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

John A. Davis, Christopher P. Davie, David B. Sable and William H. Armstrong*†

Department of Chemistry, Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, 02167-3860, USA

The vanadium(II) thiolate complex [V(tmeda)(DCTP)$_2$] [DCTP = 2,6-dichlorothiophenolate; tmeda = *N,N,N′,N′*-tetramethylethylenediamine] is obtained by the reaction of 2 equiv. of LiDCTP with [VCl$_2$(tmeda)$_2$] and reacts with azobenzene to yield the imido-containing complex [V(tmeda)(DCTP)$_2$(≡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**, [V(tmeda)(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 [VCl$_2$(tmeda)$_2$].§[4] 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 crystallographically 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**, [V(tmeda)(DCTP)$_2$(≡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 V≡NAr bonding moiety.[9] Other distances are as expected, though again it should be noted that

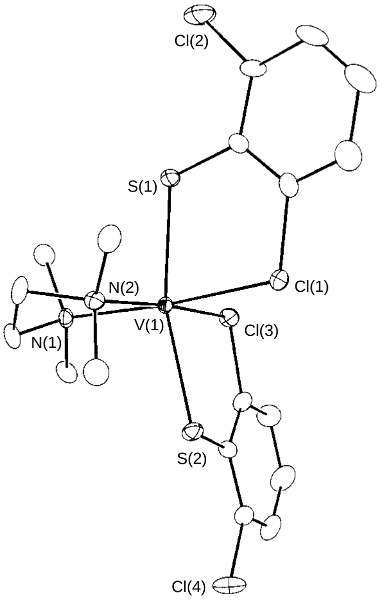

Fig. 1 ORTEP of [V(tmeda)(DCTP)$_2$], **1**, showing the 30% probability thermal ellipsoids and atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: V(1)–S(1) 2.468(2), V(1)–S(2) 2.464(2), V(1)–Cl(1) 2.515(2), V(1)–Cl(3) 2.510(2), V(1)–N(1)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

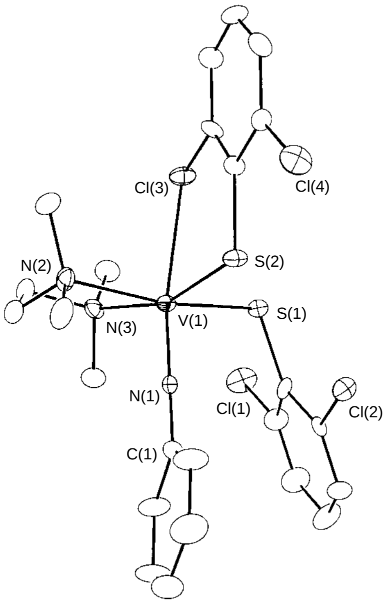

Fig. 2 ORTEP of [V(tmeda)(DCTP)$_2$(≡NPh)], **2**, showing the 30% probability thermal ellipsoids and atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: V(1)–N(1) 1.670(7), V(1)–S(1) 2.465(3), V(1)–S(2) 2.434(3), V(1)–Cl(3) 2.671(3),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

For funding this work we thank the National Science Foundation (Grant CHE-8857455). We also thank the National Institutes of Health (Grant 1 S10 RR09008) and Boston College for providing funds for the purchase of a Siemens SMART single crystal X-ray diffractometer.

Notes and References

† E-mail: william.armstrong@bc.edu

‡ 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 $[\mathrm{VCl_2(tmeda)_2}]$[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 $[\mathrm{V(tmeda)(DCTP)_2}]$ 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, CH_2Cl_2, 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 ($P6_1$, $Z = 6$) 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 $I > 2\sigma(I)$. 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 ($P2_12_12_1$, $Z = 2$) 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 $I > 2\sigma(I)$. 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.

1 R. R. Eady, in *Advances in Inorganic Chemistry*, ed. A. G. Sykes, Academic, San Diego, 1991, vol. 36, pp. 77–101 and references therein.

2 S. M. Malinak, K. D. Demadis and D. Coucouvanis, *J. Am. Chem. Soc.*, 1995, **117**, 3126.

3 W. C. A. Wilisch, M. J. Scott and W. H. Armstrong, *Inorg. Chem.*, 1988, **27**, 4333; C. R. Randall and W. H. Armstrong, *J. Chem. Soc., Chem. Commun.*, 1988, 986; L. Gelmini and W. H. Armstrong, *J. Chem. Soc., Chem. Commun.*, 1989, 1904; M. J. Scott, W. C. A. Wilisch and W. H. Armstrong, *J. Am. Chem. Soc.*, 1990, **112**, 2429; D. B. Sable and W. H. Armstrong, *Inorg. Chem.*, 1992, **31**, 161; H. H. Murray, S. G. Novick, W. H. Armstrong and C. S. Day, *J. Cluster Sci.*, 1993, **4**, 439; P. J. Bonitatebus, Jr., S. K. Mandal and W. H. Armstrong, *Chem. Commun.*, 1998, 939.

4 J. J. H. Edema, S. Gambarotta, A. Meetsma, A. L. Spek and N. Veldman, *Inorg. Chem.*, 1991, **30**, 2062.

5 D. W. Stephan and T. T. Nadasdi, *Coord. Chem. Rev.*, 1996, **147**, 147; $[\mathrm{V(pyt)_3}]^-$: G. Henkel, B. Krebs and W. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1366; $[\mathrm{V(tmeda)(pyt)_2}]$: J. G. Reynolds, S. C. Sendlinger, A. M. Murray, J. C. Huffman and G. Christou, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1253; J. G. Reynolds, S. C. Sendlinger, A. M. Murray, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1995, **34**, 5745; [V(tmeda)('S_4')]: W. Tsagkalidis, D. Rodewald and D. Rehder, *J. Chem. Soc., Chem. Commun.*, 1995, 165.

6 Values for Cl (van der Waals) and V (atomic) taken from J. Emsley, *The Elements*, Oxford University Press, Oxford, 1991, pp. 50, 210.

7 R. M. Catala, D. Cruz-Garritz, P. Sosa, P. Terreros, H. Torrens, A. Hills, D. L. Hughes and R. L. Richards, *J. Organomet. Chem.*, 1989, **359**, 219; R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa and H. Torrens, *J. Chem. Soc., Chem. Commun.*, 1987, 261; Y. A. Simonov, A. A. Dvorkin, G. S. Matuzenko, M. A. Yampol'skaya, T. S. Gifeisman, N. V. Berbeleu and T. I. Malinovskii, *Koord. Khim.*, 1984, **10**, 1247; Y. A. Simonov, G. S. Matuzenko, M. M. Botoshanskii, M. A. Yampol'skaya, N. V. Gerbeleu and T. I Malinovskii, *Zh. Neorg. Khim.*, 1982, **27**, 407; M. J. Burk, R. H. Crabtree and E. M. Holt, *J. Organomet. Chem.*, 1988, **341**, 495; J. M. Casas, L. R. Falvello, J. Forniés and A. Martín, *Inorg. Chem.*, 1996, **35**, 56.

8 V. C. Gibson, C. Redshaw, L. J. Sequeira, K. B. Dillon, W. Clegg and M. R. J. Elsegood, *Chem. Commun.*, 1996, 2151.

9 D. E. Wigley, *Prog. Inorg. Chem.*, 1995, **42**, 239, and references therein; W. A. Nugent and J. M. Mayer, *Metal Ligand Multiple Bonds*, John Wiley and Sons, New York, 1988.

10 N. Wiberg, H.-W. Häring and U. Schubert, *Inorg. Chem.*, 1978, **17**, 1880; F. Preuss, H. Becker, J. Kaub and W. A. Sheldrick, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1988, **43**, 1195; S. Gambarotta, A. Chiesi-Villa and C. Guastini, *J. Organomet. Chem.*, 1984, **270**, C49; J. H. Osborne, A. L. Rheingold and W. C. Trogler, *J. Am. Chem. Soc.*, 1985, **107**, 7945.

11 For compound $[\mathrm{V(\equiv NPh)Cl(\mu\text{-}Cl)}]_2$, M. Mazzanti, M. Khadkhodayan and W. H. Armstrong, *Abstracts of the 203rd National Meeting, ACS*, INOR No. 461, San Francisco, CA, 1992.

Received in Bloomington, IN, USA, 5th January 1998; revised manuscript received 27th May 1998; 8/04231D