

Synthesis and crystal structures of low-valent binuclear vanadium complexes using the tethering ligand *m*-xylylenebis(acetylacetonate) (*m*-xba²⁻)

Peter J. Bonitatebus, Jr., Sanjay K. Mandal and William H. Armstrong*†

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

An intriguing structural type new to low-valent vanadium chemistry and the binucleating ligand *m*-H₂xba is exhibited by the reported V^{III} dimers and the first structurally characterized bis(acetylacetonate) ligated complex of V^{II}.

Our interest in small molecule and organic functional group reduction using low-valent vanadium species featured in an anionic oxygen donor environment, as in the cases of carboxylate^{1a} and aryloxy,^{1b,c} has prompted us to investigate bis(acetylacetonates) as ligands in an attempt to synthesize binuclear complexes capable of intramolecular substrate binding and activation. Di- and tri-valent vanadium acetylacetonates are involved as undefined *in situ* intermediates in reactions ranging from epoxide deoxygenations² to dinitrogen uptake,³ yet curiously very few structurally defined examples of bis(acetylacetonate) ligated V^{III} species have been reported.⁴ Structurally characterized complexes with acetylacetonate bonded exclusively to V^{II} remain unknown,^{4e} although they have been studied spectroscopically in solution.⁵ The flexible *m*-xba²⁻ limits intermetallic distances acting as a tether, and should allow for a face-to-face approach of vanadia as observed in the chemistry of Cu^{II} where a discrete cofacial binuclear complex has been synthesized providing a cavity of well defined size and shape [Cu...Cu, 4.908(2) Å]⁶ appropriate for diatomic guest molecule incorporation (Fig. 1). Complexes of this type potentially will serve to promote and catalyze multielectron redox reactions, a strategy conceptually reminiscent of Collman's cofacial dimetalloporphyrin approach.⁷

We sought to prepare binuclear vanadium assemblies envisioning a target structure analogous to the Cu^{II} example, whereby reducible small molecules could be intramolecularly bound and activated. One obstacle in discrete dimer synthesis expected was oligomerization for these six-coordinate metal centers, yet here we report on the self-assembly and structures of novel discrete binuclear paramagnetic V^{II} and V^{III} complexes exhibiting an intriguing 'cage-like' structural type new to low-valent vanadium chemistry and the *m*-xba²⁻ ligand system. These compounds represent an important advance toward our target structure.

The reaction of [VX₃(thf)₃]⁸ (X = Cl, Br) with 1 equiv. of the disodium salt of *m*-H₂xba,⁹ generated in thf using 2 equiv. of NaH, proceeds at room temperature to produce complexes of the general formula [V₂X₂(thf)₂(*m*-xba)₂] (X = Cl, **1**, Br **2**) in 65% yield for both cases.‡ These compounds do not oligomerize upon standing in dichloromethane or thf solution over time, yet in the preparation of **1** and **2** insoluble precipitates

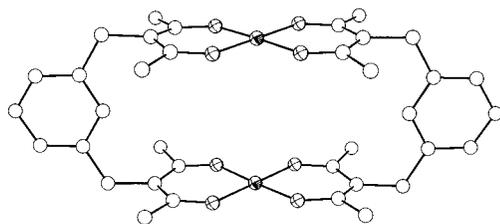


Fig. 1. Structure of [Cu₂(*m*-xba)₂]⁶

thought to be oligomeric in nature along with NaX are removed by filtration. Complexes **1** and **2** were isolated as golden yellow–brown crystalline materials from concentrated thf solutions stored at 0 °C and were characterized by X-ray crystallography. The IR spectra§ of **1** and **2** show a strong band at 1559 cm⁻¹ indicative of β-diketonate moieties chelated to the vanadia, along with two sets of doublets positioned at 867, 1020 and 918, 1065 cm⁻¹, assignable to ν_{C–O–C} stretching modes of coordinated and free thf molecules respectively.¹⁰ The structure of **1** is shown in Fig. 2.¶

The crystal structures of **1** and **2** revealed binuclear molecules with crystallographically imposed inversion symmetry. Compounds **1** and **2** are structurally analogous. The average V–O(acac) bond length of **1** [1.961(3) Å] is in good agreement with corresponding lengths of other rare acetylacetonates of V^{III} [av. 1.964(3) Å^{4a} and 1.989(4) Å^{4e}]. Considering the conformation of *m*-xba²⁻ in this structure, spanning the two vanadium atoms with a V...V distance of just over 11.66 Å and an aromatic ring-plane (centroids) separation of 5.366 Å, a structural rearrangement will be required to obtain the optimal distance for dual binding and activation of a small molecule. It is anticipated that dimers **1** and **2** will serve as useful precursors in establishing the desired *strati* conformation (see Fig. 1). Upon reduction of **1** or **2** in solution to reactive (II,II) species a structural change will be permitted to occur owing to rotational freedom about the C_{phenyl}–C_{benzyl} bond of the xylylene unit.

Our success with the synthesis of a discrete V^{II,II} dimer compound [V₂(tmeda)₂(*m*-xba)₂] **3** is very encouraging considering the intention of generating a lower-valent species from a tethered V^{III,III}₂ assembly (**1** or **2**). Compound **3** was prepared in a similar manner (53% yield) to **1** and **2** using instead [VCl₂(tmeda)₂]¹¹ as a starting material.‡ Intensely colored midnight-blue X-ray quality crystals were isolated from concentrated thf solutions after removal of insoluble precipitates and NaCl by filtration, and cooling to 0 °C. The molecular structure and selected dimensions for **3** are shown in Fig. 3.¶ A structure similar to **1** and **2** was revealed with a V...V distance of 11.444(1) Å and an aromatic ring-plane (centroids) separation of 5.426 Å, as dictated by the *m*-xba²⁻ ligand orientation which again is in an extended conformation. The remaining sites are occupied by tmeda molecules. In comparing the changes in the vanadium coordination sphere, a subtle lengthen-

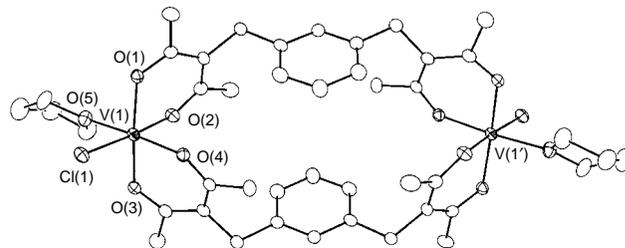


Fig. 2. Structure of **1** showing 30% probability thermal ellipsoids and atom-labeling scheme (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): V(1)–O(1) 1.941(2), V(1)–O(2) 1.962(2), V(1)–O(3) 1.985(2), V(1)–O(4) 1.955(2), V(1)–O(5) 2.097(2), V(1)–Cl(1) 2.366(1); O(1)–V(1)–O(2) 87.1(1), O(3)–V(1)–O(4) 85.4(1).

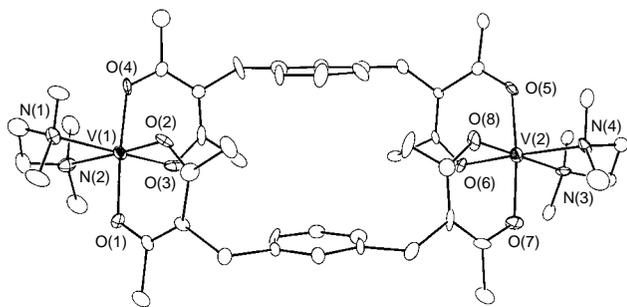


Fig. 3. Structure of **3** showing 30% probability thermal ellipsoids and atom-labeling scheme (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): V(1)–O(2) 2.035(9), V(1)–N(1) 2.23(1), V(1)–O(4) 2.04(1), V(1)–N(2) 2.26(1), V(1)–O(1) 2.03(1), V(1)–O(3) 2.00(1), V(2)–O(6) 2.020(9), V(2)–N(3) 2.20(2), V(2)–O(5) 2.06(1), V(2)–N(4) 2.22(1), V(2)–O(7) 2.02(1), V(2)–O(8) 2.05(1); O(5)–V(2)–O(6) 85.9(4), O(7)–V(2)–O(8) 86.8(5), O(1)–V(1)–O(2) 87.0(4), O(3)–V(1)–O(4) 86.8(5).

ing of the V–O(acac) bonds is observed [V–O_{av.}: **1** 1.961(3) Å, **3** 2.033(9) Å] consistent with a decrease in oxidation state. Compound **3** is, to our knowledge, the first example of a structurally characterized bis(acetylacetonate) ligated complex of V^{II}. An X-band EPR spectrum[§] in frozen (77 K) thf solution displays an intense broad signal at $g = 4$ with no higher-field absorbances detected under these conditions. The successful preparation of a (II,II) dimer is of great interest considering the application of precursors **1** and **2** toward *strati* target structure synthesis *via* reduction and terminal halide removal.

Ongoing studies focus on testing the rearrangement proposition described above in working toward a cofacial conformation. We are also interested in extending our investigations to include bis(β-diketonates) with bridging groups other than the *m*-xylylene framework.

Notes and References

† E-mail: william.armstrong@bc.edu

‡ Complexes **1–3** analyzed satisfactorily. The scale of a typical reaction was on the order of 0.54 mmol in *m*-H₂xba ligand and vanadium-containing starting materials.

§ Selected spectroscopic data: **1**; UV–VIS (CH₂Cl₂): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) = 304 (31 900), 359 (16 600); IR (Nujol, cm⁻¹) 1559vs, 1288s, 1207m, 1173m, 1065w, 1020s, 948s, 918w, 867s, 742m. **3**; EPR (thf 77 K, X-band) $g = 4$ (br); UV–VIS (thf): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) = 288 (49 800), 343 (9 110), 484 (2040), 592 (3380), 684 (2580); IR (Nujol, cm⁻¹) 1558vs, 1286s, 1201m, 1165w, 1127w, 1029s, 949s, 796s, 743m, 693w.

¶ Crystal data: **1**·thf; C₄₄H₅₆Cl₂O₁₁V₂, $M = 989.763$, monoclinic, space group C2/c, $a = 20.2285(4)$, $b = 13.0235(2)$, $c = 20.2383(4)$ Å, $\beta = 94.395(1)^\circ$, $U = 5316.0(2)$ Å³, $Z = 4$, $D_c = 1.347$ g cm⁻³, $F(000) = 2240$, $\mu = 0.515$ mm⁻¹, $T = 183$ K, $\lambda = 0.71073$ Å, $2\theta_{\max} = 56.58^\circ$, 15 553 measured reflections on a Siemens SMART CCD area-detector diffractometer, 6099 unique ($R_{\text{int}} = 0.0376$, no absorption correction). The structure was solved by direct methods and refined by FMLS methods on F^2 with statistical weighting, anisotropic displacement parameters for all non-hydrogen atoms (except those of the disordered thf solvent molecule), constrained isotropic H atoms to give $R' = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.0771$ on all data, conventional $R_1 = 0.0604$ on F values of 4997 reflections having $F_o^2 > 4\sigma F_o^2$, goodness of fit $S = 1.087$ for all F^2 values and 300 refined parameters. Final difference map features were within ± 0.920 e Å⁻³. Programs: Siemens SMART and SAINT control and integration software, Siemens SHELXTL Version 5.

2·thf; C₄₄H₅₆Br₂O₁₁V₂, $M = 1078.675$, monoclinic, space group C2/c, $a = 20.081(6)$, $b = 13.264(6)$, $c = 20.670(4)$ Å, $\beta = 95.75(2)^\circ$, U

$= 5478.0(3)$ Å³, $Z = 4$, $D_c = 1.395$ g cm⁻³, $F(000) = 2384$, $\mu = 1.857$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 183$ K. 6944 reflections measured, 3894 unique data ($2\theta_{\max} = 56.44^\circ$, $R_{\text{int}} = 0.0917$, no absorption correction). Structure solution and refinement were as for **1** including a disordered thf molecule to give 2698 reflections having $F_o^2 > 4\sigma F_o^2$ with conventional $R_1 = 0.0968$ ($wR_2 = 0.1709$) and goodness of fit $S = 1.260$ (307 parameters). Final difference map features were within 0.680 and -0.780 e Å⁻³.

3·2thf; C₅₂H₈₀N₄O₁₀V₂, $M = 934.943$, monoclinic, space group Pn, $a = 13.7459(8)$, $b = 11.1388(6)$, $c = 18.6718(5)$ Å, $\beta = 90.816(2)^\circ$, $U = 2858.6(2)$ Å³, $Z = 2$, $D_c = 1.249$ g cm⁻³, $F(000) = 1148$, $\mu = 0.385$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 183$ K. 7530 reflections measured, 6244 unique data ($2\theta_{\max} = 56.42^\circ$, $R_{\text{int}} = 0.0658$, semi-empirical absorption corrections). Structure solution and refinement performed as above including a partially disordered thf molecule to give 4173 reflections having $F_o^2 > 4\sigma F_o^2$ with conventional $R_1 = 0.0655$ ($wR_2 = 0.1223$) and goodness of fit $S = 1.092$ (644 parameters). Final difference map features were within 0.309 and -0.283 e Å⁻³. CCDC 182/763.

- (a) L. Gelmini and W. H. Armstrong, *J. Chem. Soc., Chem. Commun.*, 1989, 1904; (b) M. J. Scott, W. C. A. Wilisch and W. H. Armstrong, *J. Am. Chem. Soc.*, 1990, **112**, 2429; (c) W. C. A. Wilisch, M. J. Scott and W. H. Armstrong, *Inorg. Chem.*, 1988, **27**, 4333. Our interest in low-valent vanadium syntheses and reactivity appears elsewhere: (d) C. R. Randall and W. H. Armstrong, *J. Chem. Soc., Chem. Commun.*, 1988, 986; (e) D. B. Sable and W. H. Armstrong, *Inorg. Chem.*, 1992, **31**, 161; (f) H. H. Murray, S. G. Novick, W. H. Armstrong and C. S. Day, *J. Cluster Sci.*, 1993, **4**, 439; (g) J. A. Davis, C. P. Davie, D. P. Sable and W. H. Armstrong, *Chem. Commun.*, 1998, in press.
- Y. Hayashi and J. Schwartz, *Inorg. Chem.*, 1981, **20**, 3473.
- M. E. Vol'pin, M. A. Ilatovskaya, E. I. Larikov, M. L. Khidkele', Y. A. Shvetsov and V. B. Shur, *Dokl. Akad. Nauk SSSR*, 1965, **164**, 331.
- (a) M. Doring, H. Gørls, E. Uhlig, K. Brodersen, L. Dahlenburg and A. Wolski, *Z. Anorg. Allg. Chem.*, 1992, **614**, 65; (b) P. Knopp, K. Wiegand, B. Nuber, J. Weiss and W. S. Sheldrick, *Inorg. Chem.*, 1990, **29**, 363; (c) S. Lee, K. Nakanishi, M. Y. Chiang, R. B. Frankel and K. Spartalian, *J. Chem. Soc., Chem. Commun.*, 1988, 785; (d) V. I. Lisoivan and S. A. Gromilov, *Zh. Neorg. Khim.*, 1986, **31**, 2539; (e) E. Solari, S. De Angelis, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1992, **31**, 141. Also reported, [(thf)₃V(μ-acac)(μ-Cl)ZnCl₂], a dimeric structure of acetylacetonate bonded to V^{II} and Zn^{II} *via* one of its bridging oxygen atoms; (f) V. A. Grillo, E. J. Seddon, C. M. Grant, G. Aromi, J. C. Bollinger, K. Foltling and G. Christou, *Chem. Commun.*, 1997, 1561.
- J. M. Crabtree, D. W. Marsh, J. C. Tomkinson, R. J. P. Williams and W. C. Fernelius, *Proc. Chem. Soc.*, 1961, 336; W. P. Schaefer, *Inorg. Chem.*, 1965, **4**, 642; Y. Torii, H. Iwaki and Y. Inamura, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1550; V. A. Alekseevskii and T. A. Grabovskaya, *Russ. J. Inorg. Chem.*, 1985, **30**, 1739.
- A. W. Maverick and F. E. Klavetter, *Inorg. Chem.*, 1984, **23**, 4129.
- J. P. Collman, J. E. Hutchison, M. A. Lopez, R. Guillard and R. R. Reed, *J. Am. Chem. Soc.*, 1991, **113**, 2794; J. P. Collman, J. E. Hutchison, M. A. Lopez and R. Guillard, *J. Am. Chem. Soc.*, 1992, **114**, 8066; J. P. Collman, J. E. Hutchison, M. S. Ennis, M. A. Lopez and R. Guillard, *J. Am. Chem. Soc.*, 1992, **114**, 8074; J. P. Collman, J. E. Hutchison and P. S. Wagenknecht, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1537; R. Guillard, S. Brandes, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. P. Knop and J. P. Collman, *J. Am. Chem. Soc.*, 1995, **117**, 11721; J. P. Collman, M. S. Ennis, D. A. Oxford, L. L. Chng and J. H. Griffin, *Inorg. Chem.*, 1996, **35**, 1751.
- L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135. The bromide derivative was prepared similarly and purified by Soxhlet extraction using thf.
- The synthesis of *m*-H₂xba has been described previously: A. W. Maverick, D. P. Martone, J. R. Bradbury and J. E. Nelson, *Polyhedron*, 1989, **8**, 1549.
- F. L. Bowden and D. Ferguson, *Inorg. Chim. Acta*, 1978, **26**, 251.
- J. H. Edema, W. Stauthamer, S. Gambarotta, F. van Bolhuis, W. J. J. Smeets and A. L. Spek, *Inorg. Chem.*, 1990, **29**, 1302.

Received in Bloomington, IN, USA, 2nd December 1997; 7/08693H