr₂^{*i*}), 129.9 (*m*-C₆H₃), 135.61 (*i*-C₆H₃-2, 6-Pr₂^{*i*}), 138.00 (*p*-C₆H₃) 138.68 (*o*-C₆H₃-2, 6-Pr₂^{*i*}), 147.26 (*o*-C₆H₃).

2.3. [V(μ -SAr')I]₂ (**2**)

(LiSAr')₂ (generated in solution from 0.872 g, 2.0 mmol and LiBu^{*n*} (1.6 M in hexanes, 1.25 mL)), in THF (25 mL), was added dropwise to a stirred suspension of VI₂(THF)₄ (1.186 g, 2.0 mmol) in THF (25 mL) cooled to ca. 0 °C. The resulting dark, brown-red solution was stirred overnight while it was allowed to warm to room temperature. The solvent was removed under reduced pressure and the resulting dark red solid was extracted with hexane (30 mL) and filtered. The volume of the filtrate was reduced to ca. 5 mL under reduced pressure to afford dark red, X-ray quality crystals of **2** after storage for 3 days at ca. –20 °C. Yield: 0.768 g (63%) m.p. = 230 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.1 (br, s), 6.9 (br, s), 3.7 (br, s), 2.7 (br, m), 1.3 (br, d), 1.0 (br, d). UV/Vis (hexanes; λ_{max} , nm (ϵ , mol^{–1} L cm^{–1})): 282 (7300), 384 (2500), 466 (2000). $\mu_{\text{eff}} = 3.61 \mu_{\text{B}}$ /vanadium.

2.4. [V(SAr')₂I] (**3**)

A THF (40 mL) solution of (LiSAr')₂ (1.744 g, 4.0 mmol) in THF (50 mL) was added dropwise to a stirred suspension of VI₂(THF)₄ (1.186 g, 2.0 mmol) in THF (25 mL) with cooling in an ice bath. The resulting dark green solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and resulting dark green solid was extracted with hexane (40 mL) and filtered. The volume of the solution was reduced to ca. 10 mL which afforded green, X-ray quality crystals of **3** after 7 days at ca. 7 °C. Yield 0.552 g (23%) m.p. = 174–178 °C (dec). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 7.10 (br, d), 2.95 (br, s), 1.21 (br, s), 1.05 (br, s). UV/Vis (hexanes; λ_{max} , nm (ϵ , mol^{–1} L cm^{–1})): 328 (3050), 390 (2000), 440 (1400), 638 (1600). $\mu_{\text{eff}} = 2.64 \mu_{\text{B}}$ /vanadium.

2.5. X-ray data collection

X-ray quality crystals of **2** or **3** were removed from the Schlenk tube and immediately covered with a layer of hydrocarbon oil. A

suitable crystal was selected, attached to a glass fiber, and placed in the cold temperature stream as previously described [25]. The data were collected near 90 K using a Bruker APEX (**2**) or a SMART 1000 (**3**) diffractometer and Mo K α ($\lambda = 0.71073$ Å) radiation. Absorption corrections were applied using SADABS [26]. The structures were solved by use of direct methods in SHELXS [27] and refined by the full-matrix least-squares procedure in SHELXL. All non hydrogen atoms were refined anisotropically, while hydrogens were placed at calculated positions and included in the refinement by using a riding model. Some details of the data collection and refinement are given in Table 1. Further details are in the supplementary material.

3. Results and discussion

The use of sterically encumbering ligands has played a key role in the stabilization of low coordinate (coordination number ≤ 3) compounds throughout the periodic table [28]. Early work focused on bulky ligands attached via a second row element C, N, or O in alkyl, aryl, amido, alkoxo on aryloxo ligands. The application of ligands based on elements from the third or later rows, involving for example, silyl, phosphido, or thiolate ligands, was a later development for a number of reasons that included synthetic and steric considerations as well as weaker metal–ligand bonding [28]. Although there is now a vast chemistry of transition metal thiolates, the fact that the sulfur can carry only one organic substituent has limited their application in the stabilization of low coordination numbers. We have recently used the very large terphenyl thiolate ligand –SC₆H₃-2, 6(C₆H₂-2, 4, 6-Pr₃)₂ (–SAr^{***}) [24] to synthesize a series of divalent transition metal complexes (M(SAr^{***})₂ (M = Cr, Mn, Fe, Co)) [17] and their zinc analogue Zn(SAr^{***})₂. These feature linear or almost linear metal coordination for Cr, Mn, Co, Ni and Zn whereas Fe(SAr^{***})₂ displays a bent (S–Fe–S = 151.48(2)°) geometry and an apparent tendency to rearrange to a sandwich structure involving metal–aryl ring coordination [17]. A feature of the complexes is that, with the exception of the unique iron derivative, all the secondary metal–ligand interactions (mainly to *ipso*-carbons from a flanking aryl ring of the terphenyl ligand) are weak and exceed 2.5 Å, with the longest being observed for Mn(SAr^{***})₂ (Mn–S = 2.951(2) Å). Such distances exceed those in the corresponding η^5 or η^6 -bonded metal arene complexes by a significant margin. For example, the Cr–C interaction is 2.502(2) Å in Cr(SAr^{***})₂ whereas in Cr(η^5 -C₅H₅)₂ the Cr–C distance is 2.142(3) Å and the Cr–centroid distance is 1.61 Å [29]. The above findings encouraged us to extend the approach to vanadium and it was hoped that the employment of a bulky terphenyl thiolate ligand would allow us to obtain the first example of a two-coordinate V(II) species.

The reaction of VI₂(THF)₄ with one or two equivalents of LiSAr^{***} did not afford readily characterizable products. We turned instead to the related –SAr' ligand which has similar steric properties to –SAr^{***} and can be synthesized by a similar route. It differs from Ar^{***} only in the absence of *para*-Pr' substituents from the flanking aryl rings. The addition of one equivalent of LiSAr' to a suspension of VI₂(THF)₄ in THF at 0 °C (Eq. (1)) afforded a dark red-brown solution from which deep red crystals of **2** could be isolated in



63% yield. These were characterized by UV–Vis spectroscopy, magnetic studies and X-ray crystallography. The results of the diffraction study of **2** are illustrated in Fig. 1. It represents a very rare example of a structurally characterized vanadium (II) thiolate [4,30–33]. It is dimeric and the metals are linked by thiolate bridges to form a V₂S₂ core structure. Each vanadium is also coordinated to a terminal iodide. The V₂S₂ core is characterized by an inversion center with internal S–V–S and V–S–V angles of 100.86(4)° and

Table 1
Selected crystallographic data and collection parameters for **2** and **3**

	2	3
Formula	C ₆₀ H ₇₄ S ₂ V ₂ I ₂	C ₇₁ H ₉₈ IOS ₂ V
<i>f</i> _w	1214.99	1209.45
Color, habit	red, plate	green, rod
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.086(1)	13.4040(5)
<i>b</i> (Å)	13.278(1)	34.915(1)
<i>c</i> (Å)	16.507(2)	13.8562(5)
α (°)	90	90
β (°)	105.170(2)	92.949(1)
γ (°)	90	90
<i>V</i> (Å ³)	2768(4)	6476.1(4)
<i>Z</i>	2	4
<i>d</i> _{calc} (Mg/m ³)	1.458	1.240
θ Range (°)	2.00–27.50	1.17–25.25
μ (mm ^{–1})	1.565	0.735
Number of observed (<i>I</i> > 2 σ (<i>I</i>)) data	4435	7976
<i>R</i> ₁ (observed data)	0.0422	0.0487
<i>wR</i> ₂ (all data)	0.0897	0.1384

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