Inorg. Chem. **2007**, *46*, 5483–5485

Inorganic Chemistry

Communication

Targeted Synthesis of μ-Oxo Divanadium(V) Compounds with Asymmetry in Coordination Environments[†]

**Pabitra Baran Chatterjee,[‡] Nabanita Kundu,[‡] Subhojit Bhattacharya,[‡] Ki-Young Choi,[§]
Akira Endo,[£] and Muktimoy Chaudhury*,[‡]**

*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Kolkata 700 032, India, Department of Chemistry Education, Kongju National University,
Kongju 314-701, South Korea, and Department of Chemistry, Faculty of Science and Technology,
Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan*

Received May 4, 2007

Isovalent μ-oxo divanadium(V) compounds [$L^1VO(\mu\text{-}O)VO(salen)$] (**1**) and its bromo derivative [$L^2VO(\mu\text{-}O)VO(salen)$]·$CH_3CN$ (**2**) (both H_2L^1 and H_2L^2 are tridentate dithiocarbazate-based ONS ligands) with ligands providing donor set and coordination number asymmetry in tandem have been synthesized for the first time; confirmations in favor of these unsymmetrical molecular structures have come from single-crystal X-ray diffraction analysis, as well as from NMR (both ^1H and ^{51}V) spectroscopy.

To our knowledge, all the μ-oxo divanadium compounds containing a $V_2O_3^{n+}$ core ($n = 4$, 3, and 2) reported thus far have symmetrical structures involving identical ligand molecule(s) attached to both the metal centers.[1−6] When the vanadium centers have octahedral geometry,[1−3] the majority of these compounds[2,3] have a linear V−O−V bridge with the terminal oxo- groups in mutually trans positions (anti-linear structure).[4b] On the other hand, when the vanadium centers have square pyramidal geometry,[4−6] the bridging and terminal oxygen atoms have diverse range of arrangements, from anti-linear[5k,5l] to syn-angular[4,5a,b] through anti-angular[5c−j] and twist-angular[6] structures. Herein, we sought to explore further the electronic and molecular structures of μ-oxo divanadium(V) compounds with a heretofore unknown unsymmetrical combination involving an octahedral and a square pyramidal vanadium(V) center coupled together by a μ-oxo bridge. For this to happen, we have chosen [VO(salen)] as the precursor compound to generate the octahedral vanadium site. This compound in solution is known to get aerially oxidized to [$V^VO(salen)$]$^+$ in the presence of added anions, viz. ClO_4^-, BF_4^-, etc.[7] The vanadium centers in these oxidized compounds have octahedral geometry with the incoming anions being accommodated in to the vacant coordination site of the metal ion, trans to the terminal oxo-group. In order to generate the square pyramidal vanadium(V) center, we have chosen the tridentate biprotic ligands, *S*-methyl-3-(2-hydroxyphenyl)methylenedithiocarbazate (H_2L^1)

[†] Dedicated to Professor K. Nag on the occasion of his 65th birthday.

* To whom correspondence should be addressed. E-mail: icmc@iacs.res.in.

[‡] Indian Association for the Cultivation of Science.

[§] Kongju National University.

[£] Sophia University.

(1) (a) Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. *J. Chem. Soc. Chem. Commun.* **1979**, 707. (b) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168. (c) Schulz, D.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chim. Acta* **1995**, *240*, 217. (d) Yamada, S.; Katayama, C.; Tanaka, J.; Tanaka, M. *Inorg. Chem.* **1984**, *23*, 253. (e) Hayton, T. W.; Patrick, B. O.; Legzdins, P. *Inorg. Chem.* **2004**, *43*, 7227. (f) Nielsen, K.; Rasmus, R.; Eriksen, K. M. *Inorg. Chem.* **1993**, *32*, 4825.

(2) (a) Launay, J.-P.; Jeannin, Y.; Daoudi, M. *Inorg. Chem.* **1985**, *24*, 1052. (b) Holwerda, R. A.; Whittlesey, B. R.; Nilges, M. *Inorg. Chem.* **1998**, *37*, 64. (c) Ghosh, S.; Nanda, K. K.; Addison, A. W.; Butcher, R. J. *Inorg. Chem.* **2002**, *41*, 2243. (d) Mahroof-Tahir, M.; Keramidas, A. D.; Goldfarb, R. B.; Anderson, O. P.; Miller, M. M.; Crans, D. C. *Inorg. Chem.* **1997**, *36*, 1657. (e) Toftlund, H.; Larsen, S.; Murray, K. S. *Inorg. Chem.* **1991**, *30*, 3964.

(3) (a) Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363. (b) Gruning, C.; Schmidt, H.; Rehder, D. *Inorg. Chem. Commun.* **1999**, *2*, 57.

(4) (a) Dutta, S. K.; Kumar, S. B.; Bhattacharyya, S.; Tiekink, E. R. T.; Chaudhury, M. *Inorg. Chem.* **1997**, *36*, 4954. (b) Dutta, S. K.; Samanta, S.; Kumar, S. B.; Han, O. H.; Burckel, P.; Pinkerton, A. A.; Chaudhury, M. *Inorg. Chem.* **1999**, *38*, 1982.

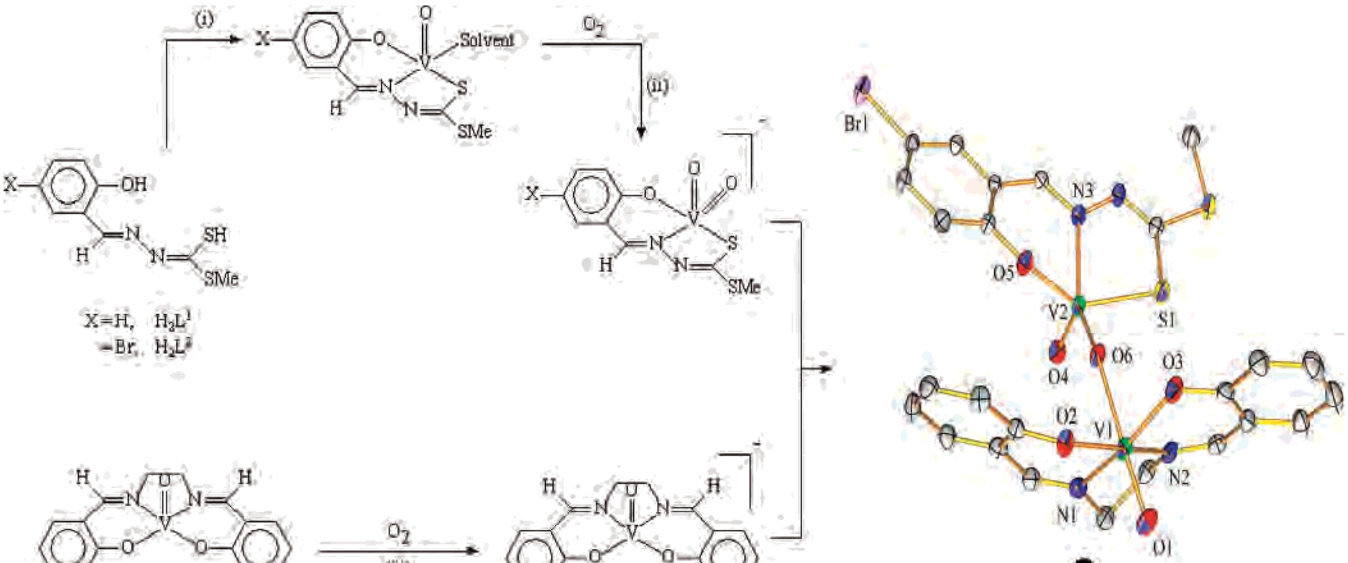
(5) (a) Pessoa, J. C.; Silva, J. A. L.; Vieira, A. L.; Vilas-Boas, L.; O'Brien, P.; Thronton, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1745. (b) Hartung, J.; Dress, S.; Greb, M.; Schmidt, P.; Svoboda, I.; Fuess, H.; Murso, A.; Stalke, D. *Eur. J. Org. Chem.* **2003**, 2388. (c) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 5343. (d) Ludwig, E.; Schilde, U.; Uhlemann, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 669. (e) Sundheim, A.; Mattes, R. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1848. (f) Chakravarty, J.; Dutta, S.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2857. (g) Ludwig, E.; Hefele, H.; Schilde, U.; Uhleman, E. Z. *Anorg. Allg. Chem.* **1994**, *620*, 346. (h) Dai, J.; Akiyama, S.; Munakata, M.; Mikuriya, M. *Polyhedron* **1994**, *13*, 2495. (i) Bellemin-Laponnaz, S.; Coleman, K. S.; Dierkes, P.; Masson, J. P.; Osborn, J. A. *Eur. J. Inorg. Chem.* **2000**, 1645. (j) Dinda, R.; Sengupta, P.; Ghosh, S.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 1684. (k) Wang, D.; Behrens, A.; Farahbakhsh, M.; Gatjens, J.; Rehder, D. *Chem. Eur. J.* **2003**, *9*, 1805. (l) Pessoa, J. C.; Calhorda, M. J.; Cavaco, I.; Correio, I.; Duarte, M. T.; Felix, V.; Henriques, R. T.; Piedade, M. F. M.; Tomaz, I. *J. Chem. Soc., Dalton Trans.* **2002**, 4407.

(6) Mandal, S.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 59.

(7) (a) Bonadies, J. A.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* **1987**, *26*, 1218. (b) Oyaizu, K.; Dewi, E. L.; Tsuchida, E. *Inorg. Chem.* **2003**, *42*, 1070.

10.1021/ic700858g CCC: \$37.00

Scheme 1. Synthetic Strategy for the Preparation of the Unsymmetrical Complexes and an ORTEP View of **2** (Acetonitrile Molecule and the Hydrogen Atoms have been Omitted for Clarity).[a]



2

[a] Conditions: (i) $VO(acac)_2$, CH_3CN, reflux; (ii) cation-assisted aerial oxidation; (iii) anion-assisted aerial oxidation in CH_3CN. Selected interatomic distances (Å) and angles (deg) in **2**: V(1)−O(1) 1.587(3), V(1)−O(2) 1.816(3), V(1)−O(3) 1.855(3), V(1)−N(1) 2.081(3), V(1)−N(2) 2.081(3), V(1)−O(6) 2.140(3), V(2)−O(4) 1.596(3), V(2)−O(5) 1.881(3), V(2)−N(3) 2.178(3), V(2)−S(1) 2.3694(13), V(2)−O(6) 1.669(3), V(1)−O(6)−V(2) 157.79(16), O(1)−V(1)−O(6) 173.25(13), O(4)−V(2)−O(6) 108.11(18).

and its bromo derivative (H_2L^2). These ligands can generate square pyramidal cis-dioxo anionic species $[LV^VO_2]^-$ when H_2L ($L = L^1$ and L^2) is refluxed with $[VO(acac)_2]$ in acetonitrile in the presence of an added cation.[8] In the synthetic strategy outlined in Scheme 1, stoichiometric amounts of $[V^{IV}O(acac)_2]$, H_2L, and $[V^{IV}O(salen)]$ (1:1:1 mol ratio) were refluxed in acetonitrile and subsequently exposed to atmospheric oxygen to get both $[V^VO(salen)]^+$ and $[LV^VO_2]^-$ species together, thus allowing the anionic species to be accommodated in to the vacant coordination site of $[VO(salen)]^+$, leading to the desired products **1** and **2** as brown crystalline solids. The formation of $[V^VO(salen)]^+$, we believe, is favored by the anion ($[LV^VO_2]^-$)-assisted oxidation of $[V^{IV}O(salen)]$,[7] while that of $[LV^VO_2]^-$ is facilitated by the cation ($[V^VO(salen)]^+$)-assisted oxidation of the putative species $[LV^{IV}O(solvent)]$.[8] The infrared spectrum of **1** displays two strong bands at 953 and 917 cm^{-1} (964 and 911 cm^{-1} for **2**) due to terminal V═O stretchings, corresponding to the individual vanadium centers.

An unambiguous description of the coordination geometry around the vanadium centers in these compounds has been obtained through single-crystal X-ray diffraction analysis.[9] An ORTEP view of **2** is displayed in Scheme 1 as a representative example. The two halves of the molecule, bridged by an oxygen atom, O6, have different geometry. The coordination environment around V1 is octahedral, while that about V2 is square pyramidal. The angles at the vanadium centers made by the bridging and terminal oxo atoms, viz. O1−V1−O6 173.25(13)° (the corresponding angle in **1** is 171.89(8)°) and O4−V2−O6 108.11(18)° (108.54(9)°) are as expected for a nearly ideal octahedral and square pyramidal geometry, respectively. The V1−O6−V2 bridge angle of 157.79(16)° (166.20(9)°) is in between the values expected for symmetric divanadium compounds with octahedral (ca. 180°)[2] and square pyramidal (ca. 145°)[4,5a,b] metal centers. The V_2O_3 core in these compounds has a rare twist-angular structure,[6] somewhat intermediate between the regular anti-linear and syn-angular modes. Of particular interest here is the trans location of the bridging oxygen atom O6 relative to the terminal oxo- atom O1 attached to the octahedral V1. Such a trans arrangement is unique in divanadium compounds containing $V_2O_3^{n+}$ core.[1−6] Consequently, the V1−O6 distance 2.140(3) Å (2.1416(16) Å) is significantly enlarged due to trans-labilizing influence of the terminal oxo- atom O1, compared to the other bridging distance V2−O6 1.669(3) Å (1.6733(16) Å). In effect, the enlarged V1···V2 separation in **2,** 3.739 Å (3.792 Å), is by far the largest among its peers (divanadium compounds containing the V_2O_3 core) reported thus far in the literature.[1−6]

To understand more about the electronic and molecular structures of these compounds in solution, both ^1H and ^{51}V NMR spectra have been measured in DMSO-d_6 solution at

---

(8) (a) Dutta, S. K.; Samanta, S.; Mukhopadhyay, S.; Burckel, P.; Pinkerton, A. A.; Chaudhury, M. *Inorg. Chem.* **2002**, *41*, 2946. (b) Samanta, S.; Ghosh, D.; Mukhopadhyay, S.; Endo, A.; Weakley, T. J. R.; Chaudhury, M. *Inorg. Chem.* **2003**, *42*, 1508. (c) Samanta, S.; Mukhopadhyay, S.; Mandal, D.; Butcher, R. J.; Chaudhury, M. *Inorg. Chem.* **2003**, *42*, 6284.

(9) Crystal data for **1**: $C_{25}H_{22}N_4O_6S_2V_2$, $M = 640.47$, triclinic, space group $P1$, $a = 9.9337(8)$ Å, $b = 10.6502(9)$ Å, $c = 13.4951(11)$ Å, $\alpha = 107.3840(10)°$, $\beta = 101.890(2)°$, $\gamma = 97.5190(10)°$, $V = 1304.67(19)$ Å^3, $Z = 2$, $D_c = 1.630$ g cm^{-3}, $F(000) = 652$, $\mu(\text{Mo } K_\alpha) = 0.926$ mm^{-1}, $T = 293(2)$ K, 6457 unique reflections [$R(\text{int}) = 0.0290$], R (on F) = 0.0607, R_w (on F^2) = 0.0983 (based on all data). Crystal data for **2**·CH_3CN: $C_{27}H_{24}BrN_5O_6S_2V_2$, $M = 760.42$, triclinic, space group $P\bar{1}$, $a = 11.1599(6)$ Å, $b = 11.5448(7)$ Å, $c = 14.1841(8)$ Å, $\alpha = 81.3900(10)°$, $\beta = 67.0010(10)°$, $\gamma = 63.1810(10)°$, $V = 1500.47(15)$ Å^3, $Z = 2$, $D_c = 1.683$ g cm^{-3}, $F(000) = 764$, $\mu(\text{Mo } K_\alpha) = 2.144$ mm^{-1}, $T = 293(2)$ K, 7426 unique reflections [$R(\text{int}) = 0.05$], R (on F) = 0.1104, R_w (on F^2) = 0.1315 (based on all data).

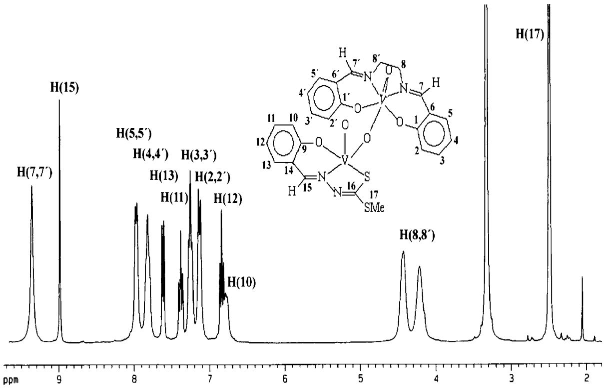


Figure 1. ^{1}H NMR spectrum of compound **1** in DMSO-d_6 solution at 293 K.

room temperature. The ^{1}H NMR spectrum of **1** (data summarized in the Supporting Information) is shown in Figure 1, which displays a pair of singlets at 9.35 and 8.98 ppm (2:1 intensity ratio) corresponding to the presence of two different kinds of azomethine moiety in this molecule. Also deserving of mention is the triplet at 7.38 ppm due to the H11 proton. Substitution of bromine at C12 in compound **2** makes the same proton (H11) to appear as a pair of doublets (Figure S1) centered at ca. 7.48 ppm ($J = 2.5$ Hz) due to ortho−meta couplings. All these and the remaining signals along with their corresponding splitting patterns are in conformity with the presence of unsymmetrical coordination environments in these molecules as exist solution.

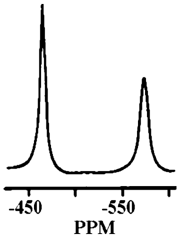


Figure 2. ^{51}V NMR spectrum of compound **1** in DMSO-d_6 solution at room temperature.

In the ^{51}V NMR spectrum, two signals have been observed as displayed in Figure 2 for compound **1**. One of these appearing at −467 ppm (relative to $VOCl_3$ as standard) is due to the vanadium center included in the V^{V}OL part,[4b] while the other at −575 ppm is arising from the V^{V}O(salen) moiety.[10] Corresponding signals in the spectrum of **2** appear at −466 and −575 ppm, respectively, and are in compliance with the unsymmetrical vanadium coordination environments. The ESI mass spectrum (Figure S2) of compound **1** in CH_3CN shows the molecular ion peak at $m/z = 641$ [M + H]$^+$ (100% relative abundance) with the expected isotope distribution.

The cyclic voltammogram (Figure S3) of **2** in DMSO shows a cathodic reversible process at $E_{1/2} = 0.45$ V vs Ag/AgCl reference (25 °C, Pt working electrode, 100 mV s^{-1} scan rate), as confirmed by steady-state voltammetry. Results of constant potential coulometry ($E_W = 0.2$ V) indicate single-electron stoichiometry for this process, thus confirming the generation of a mixed-oxidation divanadium(IV/V) product [**2**$^-$] during the course of electrolysis. The EPR spectrum at room temperature (Figure S4) of the electrolyzed solution displayed an eight-line (^{51}V, $I = 7/2$) hyperfine pattern ($<g> = 1.990$, $<A> = 88 \times 10^{-4}$ cm^{-1}) indicating a trapped-valence nature of the reduced product in the EPR time scale.[1c] Electronic spectrum of the catholyte solution failed to show any characteristic band in the NIR region, expected for a possible intervalence charge-transfer, lending support to the results of EPR spectroscopy in confiming the trapped-valence nature of the reduced mixed-oxidation species. The valence-trapped situation probably is arising here from the bent V−O−V bridge, preventing the symmetry-constrained vanadium d_{xy} orbitals, containing the odd unpaired electron, to overlap effectively via the pπ orbital of the bridging oxygen atom.[11]

In summary, a novel synthetic route has been developed for the synthesis of μ-oxo divanadium(V) compounds containing a hitherto unknown V_2O_3 core involving vanadium centers with separate donor atoms set. The identities of the compounds have been conclusively established both in solution, as well as in the solid state. The V···V separations in these compounds are by far the largest, 3.792 Å (3.739 Å for **2**), among their peers due to the trans-labilizing influence of a terminal oxo-group. The V_2O_3 core in these compounds has a twist-angular structure[6] somewhat intermediate between the anti-linear and syn-angular modes, often encountered in symmetrical divanadium compounds.[4b]

Acknowledgment. This work was supported by the Council of Scientific and Industrial Research (CSIR), New Delhi. P.B.C. and S.B. also thank CSIR for the award of research fellowships. M.C. thanks the authorities of Sophia University, Japan, for a Lecturing-Research Grant, 2006.

Supporting Information Available: Full synthetic details, ^{1}H NMR data, and CIF files for **1** and **2**, ESI mass spectrum of **1**, cyclic voltammogram followed by EPR spectrum of the catholyte solution of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700858G

---

(10) Choudhary, N. F.; Hitchcock, P. B.; Leigh, G. J. *Inorg. Chim. Acta* **2000**, *310*, 10.

(11) Young, C. G. *Coord. Chem. Rev.* **1989**, *96*, 89.