

Communications to the Editor

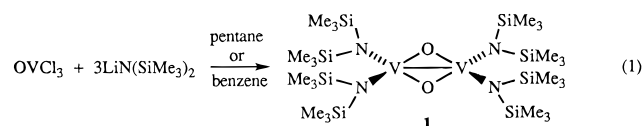
The Novel Bis(oxo-bridged) Dinuclear Vanadium(IV) Complex $\{(\mu\text{-O})_2\text{V}_2[\text{N}(\text{SiMe}_3)_2]_4\}$: An Unexpected Reaction Product

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Here we report the synthesis and characterization of the new dinuclear vanadium(IV) complex $\{(\mu\text{-O})_2\text{V}_2[\text{N}(\text{SiMe}_3)_2]_4\}$ (**1**)



and the preliminary observation of both aliphatic and aromatic carbon–hydrogen activation during the formation of this compound under mild conditions.

Of the 31 dinuclear vanadium(IV) complexes whose molecular structures have previously been determined by X-ray crystallography,^{1–29} 12 (like **1**) possess two single-atom bridges such as F, Cl, OH, OR, and NR. However, **1** is the only example of this class in which two oxide bridges are found.

Compound **1** was obtained in 22–38% yields as dark green crystals from the reaction of vanadyl trichloride with 3 equiv of $\text{LiN}(\text{SiMe}_3)_2$ in pentane,³⁰ a reaction originally carried out with the intention of synthesizing $\text{OV}[\text{N}(\text{SiMe}_3)_2]_3$. A GC-MS analysis carried out on the volatile components collected in a liquid-nitrogen-cooled trap after the reaction was completed revealed the presence of $\text{HN}(\text{SiMe}_3)_2$, cyclopentane, 1-pentene, 2-pentene (isomers were not identified), and several unidentified species. When the reaction was carried out in refluxing benzene, **1** was obtained in 15–25% yields. After the isolation of crystalline **1**, the oily residual product was dissolved in chloroform and hydrolyzed with hydrochloric acid to determine the oxidation state of vanadium. The observed visible spectrum confirmed that V(IV) is the major if not exclusive vanadium product in our reactions. Chloroform extracts of the aqueous phase obtained from the reaction in refluxing benzene were observed by both ¹H and ¹³C NMR spectroscopy to contain biphenyl.

The molecular structure of **1**³¹ shown in Figure 1 is the first

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(1) Preuss, F.; Becker, H.; Kaub, J.; Sheldrick, W. S. *Z. Naturforsch.* **1988**, *43b*, 1195.

(2) Preuss, F.; Overhoff, G.; Becker, H.; Häusler, H. J.; Frank, W.; Reiss, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1827.

(3) Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 214.

(4) Herberhold, M.; Kuhnlein, M.; Schrepfermann, M.; Ziegler, M. L.; Nuber, B. *J. Organomet. Chem.* **1990**, *398*, 259.

(5) Berno, P.; Gambarotta, S. *Angew. Chem.* **1995**, *107*, 871; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822.

(6) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321.

(7) Forrest, J. G.; Prout, C. K. *J. Chem. Soc. A* **1967**, 1312.

(8) Tapscott, R. E.; Belford, R. L.; Paul, I. C. *Inorg. Chem.* **1968**, *7*, 356.

(9) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.

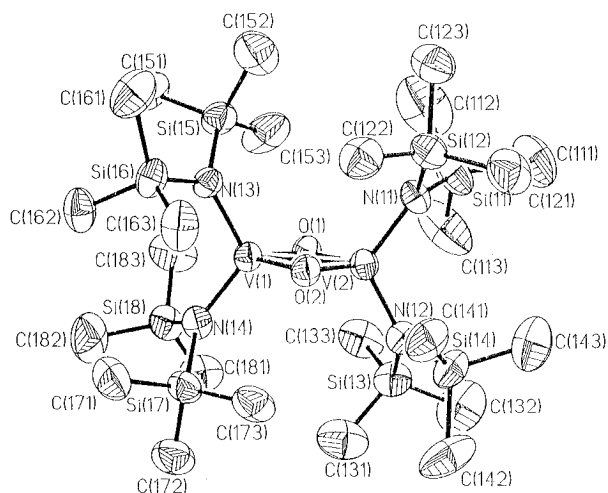


Figure 1. X-ray structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Some average bond distances (Å) are as follows: V–V, 2.612(2); V–O, 1.802(4); V–N, 1.885(6); N–Si, 1.771(6).

example of a bis(oxo-bridged) vanadium(IV) dimer. There are two well-separated dimeric molecules of virtual D_{2h} symmetry in the asymmetric unit, and the two vanadium and two bridging oxygen atoms in each dimer are planar with mean deviations from the planes of 0.0036 and 0.0004 Å, respectively. The average N–V–O, N–V–N, O–V–O, and V–O–V angles are 112.7(2), 115.7(2), 87.1(2), and 92.9(2)°, respectively. All of the V–O and the V–N bond lengths are equal within experimental error, respectively.

In bridged dimetallic complexes, the metal–metal distance is of special interest. In dinuclear analogues of **1**, V–V distances between 2.459 and 2.970 Å^{1–4,6} have been assumed

(10) Carrano, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944.

(11) Castro, S. L.; Cass, M. E.; Hollander, F. J.; Bartley, S. L. *Inorg. Chem.* **1995**, *34*, 466.

(12) Roesky, H. W.; Anhaus, J.; Schmidt, H. G.; Sheldrick, G. M.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1983**, 1207.

(13) Hahn, C. W.; Rasmussen, P. G.; Bayón, J. C. *Inorg. Chem.* **1992**, *31*, 1963. The V–O (pyrazole) abbreviation is apparently a typographical error in this paper and it should be V–N (pyrazole).

(14) Musiani, M. M.; Milani, F.; Graziani, R.; Vidali, M.; Casellato, U.; Vigato, P. A. *Inorg. Chim. Acta* **1982**, *61*, 115.

(15) (a) Théobald, P. F.; Galy, J. *Acta Crystallogr.* **1973**, *B29*, 2732. (b) Théobald, F.; Tachez, P. M. *Acta Crystallogr.* **1980**, *B36*, 2873.

(16) Fallon, G. D.; Gatehouse, B. M. *Acta Crystallogr.* **1976**, *B32*, 71.

(17) Bukovec, P.; Miličević, S.; Demšar, A.; Golic, L. *J. Chem. Soc., Dalton Trans.* **1981**, 1802.

(18) Waltersson, K. *Cryst. Struct. Commun.* **1978**, *7*, 507.

(19) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 378.

(20) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168.

(21) Wiegardt, K.; Bossek, U.; Volckmar, K.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 1387.

(22) Neves, A.; Wiegardt, K.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1988**, *150*, 183.

(23) Collison, D.; Eardley, D. R.; Mabbs, F. E.; Powell, A. K.; Turner, S. S. *Inorg. Chem.* **1993**, *32*, 664.

(24) Helbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.

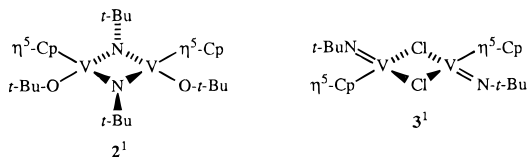
(25) Duraj, S. A.; Andras, M. T.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 1232.

(26) Tiekink, E. R. T.; Yan, X.-F.; Young, C. G. *Aust. J. Chem.* **1992**, *45*, 897.

(27) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204.

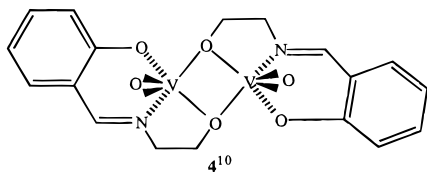
(28) Gilson, T. R.; Thom-Postlethwaite, I. M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1986**, 895.

to represent a metal–metal single bond. The average V–V distance of 2.612(2) Å in **1** is slightly longer than twice the single-bond radius of vanadium (2.45 Å)³² and lies well within the aforementioned range. However, contrary to expectation for the presence of such a bond, **1** is paramagnetic as observed by solution NMR and EPR spectroscopies and also by solid state magnetic susceptibility measurements to be discussed shortly. By contrast compound **2**, which has a longer V–V



distance (2.970(3) Å) than that in **1**, is diamagnetic.¹

The ¹H and ¹³C{¹H} NMR spectra of **1** in benzene-*d*₆ displayed a broad singlet at 4.18 and 52.53 ppm, respectively, consistent with the paramagnetism of this compound. Its EPR spectrum in benzene-*d*₆ at room temperature exhibited the 15-line pattern expected for a vanadium dimer. It is noteworthy that vanadium dimers display a variety of EPR spectral characteristics upon changing the bridging ligands or the V–V distances. Thus, in contrast to **1**, **3** showed an 8-line signal,¹ consistent with a longer V–V distance than that in **1** and the absence of an observable V–V interaction. By contrast, **4** is EPR silent in solution.¹⁰



Compound **1** exhibits nearly ideal Curie–Weiss paramagnetism. The effective magnetic moment of 2.77 μ_B per dimer is

(29) (a) Allman, R.; Bauman, I.; Kutoglu, A.; Rosch, H.; Hellner, E. *Naturwissenschaften* **1964**, *51*, 263. (b) Klemm, W.; von Schnering, H. G. *Naturwissenschaften* **1965**, *52*, 12. (c) Plass, W. *Angew. Chem.*, in press and private communication.

independent of temperature between 2 and 296 K and is in good agreement with the spin-only value (2.83 μ_B) for an *S* = 1 (triplet) system. The nature of the orbital interactions that lead to the spin triplet ground state of **1** is illuminated by EHMO calculations.³³ For the model compound {(μ-O)₂V₂[N(SiH₃)₂]₄}³⁴ the HOMO's are a pair of singly occupied MO's separated by only 0.15 eV. The next occupied MO is 2.97 eV lower in energy, while the first unoccupied level is 0.49 eV higher in energy. Both of the HOMO's are primarily metal-centered and V–V bonding, one σ and the other π in character, but both also are antibonding with respect to the bridging O atoms. Thus the near degeneracy of these two MO's accounts nicely for the presence of two unpaired electrons and the spin triplet ground state. The low total V–V overlap population reflects a relatively weak V–V bond and is consistent with the relatively long V–V bond distance observed here.

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Supporting Information Available: Tables of crystallographic data, experimental details, and spectroscopic characterization data (16 pages). Ordering information is given on any current masthead page.

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(30) To a stirred, –78 °C suspension of LiN(SiMe₃)₂ (6.02 g, 34.9 mmol) in 100 mL of pentane was added 1.10 mL (2.02 g, 11.6 mmol) of VOCl₃. The mixture was allowed to warm to room temperature over 1.5 h and further stirred at room temperature for 17 h. A grey solid was filtered off and washed copiously with pentane. The filtrate and the washings were combined and concentrated to ca. 10 mL, and the solution was kept in a freezer for 1 day. After filtration of the dark green crystals at –78 °C and washing with cold pentane, the solid was recrystallized from pentane to give **1** in 22–38% yield.

(31) Crystal data: dark green, orthorhombic, *a* = 27.923(10) Å, *b* = 18.113(6) Å, *c* = 36.095(12) Å, *V* = 18256(10) Å³, *Z* = 16, space group *Pbcn*, *R* = 5.06%, GOF = 1.16.

(32) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, **1960**; p 256.

(33) (a) Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Atomic orbital zeta parameters were taken from the following: Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 177. (c) H_{ii} parameters were taken from the following: Moore, C. Circular 467 U.S. Department of Commerce, National Bureau of Standards, Vol. 1, 1949.

(34) MO calculations were performed on the model compound V₂O₂–[N(SiH₃)₂]₄ with all bond distances and angles for the V₂O₂N₄Si₈ framework the same as those in **1**. The CH₃ groups of **1** were replaced by H atoms with a Si–H distance of 1.48 Å.