Vanadium(II) Carboxylate Chemistry. Synthesis, Structure, and Properties of $[(thf)_3V(\mu\text{-}Cl)(\mu\text{-}CF_3CO_2)_2V(thf)_3][ZnCl_3(thf)]$ (thf = tetrahydrofuran)

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A dinuclear V^{II} carboxylate complex, $[(thf)_3V(\mu\text{-}Cl)(\mu\text{-}CF_3CO_2)_2V(thf)_3][ZnCl_3(thf)]$ (thf = tetrahydrofuran) has been prepared and characterized by *X*-ray crystallography, magnetic susceptibility, UV-VIS, EPR, and IR spectroscopic measurements.

Reaction mixtures containing vanadium(II) and carboxylate ligands have been reported to carry out dinitrogen fixation.[1] In the light of this observation, it is interesting to note that there are no examples of well-defined mononuclear or polynuclear carboxylate complexes in which vanadium exists solely in the +2 oxidation state. Furthermore, carboxylate-bridged vanadium(II) dimers (d^3–d^3) are important synthetic targets that would contribute to the investigation of trends in properties of metal–metal bonded species such as $M_2(O_2CR)_6$ (M = Cr, Mo, W).[2] Previous attempts[3,4] to prepare low valent vanadium carboxylate complexes resulted in the isolation of several oxo-bridged trinuclear species, among which the lowest average V oxidation state is + 2 2/3. It was postulated that low valent vanadium in a carboxylate oxygen co-ordination environment is sufficiently oxophilic to carry out O atom abstraction from carboxylates.[4] The results described herein demonstrate the existence of a stable carboxylate-bridged V^{II} binuclear species, $[(thf)_3V(\mu\text{-}Cl)(\mu\text{-}O_2CCF_3)_2V(thf)_3]$-$[ZnCl_3(thf)]$ (**1**) (thf = tetrahydrofuran).

Compound (**1**) was prepared from either V^{II} or V^{III}† starting materials. In the first case, a mixture containing $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (**2**) (2.600 g, 1.600 mmol),[6–8] $Na(CF_3CO_2)$ (0.870 g, 6.40 mmol), and dry THF (20 ml) was allowed to stir overnight then filtered to remove NaCl. Purple crystals were obtained from the green–purple dichroic solution after cooling to −35 °C. Addition of hexane (2 ml) and

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† Compound (**1**) was also prepared by mixing $VCl_3(thf)_3$ with one equivalent of $Ag(CF_3CO_2)$ in thf solution, then carrying out a reduction using excess metallic Zn. The material was isolated in 60% yield by concentration of the reaction mixture, followed by cooling to −35 °C.

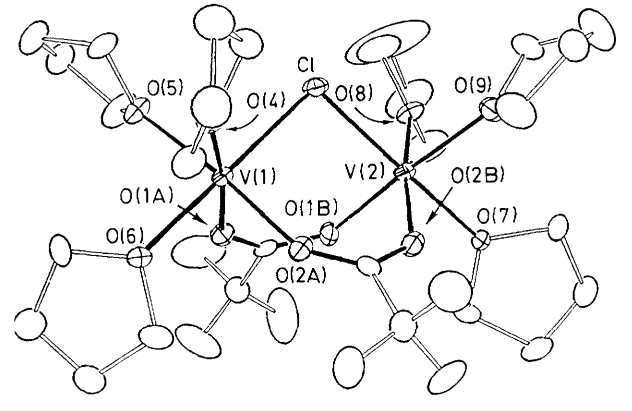

Figure 1. Structure of $[V_2Cl(CF_3CO_2)_2(thf)_6]^+$ showing the 30% probability thermal ellipsoids and atom-labelling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°) are as follows: V(1) · · · V(2) 3.796(2), V(1)–Cl(1) 2.473(2), V(2)–Cl(1) 2.472(2), V(1)–O(1A) 2.087(4), V(1)–O(2B) 2.087(5), V(2)–O(1B) 2.093(4), V(2)–O(2B) 2.097(3), V–O_{thf} 2.132(4)—2.148(4); V(1)–Cl(1)–V(2) 100.3(1), O(1a)–V(1)–O(2A) 94.0 (2), O(1B)–V(2)–O(2B) 93.3(1), O(1A)–V(1)–Cl(1) 94.0(1), O(2A)–V(1)–Cl(1) 94.8(1), O(1B)–V(2)–Cl(1) 95.0(2), O(2B)–V(2)–Cl(1) 95.6(1), O_{tfa}–V–O_{thf} *cis* 84.8(2)—88.8(1), *trans* 171.4(2)—174.2(2), O_{thf}–V–O_{thf} 86.6(2)—90.5(2), O_{thf}–V–Cl(1) *cis* 90.1(1)—92.9(1), *trans* 178.2(1), 178.7(1).

storing at −35 °C overnight led to the precipitation of a second crop of (**1**), from which *X*-ray quality crystals were obtained.‡ This procedure afforded the novel binuclear V^{II} carboxylate species (**1**) (2.84 g, 85% yield).

The solid state structure of $[V_2Cl(CF_3CO_2)_2(thf)_6]^+$ (**1**) (Figure 1) consists of two six-co-ordinate V^{II} centres bridged by one chloride and two trifluoroacetate groups and co-ordinated terminally by thf molecules. No remarkable deviations from octahedral symmetry at the vanadium centres are apparent. The V–O_{thf} (av. 2.140 Å) and V–Cl (av. 2.473 Å) bond lengths are in good agreement with the corresponding lengths in $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (**2**) (V–O_{thf} 2.143,[8] 2.139;[6] V–Cl 2.477,[8] 2.477[6]). Consistent with the II,II oxidation state assignment for vanadium, V–O_{tfa} (tfa = trifluoroacetate) bond lengths in (**1**) (av. 2.091 Å) are substantially longer than corresponding distances in higher valent trinuclear vanadium complexes, $[V_3O(CF_3CO_2)_6(thf)_3]$ (av. 2.038,[4] 2.040[3]) and $[V_3O(ClCH_2CO_2)_6(H_2O)_3]$ (CF_3SO_3) (av. 2.011 Å).[4] The V · · · V separation of 3.796 (2) Å in (**1**) is significantly longer than in (**2**) (2.973,[8] 2.993 Å[6]), and well outside of the range within which significant metal–metal bonding interactions occur. Substitution of two chlorides in (**2**) with two $CF_3CO_2^-$ groups effects this larger separation which in turn accounts for the widened V–Cl–V angle in (**1**) [100.3(1)°] as compared to (**2**) (73.8,[8] 74.4°).[6] In contrast to this situation, the bis-chloride-bridged binuclear vanadium(II) complex $[CpV(\mu\text{-}Cl)(PEt_3)]_2$ (Cp = C_5H_5) exhibits a somewhat shorter V · · · V separation (3.255 Å) in the solid state.[8]

In order to confirm the $V^{II}V^{II}$ oxidation state assignment for a bulk sample of (**1**) and to probe the extent of magnetic interaction between vanadium ions, temperature dependent magnetic susceptibility measurements were carried out. The room temperature (295 K) magnetic moment per vanadium for (**1**) (μ_{eff}/V = 3.41 μ_B) was lower than the spin-only value expected for two isolated V^{II} ions (μ_{eff}/V = 3.87 μ_B), indicating the presence of an antiferromagnetic interaction. Susceptibility data in the 5—300 K range were fitted to the expression for X_M *vs.* T derived from an isotropic exchange Hamiltonian,[9] $H = -2JS_1S_2$ with $S_1 = S_2 = 3/2$, $g = 1.97$, $J = -21$ cm^{-1}. Contribution from a 0.2% paramagnetic impurity ($S = 1/2$) was also included in the calculated fit. Magnetic interaction between V atoms in (**1**) is substantially less than in (**2**) ($J = -75$ cm^{-1}).[8] This decrease in magnetic coupling may be due to the loss of incipient metal–metal bonding, which has been proposed to exist for (**2**),[8] or to the difference in V–Cl–V bond angles for the two compounds.

Spectroscopic properties of bulk samples of (**1**) are as expected for a V^{II} complex. The UV-VIS spectrum of (**1**) in thf has d–d absorption bands at 877 (ε = 15 cm^{-1} M^{-1}), 576 (ε = 21), and 418 nm (sh) which by comparison to (**2**)[6,8] and other V^{II} complexes such as $[VCl_6]^{4-}$ and $[V(H_2O)_6]^{2+}$,[6,10] and assuming idealized octahedral symmetry, can be assigned as $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions, respectively. There is no evidence for the double spin-flip transition that was observed for (**2**) in thf.[6] An EPR spectrum of a frozen thf solution of (**1**) displays an intense broad signal centred at $g = 2$ and a smaller absorbance at $g = 3.9$ in contrast to (**1**), which has the $g = 2$ absorption but does not exhibit the low field signals under these conditions. IR spectroscopy for (**1**) is consistent with the formulation provided by the *X*-ray analysis.§

In conclusion, despite the oxophilic nature of low valent vanadium, this work demonstrates that a bis-carboxylate-bridged V^{II} dimer can be prepared in good yield under the appropriate reaction conditions. Spectroscopic and magnetic measurements confirm the $V^{II}V^{II}$ oxidation state assignment for (**1**). Ongoing studies are directed towards expanding this potentially large class of molecules using other carboxylate ligands, and towards examining the reactivity properties of (**1**) and related species.

Funding for this work was provided by the University of California, Berkeley Biomedical Research Support Grant (no. 88–4). L. G. is grateful for the award of an N.S.E.R.C. postdoctoral scholarship.

Received, 31st May 1989; Com. 9/02269D

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‡ *Crystal data* for compound (**1**): triclinic space group $P\bar{1}$, a = 10.205(4), b = 16.620(8), c = 17.793 (10) Å, α = 118.31(3), β = 98.34(3), γ = 104.17(3)°, U = 2462(3) Å^3, D_c = 1.40 g cm^{-3}, Z = 2. Data were collected at 130 K with Mo-K_α radiation out to 2θ = 50°, yielding 5149 reflections with $I > 3\sigma(I)$. The structure was solved by a combination of Patterson and direct methods (SHELX86) and refined using anisotropic thermal parameters for all non-hydrogen atoms to $R(R_w)$ values of 4.45% (4.65%). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *IR spectroscopic data:* 1695 (ν_{OCO} asym), 1457 cm^{-1} (ν_{OCO} sym).