

Directed reactivity at a vanadium(II) thiolate center: synthesis and structure of a novel vanadium thiolate complex and its reaction product with azobenzene

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The vanadium(II) thiolate complex $[\text{V}(\text{tmeda})(\text{DCTP})_2]$ [DCTP = 2,6-dichlorothiophenolate; tmeda = *N,N,N',N'*-tetramethylethylenediamine] is obtained by the reaction of 2 equiv. of LiDCTP with $[\text{VCl}_2(\text{tmeda})_2]$ and reacts with azobenzene to yield the imido-containing complex $[\text{V}(\text{tmeda})(\text{DCTP})_2(\equiv\text{NPh})]$.

Low-valent vanadium thiolate complexes are of interest due in part to their potential relevance to the functioning of the alternative nitrogenase cofactor,¹ and to their presumed reactivity toward small reducible molecules in general. Recently, Coucouvanis and coworkers have shown that vanadium in a sulfur- and nitrogen-containing environment can catalyze the reduction of hydrazine to ammonia.² We have had considerable interest in lower-valent vanadium chalcogenide complexes, particularly with respect to their reactivity toward small molecules.³ Herein we report the synthesis and structural characterization of a novel and rare mononuclear vanadium(II) thiolate complex containing labile coordination sites. We also provide an initial report on its reactivity with a substrate of relevance to dinitrogen reduction.

Complex **1**, $[\text{V}(\text{tmeda})(\text{DCTP})_2]$ (DCTP = 2,6-dichlorothiophenolate; tmeda = *N,N,N',N'*-tetramethylethylenediamine), is formed from the reaction of 2 equiv. of the lithium salt of 2,6-dichlorothiophenol (LiDCTP)[‡] with 1 equiv. of $[\text{VCl}_2(\text{tmeda})_2]$.[§] The crystal structure of **1** is shown in Fig. 1.¶ Bond distances and angles for **1** are consistent with those observed for other complexes of this sort, though crystallo-

graphically characterized vanadium(II) thiolates are still quite uncommon.⁵ The structure of **1** reveals as well the presence of two dative, aryl-halide bonds. The observed V–Cl distances [2.515(2) Å, 2.510(2) Å] are well within the sum of radii of the atoms (3.131 Å),⁶ and there is a slight lengthening of the Cl–C bond [1.758(9) Å] relative to the bond for the non-coordinated chlorine [1.727(9) Å]. While the ability of DCTP[–] to act as a bidentate ligand through sulfur and chlorine is unknown in the literature, such dative bonds with other halides are not unprecedented,⁷ including one at a vanadium center.⁸ The occurrence of such potentially labile bonds at a vanadium(II) center, and particularly at an electron-rich vanadium(II) thiolate center, gives hope that these might be sites for reactivity.

These hopes were realized in the reaction that yields complex **2**, $[\text{V}(\text{tmeda})(\text{DCTP})_2(\equiv\text{NPh})]$. Complex **2**, whose ORTEP is shown in Fig. 2,¶ is obtained from the reaction of **1** with 0.5 equiv. of azobenzene.¶ The azobenzene is cleaved to give one phenylimido group per vanadium, with concomitant dissociation of one of the chlorine dative bonds of **1**. The other dative chlorine bond is now located *trans* to the imido group, and the V–Cl bond distance is, as expected from the strongly electron donating nature of the imido functionality, significantly lengthened relative to that seen in **1** [2.671(3) vs. 2.510(2) Å]. Structurally, **2** is quite similar to other vanadium(IV) and vanadium(V) arylimido complexes,⁹ with the short V–N distance [1.670(7) Å] and nearly linear V–N–C angle [171.2(7)°] indicating a $\text{V}\equiv\text{NAr}$ bonding moiety.⁹ Other distances are as expected, though again it should be noted that

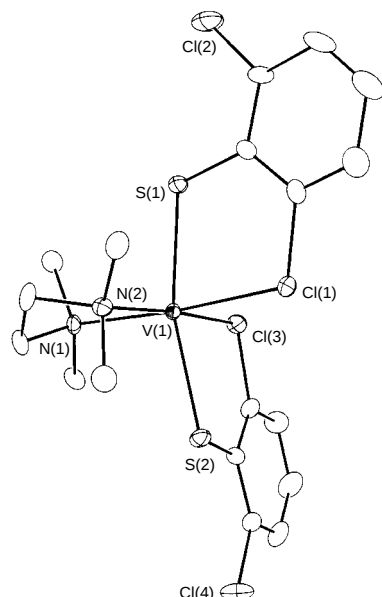


Fig. 1 ORTEP of $[\text{V}(\text{tmeda})(\text{DCTP})_2]$, **1**, showing the 30% probability thermal ellipsoids and atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: V(1)–S(1) 2.468(2), V(1)–S(2) 2.464(2), V(1)–Cl(1) 2.515(2), V(1)–Cl(3) 2.510(2), V(1)–N(1) 2.206(6), V(1)–N(2) 2.220(7), S(1)–V(1)–S(2) 165.19(7), Cl(1)–V(1)–Cl(3) 92.84(6).

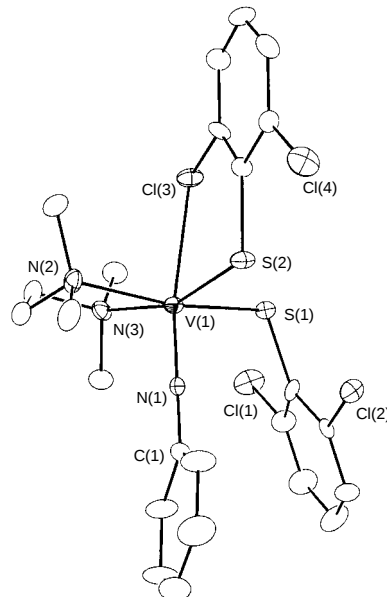


Fig. 2 ORTEP of $[\text{V}(\text{tmeda})(\text{DCTP})_2(\equiv\text{NPh})]$, **2**, showing the 30% probability thermal ellipsoids and atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: V(1)–N(1) 1.670(7), V(1)–S(1) 2.465(3), V(1)–S(2) 2.434(3), V(1)–Cl(3) 2.671(3), V(1)–N(2) 2.245(8), V(1)–N(3) 2.243(7), V(1)–N(1)–C(1) 171.2(7).

very few vanadium(IV) imido complexes have been structurally characterized.¹⁰ Perhaps more interestingly, of those that have, none have been prepared from reduction of a diazo moiety. In fact, of all reported vanadium imido complexes, only one other is formed as the result of the reductive cleavage of a dinitrogen analogue.¹¹

Compound **1** has also shown reactivity with many other small molecules such as *tert*-butyl isocyanide, 1,2-diphenylhydrazine and organic aldehydes. Elucidation of other reaction products and details of the reactivity of related compounds will be reported elsewhere. Further development of chemistry at other low-valent vanadium thiolate centers is under way.

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Notes and References

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‡ In a typical preparation, 5.372 g (30.00 mmol) of 2,6-dichlorothiophenol (Lancaster) were added to 20 ml of toluene. 18.75 ml (30.00 mmol) of 1.6 M *n*-butyllithium (Aldrich, in hexanes) were added over 0.5 h to the thiol solution with vigorous stirring. The resulting white precipitate was washed with hexane and dried, affording an approximately quantitative yield.

§ In a typical preparation, 1.00 g (2.82 mmol) of [VCl₂(tmeda)₂]⁴ was dissolved in 20 ml of THF. Then 1.04 g (5.65 mmol) of LiDCTP were added at once with stirring. The light blue solution turned homogeneous and emerald green. Over 0.2 h a light green precipitate of [V(tmeda)(DCTP)₂] appeared. The precipitate was filtered off, washed with diethyl ether and dried *in vacuo* to give analytically pure product in 68% yield. The yield could be improved by treating the remaining filtrate with pentane. The green precipitate was filtered off and rinsed with 5 ml of diethyl ether and then 5 ml of THF. The combined solids then afforded an 82% yield. Elemental analysis was satisfactory. EPR (X-band, CH₂Cl₂, 77 K): *g* = 5.33, multiline.

¶ Crystal data for **1**: a single crystal was mounted under the cold stream (−90 °C) of a Siemens SMART system. An initial collection of 60 frames of data yielded the crystal system (hexagonal) and unit cell [*a* = 7.6735(1), *c* = 65.3685(2) Å]. 20749 reflections were collected, of which 5003 were unique. The space group (*P*6₁, *Z* = 6) was chosen by systematic absences and successful refinement of the structure. No absorption correction was used. The structure was solved using SHELX 5.0 using anisotropic thermal parameters for all non-hydrogen atoms to values of *R*₁ = 7.35%, *wR*₂ = 15.7% for *I* > 2σ(*I*). For 2·thf: a single crystal was mounted under the cold stream (−90 °C) of a Siemens SMART system. An initial collection of 60 frames of data yielded the crystal system (orthorhombic) and unit cell [*a* = 13.621(4), *b* = 15.254(4), *c* = 30.410(7) Å]. 17675 reflections were collected, of which 10152 were unique. The space group (*P*2₁2₁2₁, *Z* = 2) was chosen by systematic absences and successful refinement of the structure. No absorption correction was used. The structure was solved using SHELX 5.0 using anisotropic thermal parameters for all non-hydrogen atoms to values of *R*₁ = 8.40%, *wR*₂ = 13.72% for *I* > 2σ(*I*). CCDC 182/902.

|| In a typical preparation, 0.25 g (0.478 mmol) of **1** was suspended with stirring in 20 ml of THF. Addition of 0.044 g (0.239 mmol) of azobenzene (Aldrich) yielded a yellow–green heterogeneous mixture which was then

refluxed and became dark brown and homogeneous over 2 h. The solution was filtered, concentrated and cooled, affording brown crystals in 65% yield. Analysis was satisfactory. EPR (X-band, THF, 77 K): *g* = 2.0, 8 lines.

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