JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 23
1983

Structural Studies of the Vanadium(II) and Vanadium(III) Chloride Tetrahydrofuran Solvates

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While the composition of $VCl_3{\cdot}3thf$ (thf = tetrahydrofuran) is confirmed by *X*-ray crystallography, and the structure shown to consist of *mer*-$VCl_3(thf)_3$ molecules, both crystallography and analysis reveal that the $VCl_2{\cdot}2thf$ previously reported is actually $[V_2(\mu\text{-}Cl)_3(thf)_6]_2[Zn_2(\mu\text{-}Cl)_2Cl_4]$.

There is much interest and importance in the compounds $VCl_3{\cdot}3thf$[1] and $VCl_2{\cdot}2thf$,[2–4] because they are reagents for entry into the nonaqueous chemistry of lower-valent vanadium compounds. In view of this and because divalent vanadium is potentially able to form V–V bonds[5] we deemed it worthwhile to characterize these substances structurally.

The compound $VCl_3{\cdot}3thf$ has a crystal structure† made up of discrete octahedral *mer*-$VCl_3(thf)_3$ molecules, illustrated in Figure 1. This is one of the two foreseeable molecular structures and is consistent with the chemistry and solubility properties of this compound.

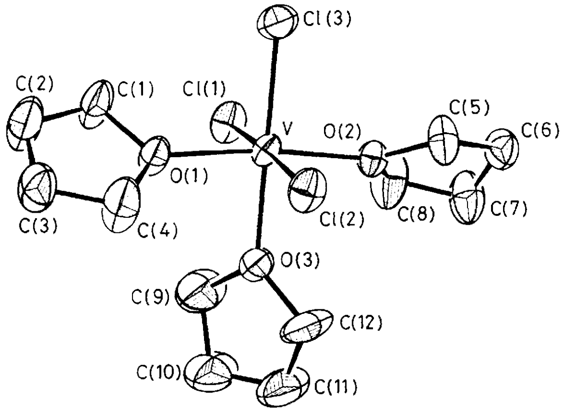

Figure 1. The $VCl_3(thf)_3$ molecule. The V–Cl(1) and V–Cl(2) distances have a mean value of 2.330[3] Å while V–Cl(3) = 3.297(2) Å. The V–O(1) and V–O(2) distances have a mean value of 2.061[8] Å while V–O(3) = 2.102(3) Å. *cis* Cl–V–Cl angles average 92.0[5]° and *cis* O–V–O angles average 86.2[2]°.

For $VCl_2{\cdot}2thf$ prepared by reduction of VCl_3 in thf with zinc[2,3] we find that the composition is not that given by the above formula. The compound as prepared is very difficult to obtain in suitable crystalline form for *X*-ray crystallography, but in the course of an attempt to crystallize $VCl_2(PEt_3)_2$[2] from thf some excellent crystals were formed, presumably by slow solvolysis of the phosphine complex. Their i.r. spectrum was identical to that of the bulk material. An *X*-ray crystallographic study† showed that the compound is made up of $[V_2(\mu\text{-}Cl)_3(thf)_6]^+$ ions and $[Zn_2(\mu\text{-}Cl)_2Cl_4]^{2-}$ ions, shown in Figure 2. The atoms refined successfully as zinc atoms cannot be satisfactorily treated as vanadium atoms. It is to be noted that the formulae $V_4Zn_2Cl_{12}(thf)_{12}$ and $VCl_2(thf)_2$ have very similar analytical percentages except of course for vanadium. The earlier analysis[2] for vanadium was not specific but based

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† *Crystal data:* For $VCl_3{\cdot}3thf$, $C_{12}H_{24}Cl_3O_3V$, $M = 372.6$, monoclinic, $P2_1/c$, $a = 8.847(2)$, $b = 12.861(5)$, $c = 15.134(3)$ Å, $\alpha = 90.0$, $\beta = 91.94(2)$, $\gamma = 90.0°$, $U = 1721(1)$ Å^3, $D_c = 1.422\ g\ cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 10.285\ cm^{-1}$, $Z = 4$, $\lambda = 0.71073$ Å, crystal dimensions $0.8 \times 0.4 \times 0.3\ mm^3$, $R = 0.053$ and $R_w = 0.080$ for 1690 reflections with $F \geqslant 3\sigma(F)$ collected at 22 °C on a Syntex $P\bar{1}$ diffractometer. For $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, $C_{24}H_{48}Cl_6O_6V_2Zn$, $M = 812.6$, triclinic, $P\bar{1}$, $a = 11.485(4)$, $b = 15.312(2)$, $c = 10.786(2)$ Å, $\alpha = 71.07(2)$, $\beta = 99.10(2)$, $\gamma = 104.41(2)°$, $U = 1731(1)$ Å^3, $D_c = 1.56\ g\ cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 17.61\ cm^{-1}$, $Z = 2$, $\lambda = 0.71073$Å, crystal dimensions $0.3 \times 0.3 \times 0.15\ mm^3$, $R = 0.04$ and $R_w = 0.067$ for 6407 reflections with $F \geqslant 3\sigma(F)$ collected at −105 °C on a CAD-4 diffractometer.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

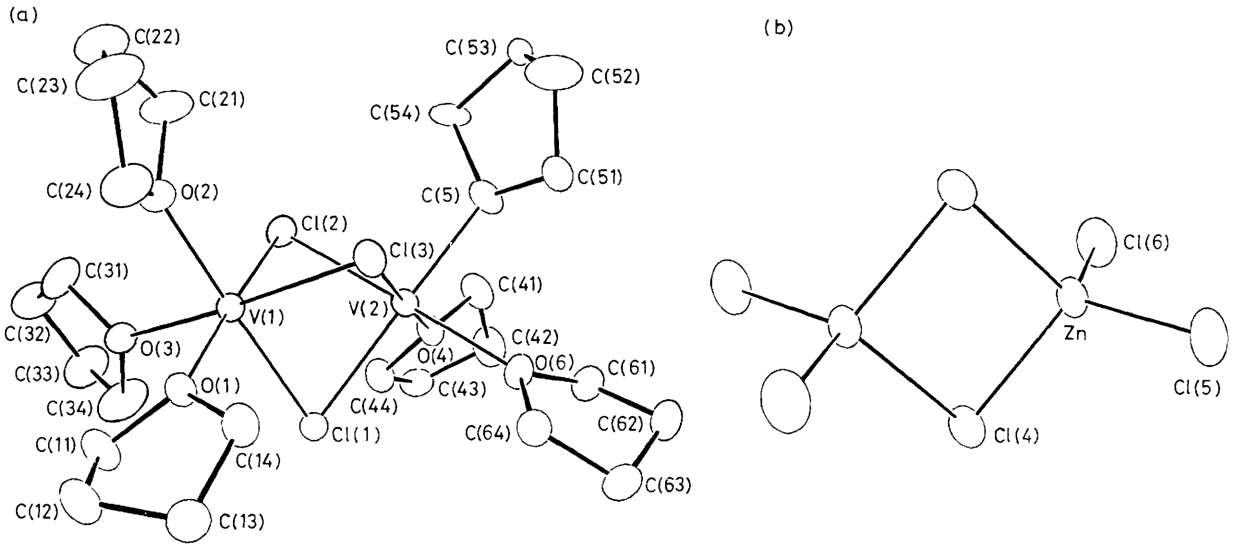

Figure 2. (a) The $[V_2(\mu\text{-Cl})_3(thf)_6]^+$ ion. The mean V–Cl and V–O distances are 2.478[3] and 2.147[7] Å, respectively. (b) The centrosymmetric $[Zn_2(\mu\text{-Cl})_2Cl_4]^{2-}$ ion. The mean bridging and terminal Zn–Cl distances are 2.355[6] and 2.211[1] Å, respectively, while the Zn · · · Zn distance is 3.251(1) Å.

on the weight of residue following combustion analysis for C and H. We have obtained direct analyses for both V and Zn by *X*-ray fluorescence on the '$VCl_2 \cdot 2thf$' prepared by the method of Hall *et al.* and the weight ratio, 1.49, was close to that calculated (1.56) for a 2:1 atomic ratio of V to Zn. The electrolytic preparation[4] of $VCl_2(MeOH)_2$ from which $VCl_2(thf)_2$ and other VCl_2L_2 compounds were then made may give authentic $VCl_2(thf)_2$, but we have not yet examined this question.

The dimensions of the $[(thf)_3V(\mu\text{-Cl})_3V(thf)_3]^+$ structure are reasonable when compared with other such chlorine-bridged bioctahedral structures,[6] especially that of $[Cr_2Cl_9]^{3-}$ which also contains d^3 cations. The distortions from an ideal structure consisting of two regular octahedra sharing a face are in the directions indicative of repulsion between the metal ions, but indicate a smaller repulsive force here between V^{2+} ions than that between the Cr^{3+} ions, as might be expected. Thus, while the ideal values for Cl_b–M–Cl_b and M–Cl_b–M (Cl_b = bridging chlorine atom) angles are 90° and 70.53° respectively, we find here angles of 87.2° and 74.4°, while in $[Cr_2Cl_9]^{3-}$ these angles were a little further from the ideal values, *viz.*, 85.8° and 76.4°. The V · · · V distance, 2.993(1) Å is shorter than the Cr · · · Cr distance of 3.12 Å.

The $[Cl_2Zn(\mu\text{-Cl})_2ZnCl_2]^{2-}$ ion, while apparently novel, is not surprising and is in keeping with the tendency of Zn^{II} to exhibit tetrahedral co-ordination, particularly in halogeno complexes.

Since we previously[7] used '$VCl_2 \cdot 2thf$' prepared according to Hall *et al.* to prepare $V_3(\mu_3\text{-O})(CH_3CO_2)_6(thf)_3$, we have checked a sample of the latter for the presence of zinc; none was found.

This work was supported by a grant from the U.S. National Science Foundation. We thank Professor Emil Schweikert of this department for the *X*-ray fluorescence measurements.

Received, 22nd July 1983; Com. 990

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