A Linear Tetranuclear Vanadium–Oxygen Assembly

Adrian Hills, David L. Hughes, G. Jeffery Leigh* and J. Roger Sanders
AFRC IPSR Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK

The reaction of [VO(salen)] with controlled quantities of species able to extract the oxygen atom, such as trityl fluoroborate or fluoroboric acid–diethyl ether (1/1) leads to the novel tetranuclear cation $[\{V(salen)\}_4(\mu\text{-}O)_3]^{2+}$, which contains a linear vanadium–oxygen chain.

A large number of complexes containing VO(Schiff base dianion)$^{n+}$ (n = 0 or 1) moieties has been reported.[1] To date these have always been mononuclear or polymeric with single oxygen bridges, although a few dinuclear species with single oxygen bridges are known for VO systems with anions other than Schiff-base dianions.[2]

Recently, we showed[3] the first exception to this generalization, $[\{V(salen)\}\{VO(salen)\}(\mu\text{-}O)]^+$ (H_2salen = *N,N'*-bis(salicylidene)ethylenediamine), a compound best formulated as $[V^{IV}{=}O{\rightarrow}V^{V}{=}O]^+$. This exists only in the solid state, and dissociates in solution. We now report a novel tetranuclear species.

Reaction of [VO(salen)] with trityl tetrafluoroborate or with $HBF_4{\cdot}Et_2O$ in the molar ratio of 2 : 1 (in an attempt to abstract an oxygen atom) yielded not the expected [{V(salen)}{VO(salen)}(μ-O)]BF_4 but black crystals of what proved to be [{V(salen)}$_4$(μ-O)$_3$]$(BF_4)_2$ (Fig. 1). The magnetic susceptibility measured between 294 and 90 K shows a roughly linear dependence of $1/\chi_A$ upon T, with an extrapolated value of θ of *ca.* −10 K. Using the spin-only formula, the data are consistent with μ_{eff} = 1.53 μ_B per vanadium at 294 K, dropping to 1.33 μ_B at 90 K. The anti-ferromagnetic coupling is not very extensive at room temperature. We have so far been unable to obtain crystals suitable for EPR spectroscopy, and dispersion to make a magnetically dilute solid is not feasible as yet. The compound shows ν(V=O) at 945 and 910 cm^{-1} in the IR spectrum in the solid state. In both [VO(salen)] and [VO(salen)]$^+$ this band is observed at 981 cm^{-1},[4] and it is observed at 870 cm^{-1} in [{V(salen)}{VO(salen)}(μ-O)]$^+$.[3] The tetranuclear species is clearly very different from any of these.

The X-ray crystal structure reveals a centrosymmetric linear tetranuclear chain,† in which the outer vanadium atoms can be regarded as part of {V^{IV}O(salen)} units, bound to a central {V(salen)}$_2$O^{2+} unit. This is supported by the following observations. In the almost linear V(1)–O(1)–V(2)–O(2)–V(2′)–O(1′)–V(1′) chain, V(1)–O(1) is 1.625(2) Å. This compares with 1.67(5) Å for the V^{IV}=O separation in the $V^{IV}{=}O{\rightarrow}V^{V}{=}O$ chain in [{V(salen)}{VO(salen)}(μ-O)]$^+$.[3] Similarly, O(1)-V(2) is 2.059(2) Å, compared with 2.06(5) Å for $O{\rightarrow}V^V$ in the dinuclear entity. The square-pyramidal geometry around the vanadium atoms in these {VO(salen)} units is very similar to that in [VO(salen)] (V^{IV}=O = 1.588 Å) and in [VO(salen)]ClO_4 (V^V=O=1.576 Å).[4]

The central {V(salen)}$_2$O^{2+} unit is not so easily defined. V(2)–O(2) is 1.763 Å, longer than the V^V=O separation of 1.58(3) Å, and its essential structure is best represented by V$\doteq$O$\doteq$V, V–O bond order 1.5, with nearly ideal octahedral coordination about each vanadium.

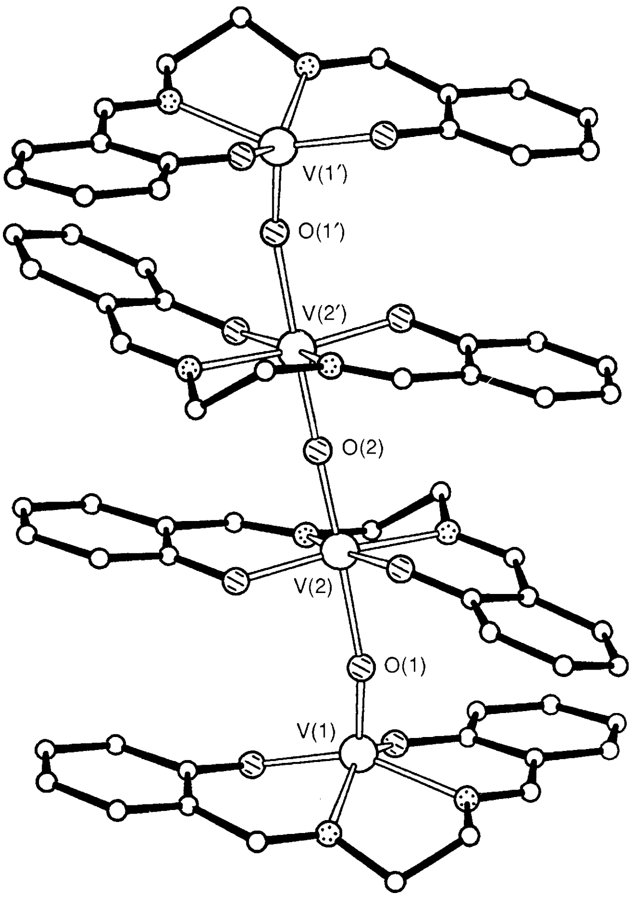

Fig. 1 The structure of the ion [{V(salen)}$_4$(μ-O)$_3$]$^{2+}$. The angle V(1)–O(1)–V(2) is 162.2(1)°. The ion is centrosymmetric, and hence V(2)–O(2)–V(2′) must be 180°.

The EPR spectrum of the tetranuclear salt when dissolved in acetonitrile at 20 °C shows signals assignable only to [VO(salen)], with an intensity corresponding to two [VO(salen)] molecules for each of the four vanadium atoms initially present. The addition of water to this acetonitrile solution yields altogether four moles of [VO(salen)], as judged by EPR and UV spectroscopy. The addition of 2 equiv. of $[PPh_4]Br$ converts the acetonitrile solution to a mixture of three molecules of [VO(salen)] and one molecule of [VBr_2(salen)],[5] again determined by UV and EPR spectroscopy.

The reason for the formation of our tetranuclear cation would appear to be that the preparative reaction protonates a V=O moiety to yield a labile coordinated water molecule $V{\leftarrow}OH_2^{2+}$ in the absence of any strongly coordinating anion. What crystallises is the least soluble species. It is already known that if an acid with a more strongly coordinating anion, such as HCl, is used then the oxygen is similarly protonated and an excess of this acid produces [VCl_2(salen)].[4] If we use a 1 : 2 molar ratio of [VO(salen)] : $HBF_4{\cdot}Et_2O$ (rather than 2 : 1, as above) we obtain a 90% yield of a material with spectroscopic and analytical properties consistent with the formulation [V(H_2O)(salen)]$(BF_4)_2$. With a molar ratio of 1 : 1, the product is formulated on the basis of analysis and spectroscopic properties as [{V(salen)$_2$}O]$(BF_4)_2$. This last material contains a cation corresponding to the central unit of our tetranuclear species. We are currently attempting to obtain suitable crystals to confirm these formulations.

Our tetranuclear species, like the [{V(salen)}{VO(salen)}-(μ-O)]$^{2+}$, is labile in solution but stable in the solid. We have evidently established a new area of vanadium–oxygen chemistry of polynuclear species, which we are currently exploring.

---

† *Crystal structure analysis* of [{V(salen)}$_4$(μ-O)$_3$]$(BF_4)_2{\cdot}$2MeCN. *Crystal data*: $C_{68}H_{62}B_2F_8N_{10}O_{11}V_4$, M = 1572.7. Triclinic, space group $P\bar{1}$ (no. 2), a = 10.511(1), b = 13.349(1), c = 14.831(1) Å, α = 70.489(9), β = 109.413(7), γ = 79.442(7)°, V = 1745.7 Å^3. Z = 1, D_c = 1.496 g cm^{-3}, $F(000)$ = 802, μ(Mo-Kα) = 5.9 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Crystals are air-stable, very dark, thick needles. After photographic examination, one was transferred to an Enraf-Nonius CAD4 diffractometer for determination of accurate cell parameters (by refinement from settings of 25 reflections, θ *ca.* 10.5°, each centred in four orientations) and measurement of diffraction intensities (to θ_{max} = 25°).

During processing, intensities were corrected for Lorentz-polarisation effects, slight deterioration, absorption and to ensure no negative net intensities. 6138 Unique reflections were entered into the SHELX system.[6]

The structure was determined, eventually, by direct methods (in SHELXS[7]) in the space group $P\bar{1}$. After conversion to the centrosymmetric symmetry, refinement (by full-matrix least-squares methods in an extended version of SHELX[6]) to convergence was rapid, giving R = 0.053, R_g = 0.050[6] for all data weighted equally. In the cation, all non-hydrogen atoms were refined anisotropically and H atoms were included in idealised positions with independent isotropic thermal parameters. The BF_4^- ion is disordered in several orientations; four idealised BF_4 tetrahedra, with a common B atom and equal occupancies but with independent atomic isotropic thermal parameters, were included in the refinement. The acetonitrile molecule is disordered equally in two orientations, sharing a common centre C atom. In a final difference map the only peaks of significance (*ca.* 0.6 eÅ^{-3}) are in the region of the anion.

Scattering factors for neutral atoms were taken from Ref. 8. Computer programs have been noted above or in Table 4 of Ref. 9, and were run on the MicroVAXII machine in this laboratory.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank Dr L. F. Larkworthy, University of Surrey, for obtaining magnetic data.

Received, 10th January 1991; Com. 1/00113B

References

1 L. Vilas Boas and J. Costa Pessoa, in *Comprehensive Coordination Chemistry*, vol. 3, ed. Sir G. Wilkinson, Pergamon Press, Oxford, 1987, p. 453.

2 (*a*) A. Kojima, K. Okazaki, S. Ooi and K. Saito, *Inorg. Chem.*, 1983, **22**, 1168; (*b*) S. Yamada, C. Katayama, J. Tanaka and M. Tanaka, *Inorg. Chem.*, 1984, **23**, 253; (*c*) T. L. Riechel and D. T. Sawyer, *Inorg. Chem.*, 1975, **14**, 1869; (*d*) M. Nishizawa and K. Saito, *Inorg. Chem.*, 1980, **19**, 2284; (*e*) T. K. Myser and R. E. Shepherd, *Inorg. Chem.*, 1987, **26**, 1544.

3 A. Hills, D. L. Hughes, G. J. Leigh and J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1991, 61.

4 J. A. Bonadies, W. M. Butler, V. L. Pecoraro and C. J. Carrano, *Inorg. Chem.*, 1987, **26**, 1218.

5 K. P. Callahan and P. J. Durand, *Inorg. Chem.*, 1980, **19**, 3211.

6 G. M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, 1976.

7 G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, 175.

8 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, vol. 4, 1974, pp. 99 and 149.

9 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.