Aggregation/deaggregation processes in vanadium(II) carboxylate chemistry

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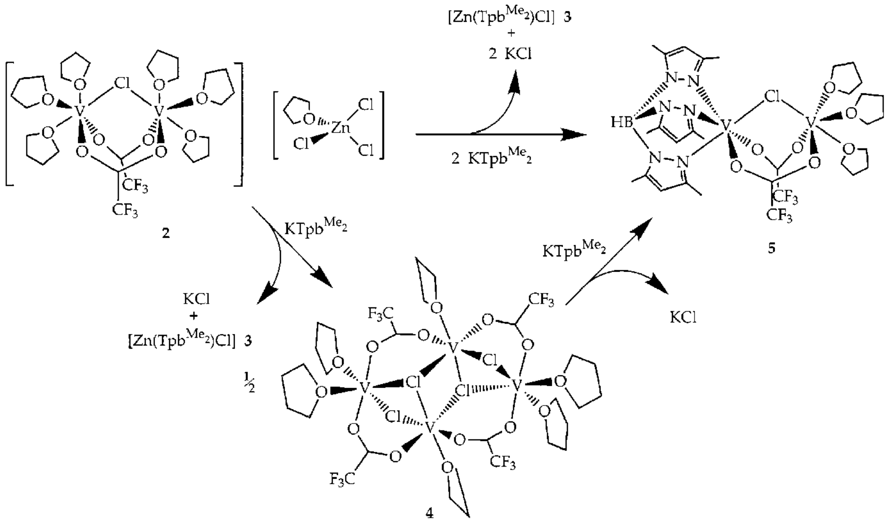
Reactions of potassium tris(3,5-dimethylpyrazolyl)borate (KTpb^{Me_2}) with the low-valent mixed-metal complex [(thf)$_3$V(μ-Cl)(μ-tfa)$_2$V(thf)$_3$][ZnCl$_3$(thf)] resulted first in ZnCl$^+$ abstraction and tetramer formation, then in asymmetric binuclear product formation through ligand substitution.

Our efforts in developing the chemistry of low-valent vanadium in an anionic oxygen ligand donor environment,[1–4] including that of vanadium(II) carboxylate coordination chemistry,[1] stems from the reported reducing and oxophilic character of these types of V^{II} complexes in both protic and aprotic media. For example, α,ω-dicarboxylic acids have been shown to promote the reaction between N$_2$ and vanadium(II) to yield N$_2$H$_4$ in the presence of hydroxide *via* by a proposed carboxylato-bridged V^{II} aggregate.[5] These reported conditions are mild, aqueous and heterogeneous in nature. Studies in organic, aprotic media of the interaction of V^{II} and trifluoroacetate (tfa) by Cotton *et al.* in an attempt to synthesize a multiply-bonded metal species, '$V{\equiv}V^{4+}$', resulted instead in the isolation of an oxidized oxo-centered triangular core, [V$_3$(μ$_3$-O)(μ-tfa)$_6$(thf)$_3$] **1**.[6,7] Carboxyl group O-atom abstraction was postulated as the source of the (μ$_3$-O) atom in **1**, a conclusion based on the high oxophilicity of V^{II}. Although this latter report presented results of a synthetic strategy directed toward a '$V{\equiv}V^{4+}$' compound, it also served as an initial effort to homogenize and probe the original interesting N$_2$-fixing system.[5] Later efforts in our laboratory, under rigorously anaerobic and dry conditions using a similar preparation to that reported for **1**, demonstrated the existence and relative thermal stablility of a V^{II} carboxylate dimer, [(thf)$_3$V(μ-Cl)(μ-tfa)$_2$V(thf)$_3$][ZnCl$_3$(thf)], **2** (Scheme 1), isolated as a highly air- and moisture-sensitive compound in good crystalline yield.[1] Herein we describe our continued effort and interest in vanadium(II) carboxylate coordination chemistry by reporting on the synthesis, structure and some properties of a novel binuclear carboxylate complex along with its tetrameric precursor—an unprecedented example of vanadium(II) isolated at this nuclearity. These new 'zinc-free' and halide-bridged multinuclear V^{II} compounds represent an important advance in probing the N$_2$-fixing system of Folkesson and Larsson by serving as starting materials for reactions with hydroxide or alkoxide ligands. Alkoxide donors, in conjunction with carboxylato-bridged V^{II} aggregates, are conceivably required for efficient homogeneous small molecule multielectron reduction, as were hydroxide ions in the original heterogeneous V^{II} carboxylate N$_2$-fixing system.[5]

Treating green-purple **2** (0.22 mmol scale) with one equivalent of potassium tris(3,5-dimethylpyrazolyl)borate (KTpb^{Me_2}) in 15 mL of THF (Scheme 1) and stirring overnight gave deposition of a white precipitate (KCl) which was removed by filtration. Layering the resulting blue-green filtrate with 3–5 mL of pentane and allowing it to stand for 12 h at 0 °C discharged another colorless solid, but in crystalline form, which was filtered off and identified by X-ray crystallography to be [Zn(Tpb^{Me_2})Cl], **3**.† Layering and cooling the filtrate again completed the isolation of crystalline sky-blue [V$_4$(μ$_3$-Cl)$_2$(μ-Cl)$_2$(μ-tfa)$_4$(thf)$_6$] **4** (Fig. 1).‡ Apparently, this reaction involves scavenging the Zn^{II} of **2** as [Zn(Tpb^{Me_2})Cl], **3**, using KTpb^{Me_2}, with concomitant KCl formation and chloride ion liberation. This freed Cl drives the cationic core of **2** to dimerize assembling a [V$_4$tfa$_4$]$^{4+}$ aggregate, compound **4**.§

The crystal structure of **4** (Fig. 1) revealed a tetramer with crystallographically imposed inversion symmetry.† Selected dimensions, listed in Fig. 1, show V–O$_{thf}$ and V–O$_{tfa}$ bond lengths (av. 2.139, av. 2.101 Å, respectively) to be in good agreement with those of **2** (av. 2.140, av. 2.091 Å, respectively).[1] The apical (μ$_3$) chloride distances in **4** (av. 2.506 Å) are only slightly shorter than similar bonds seen for the *triangulo*-trinuclear species [V$_3$(μ$_3$-Cl)$_2$(μ-Cl)$_3$]$^+$ (av. 2.519 Å).[8] The V···V separations in **4** (4.169, 3.637, 3.351 Å) vary within a relatively large range (0.818 Å) as a consequence of the different numbers and types of bridging groups between vanadium centers. The angle made by V(1)–Cl(1)–V(2) is also significantly widened [112.81(4)°] compared with the V–Cl–V



Scheme 1 Synthesis of carboxylato-bridged vanadium(II) aggregates.

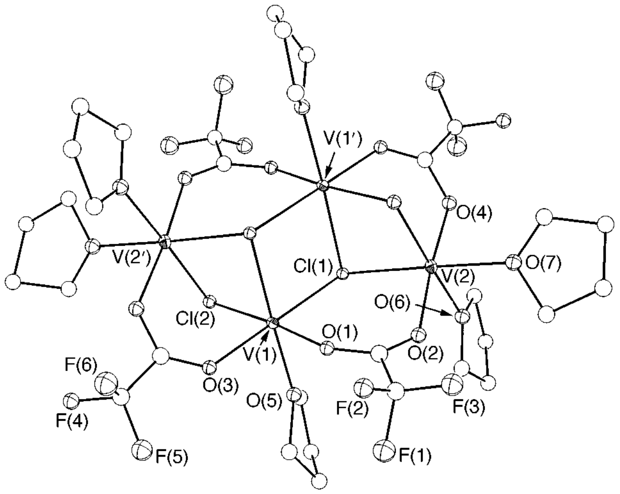


Fig. 1 Structure of **4** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°) are: V(1)–Cl(1) 2.515(1), V(1)–Cl(2) 2.481(1), V(2)–Cl(1) 2.489(1), V(1)–O(1) 2.109(3), V(2)–O(2) 2.090(3), V(1)–O(5) 2.129(3), V(2)–O(7) 2.140(4), V(1)–V(2) 4.169, V(1)–V(1′) 3.637, V(2)–V(1′) 3.351; V(1)–Cl(1)–V(2) 112.81(4), V(1)–Cl(1)–V(1′) 92.59(4), V(1)–Cl(2)–V(2′) 85.20(4), O(7)–V(2)–O(6) 86.4(2), O(1)–V(1)–Cl(2) 175.86(9), O(3)–V(1)–Cl(1) 179.90(9).

angle of **2** [100.3(1)°].[1] Compound **4** is the first example of an isolated vanadium(II) tetramer, and is resembled closest in terms of vanadium–ligand core connectivity and oxidation state by the methoxide-containing V_4^{10+} catecholato-bridged aggregate of Shilov and coworkers, the only structure reported to date from their vanadium-based N_2-fixing system.[9]

The aggregation of **2** $\longrightarrow$ **4** invites a question regarding the outcome of a reaction involving **4** with one more equivalent of $\mathrm{KTpb}^{\mathrm{Me}_2}$. Reaction of **4** with $\mathrm{KTpb}^{\mathrm{Me}_2}$ in THF [or treatment of **2** with two equivalents (0.45 mmol scale) of $\mathrm{KTpb}^{\mathrm{Me}_2}$, Scheme 1] develops a light-brown solution from which KCl precipitates after 12 h of stirring. Filtration, pentane layering, and cooling overnight produced the neutral, asymmetric dimer $[(\mathrm{Tpb}^{\mathrm{Me}_2})\mathrm{V}(\mu\text{-Cl})(\mu\text{-tfa})_2\mathrm{V}(\mathrm{thf})_3]$, compound **5** (Fig. 2), in crystalline form.‡ Evidently this reaction converts the $[\mathrm{V}_4\mathrm{tfa}_4]^{4+}$ aggregate back to a $[\mathrm{V}_2\mathrm{tfa}_2]^{2+}$ core.§

The structure of **5** (Fig. 2), the first asymmetric $\mathrm{V}_2^{\mathrm{II,II}}$ dimer reported to date, consists of two V^{II} ions bridged by one chloride and two trifluoroacetate groups and coordinated terminally by a $\mathrm{Tpb}^{\mathrm{Me}_2}$ group on one side and by THF molecules on the other.† The $\mathrm{V–O_{tfa}}$ (av.) and V–Cl bond lengths are slightly different for each vanadium [V(1): 2.118, 2.507; V(2): 2.092, 2.456 Å respectively] reflecting the asymmetry in the molecule. These differences affect the V···V separation [3.868(1) Å] and the V–Cl–V angle [102.40(6)°] which are longer and wider as compared to **2** [3.796(2) Å, 100.3(1)°].[1]

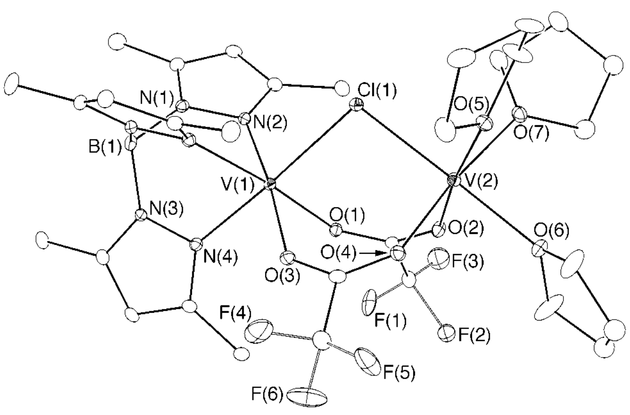


Fig. 2 Structure of **5** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°) are: V(1)–Cl(1) 2.507(2), V(2)–Cl(1) 2.456(2), V(1)–O(3) 2.122(4), V(2)–O(4) 2.091(4), V(1)–N(4) 2.150(5), V(2)–O(6) 2.152(4), V(1)–V(2) 3.868(1); V(1)–Cl(1)–V(2) 102.40(6), O(3)–V(1)–N(2) 174.7(2), O(4)–V(2)–O(7) 172.8(2).

Use of the $\mathrm{Tpb}^{\mathrm{Me}_2-}$ ligand in reactions with **2**, has resulted in a doubling of the number of known bridged V^{II} carboxylates in the literature[1,10] and has encouraged aggregation/deaggregation behavior in vanadium(II) carboxylate chemistry. The first examples of a tetrameric and an asymmetrical dimeric V^{II} species were unveiled. We are currently examining the reaction chemistry of the carboxylato-bridged aggregate **4**, as a halide-rich and 'zinc-free' starting material, especially with alkoxides in the presence of reducible small molecules. Also, the use of $\mathrm{KTpb}^{\mathrm{Me}_2}$ for scavenging inner-sphere charge-sharing $\mathrm{Zn}^{\mathrm{II}}$ ions present in other potentially reactive low-valent mixed-metal V–Zn alkoxide compounds synthesized recently in our laboratory,[11] is currently under investigation. Application of this unusual synthetic avenue, along with directed reactivity at the solvated face of **5**, will be reported elsewhere.

Notes and references

† *Crystal data* for **3**: $C_{15}H_{22}N_6B_1Cl_1Zn_1$, M = 398.01, a = 13.087(2), b = 8.054(1), c = 17.313(4) Å, V = 1824.9(6) Å^3, T = 183(2) K, μ = 1.499 mm^{-1}, orthorhombic, $Pmc2_1$, Z = 2, 2064 reflections total, R indices of $R_1 = 3.85\%$ and $wR_2 = 10.45\%$ for $I > 2\sigma(I)$. For **4**: $C_{32}H_{48}O_{14}F_{12}Cl_4V_4$, M = 1230.23, a = 12.9139(1), b = 12.6158(2), c = 16.3596(2) Å, β = 111.048(1)°, V = 2487.46(5) Å^3, T = 183(2) K, monoclinic, $P2_1/c$, Z = 2, 14099 reflections total, 5403 unique. A semi-empirical absorption correction from ψ-scans was applied (μ = 1.044 mm^{-1}). The structure was solved using anisotropic thermal parameters for all non-hydrogen atoms and a model including 2-fold rotational disorder for both the four THF carbons of O(7) and the two CF_3 groups, to values of $R_1 = 6.75\%$ and $wR_2 = 16.37\%$ for $I > 2\sigma(I)$. Final difference map features were within 0.672 and −0.541 e Å^{-3}. For **5**·THF: $C_{31}H_{46}N_6O_7B_1F_6Cl_1V_2\cdot C_4H_8O_1$, M = 948.93, a = 12.1724(1), b = 18.4139(3), c = 19.207 Å, β = 92.799(1)°, V = 4299.92(8) Å^3, T = 183(2) K, monoclinic, $P2_1/n$, Z = 4, 16,507 reflections total, 5547 unique. A semi-empirical absorption correction from ψ-scans was applied (μ = 0.573 mm^{-1}). The structure was solved using anisotropic thermal parameters for all non-hydrogen atoms and a model including 2-fold rotational disorder for both CF_3 groups and a THF solvate to values of $R_1 = 6.77\%$ and $wR_2 = 13.90\%$ for $I > 2\sigma(I)$. Final difference map features were within 0.416 and −0.303 e Å^{-3}. CCDC 182/1071.

‡ **4**: Anal. (calc.) C 31.34 (31.24), H 4.21 (3.93), N 0.00 (0.02)%; 45% yield. **5**: Anal. (calc.) C 43.42 (42.46), H 5.52 (5.29), N 9.21 (9.58)%; 47% yield. Analyses of non-crystalline samples often suggested inadequate removal of **3**.

§ *Selected spectroscopic data* for **4**: EPR [THF (77K), X-band] g = 2 (br), with a small absorbance at g = 3.9; IR (Nujol, cm^{-1}) 1698 (ν_{OCO} asym), 1575 (ν_{OCO} sym). Given the similarity in EPR spectra of **4** and **2** it is possible **4** may be dissociating in solution, to exist perhaps as the chloride salt, $[(\mathrm{thf})_3\mathrm{V}(\mu\text{-Cl})(\mu\text{-tfa})_2\mathrm{V}(\mathrm{thf})_3][\mathrm{Cl}]$. For **5**: EPR [THF (77K), X-band] g = 2 (br, superimposed 8-line), with a small absorbance at g = 4; IR (Nujol, cm^{-1}) 2521 (ν_{BH}), 1709 (ν_{OCO} asym), 1545 (ν_{OCO} sym).

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