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An Octanuclear Basic Benzoate Containing Four Vanadium(III) and Four Zinc(II) Atoms: $[VZnO(O_2CC_6H_5)_3(THF)]_4 \cdot 2THF$

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Reaction of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ with sodium benzoate in THF solution at room temperature for 48 h gave a red-black solution from which the red-black, crystalline title compound was isolated in 45% yield. The composition and structure were established by X-ray crystallography. The structure was refined in space group *C*2/*c* with the following unit cell parameters: $a = 22.780$ (5) Å; $b = 23.492$ (4) Å; $c = 20.222$ (4) Å; $\beta = 91.45$ (3)°; $V = 10819$ (7) Å^3; $Z = 4$. Refinement converged to an unweighted *R* value of 0.0484. The molecule consists of a central tetrahedron of vanadium atoms (with V–V distances ranging from 2.938 (1) to 2.987 (1) Å), each face of which is capped by a zinc atom (with Zn–V distances ranging from 3.417 (1) to 3.495 (1) Å). At the center of each of the four ZnV_3 pyramids is an oxygen atom, essentially equidistant from all four metal atoms (mean M–O distance ca. 2.00 Å), and each Zn–V edge is bridged by a benzoate anion. Finally, there is a tetrahydrofuran molecule coordinated to each zinc atom trans to the oxygen atom that it shares with its neighboring vanadium atoms. Each vanadium atom is surrounded by a distorted octahedron of oxygen atoms and each zinc atom by a distorted trigonal bipyramid. Although only a crystallographic, twofold axis is imposed on the molecule, the idealized symmetry (neglecting the terminal THF carbon atoms) is fully tetrahedral (T_d).

Introduction

The fact that a conveniently prepared[1] and often-used form of "$VCl_2 \cdot 2THF$" is in reality[2] $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (**1**) can be considered as either (or both) good news or bad news. In some cases the presence of zinc will be a drawback, in others it may make no difference,[3] and in still others it may lead to the preparation of interesting compounds containing both zinc and vanadium. An example of this last possibility has recently been reported,[4] and others have turned up in our laboratory.[5] One of these mixed products contains a remarkable array of two concentric tetrahedra, V_4 within Zn_4, and is described in this paper. This extraordinary compound, **2**, discovered during a study of the reactions of **1** with carboxylato ligands when sodium benzoate was employed, has the formula $[VZnO(O_2CC_6H_5)_3(C_4H_8O)]_4 \cdot 2C_4H_8O$.

As noted in earlier publications from this laboratory,[6] our knowledge of the chemistry of vanadium complexes with carboxylic acids is still very fragmentary. Few general reaction patterns have been recognized, and the true nature of several compounds remains uncertain. Vanadium often forms complicated polynuclear complexes with carboxylic acids.[6-8] Typical and relatively simple carboxylates of vanadium in low oxidation states are the oxo-centered trinuclear species[6,9] and the dimeric tetracarboxylato-bridged complexes with cyclopentadienyl anion (Cp) in the axial position.[10]

Table I. Crystallographic Data

formula	$Zn_4V_4O_{34}C_{108}H_{108}$
fw	2415.29
space group	*C*2/*c*
systematic absences	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$
a, Å	22.780 (5)
b, Å	23.492 (4)
c, Å	20.222 (4)
α, deg	90.0
β, deg	91.45 (3)
γ, deg	90.0
V, Å^3	10,819 (7)
Z	4
d_{calcd}, g/cm^3	1.483
cryst size, mm	0.3 × 0.4 × 0.4
μ(Mo Kα), cm^{-1}	12.896
data collecn instrument	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
orientation raflcns: no.; range (2θ), deg	25; $12 \leqslant 2\theta \leqslant 18.5$
temp, °C	−100
scan method	ω-2θ
data collecn range, 2θ, deg	$4 \leqslant 2\theta \leqslant 37$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6725, 6277
no. of parameters refined	647
R^a	0.0484
$R_w{}^b$	0.0718
quality-of-fit indicator^c	1.763
largest shift/esd, final cycle	0.07
largest peak, e/Å^3	1.149

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

Experimental Section

All operations were performed under an atmosphere of argon, with use of standard Schlenk techniques and a double-manifold vacuum line. Tetrahydrofuran was freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulae and/or syringes. Sodium benzoate was deaerated under vacuum at 80 °C. $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (**1**) was prepared according to the published procedure.[1]

$[ZnVO(O_2CC_6H_5)_3(THF)]_4 \cdot 2THF$. $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (1.33 g, 0.82 mmol) was placed in a 100-mL round-bottomed, side-neck flask equipped with a magnetic stirrer. Fifty milliliters of THF was added, and the bright-green slurry was stirred for about 15 min. Sodium benzoate (1.44 g, 10 mmol) was then added, and the reaction

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(1) Hall, V. H.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.

(2) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.

(3) (a) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4113.

(4) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

(5) The linear trimer $Zn_2VCl_6(THF)_2(PPh_3)_2$ has been prepared and characterized: Cotton, F. A.; Duraj, S. A.; Roth, W. *Inorg. Chem.*, in press.

(6) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3127 and references therein.

(7) Cotton, F. A.; Lewis, G. E., Mott, G. N. *Inorg. Chem.* **1983**, *22*, 1825.

(8) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.

(9) Glowiak, T.; Kubiak, M.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1977**, *25*, 359.

(10) (a) Lann, G. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Y. T.; Pasynskii, A. A.; Kolobova, N. E. *J. Organomet. Chem.* **1971**, *27*, 53.

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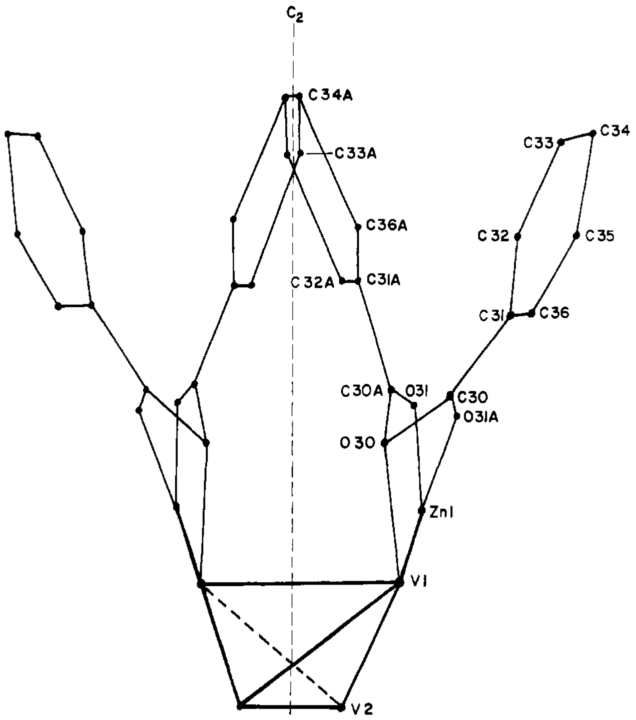

Figure 1. Schematic drawing of the disorder displayed by one benzoate ligand. C_2 is a crystallographic twofold axis.

mixture turned deep red immediately. The reaction mixture was stirred at room temperature for 48 h, and after that period the red-black solution was filtered through Celite 545 (Fisher Scientific). The filtrate was evaporated to ca. 15 mL, and the flask was placed in a freezer for several days. Dark red-black, blocklike crystals were obtained; yield 0.45 g, 45%.

Crystallographic quality crystals can also be prepared by careful layering, with hexane, of the filtrate. Large, dark red-black, blocklike crystals of $[ZnVO(O_2CC_6H_5)_3(THF)]_4 \cdot 2THF$ are formed upon slow mixing of the solvents within several weeks. These were shown by X-ray examination to be identical in composition with the crystals mentioned above.

X-ray Crystallography. General procedures have already been described elsewhere.[11] Basic information about data collection and structure refinement is given in Table I. The intensity data were corrected for Lorentz and polarization effects. No correction for absorption was made since ψ scans showed less than 10% variation in the intensities of selected reflections.

The structure was solved and partially developed in space group *Cc*. A three-dimensional Patterson map indicated the presence of several triangular arrays of metal atoms. After one such triangle was properly positioned in the cell, the remaining atoms were located by a series of alternating least-squares refinements and difference Fourier syntheses. Since the arrangement of atoms was consistent with the presence of a C_2 axis, refinement was continued in the centrosymmetric space group *C*2/*c*. One of the six benzoato ligands was found to be disordered over two positions, and equal fractional occupancy of $^1/_2$ was assigned to each orientation. This disorder was not a result of raising the symmetry from *Cc* to *C*2/*c*. A schematic drawing of the disordered part of the molecule is shown in Figure 1. A molecule of solvent, THF, present in the lattice was also partially disordered. Three atoms, namely C(91), C(92), and C(93), had occupancies of 1, but the rest were assigned fractional occupancies by trial and error. It was not clear which atoms in the rings should be treated as oxygen atoms. Initially all were refined as carbon atoms and then one with occupancy 0.6 was changed to oxygen while C(92) was treated as 60% carbon and 40% oxygen by raising its multiplicity to 1.13. The two partially overlapping THF rings are defined by the following sets of atoms: O(90)–C(91)–C(92)–C(93)–C(94) and C(91)–C(92)–C(93)–C(96)–C(95) with multiplicities equal to 0.6 and 0.4, respectively.

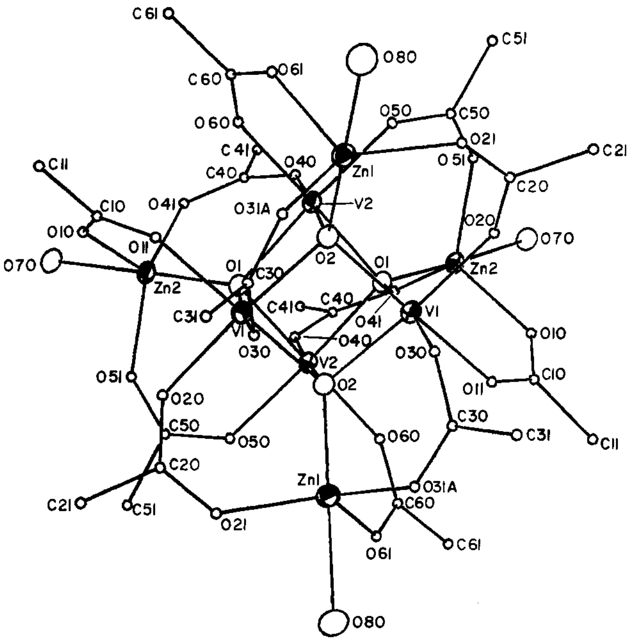

Figure 2. ORTEP drawing of the entire $[ZnVO(O_2CC_6H_5)_3(C_4H_8O)]_4$ molecule. The thermal ellipsoids represent 30% of electron density. Atoms in the benzoate ligands are assigned arbitrarily small thermal ellipsoids. Phenyl rings are omitted for clarity and are represented by a carbon atom only. Symmetry-related atoms have the same designations.

Anisotropic thermal parameters were assigned to all atoms except those in the molecule of free THF and in the disordered benzoate ligand. The final difference Fourier map contained one peak above 1 e/Å^3 located on a twofold axis while the rest had intensity below this value.

Results and Discussion

The crystallographically determined composition of the compound reported here corresponds to the following formula: $Zn_4V_4O_4(O_2CC_6H_5)_{12}(C_4H_8O)_4 \cdot 2C_4H_8O$. Final values of positional and isotropic equivalent thermal parameters are listed in Table II. Important interatomic distances and angles are presented in Tables III and IV, respectively. Less important dimensions are included in the supplementary material. ORTEP drawings of the molecule defining the numbering scheme and showing its essential structural features are shown in Figures 1–3.

The octanuclear molecule resides on a crystallographic twofold axis passing through the center of opposite edges of the tetrahedron defined by the four vanadium atoms. Each face of the tetrahedron is capped by a zinc atom, and there is an oxygen atom, O_c, inside every V_3Zn pyramid, ca. 2 Å from the metal atoms. Each of the 12 V–Zn edges is bridged by a benzoate anion, and one molecule of THF completes the coordination sphere around each zinc atom. Thus, this large molecule has a very high virtual symmetry, T_d. The averaged values of important interatomic distances (in angstroms) are as follows: Zn–V, 3.458 [13]; V–V, 2.965 [4]; Zn–O_c, 1.990 [12]; V–O_c, 1.988 [5]; Zn–O_{carb}, 2.007 [6]; V–O_{carb}, 2.009 [3]. When angles are calculated from the above distances, with use of T_d symmetry, the following ideal angles (in degrees) are obtained: V–V′–V″, 60.0;: V–Zn–V′, 50.77; Zn–V–V′, 64.61; Zn–O–V, 120.75; V–O–V′, 94.44. The average distance from O_c to its V_3 plane in this idealized model is 1.01 Å.

The effective coordination of vanadium and zinc atoms is octahedral and trigonal bipyramidal, respectively. The assignment of oxidation state is straightforward: with 20 negative charges contributed by ligands, and zinc being necessarily dipositive, vanadium has to be in the +3 oxidation state. The distance between vanadium atoms, which is just below 3 Å,

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(11) See for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table II. Positional and Isotropic Equivalent Thermal Parameters for $[ZnVO(O_2CC_6H_5)_3(C_4H_8O)]_4 \cdot 2C_4H_8O^a$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Zn(1)	0.11623 (2)	0.32178 (2)	0.18471 (2)	1.93 (1)	C(30A)	−0.0160 (4)	0.4013 (4)	0.3122 (4)	2.2 (2)*
Zn(2)	0.06295 (2)	0.14395 (2)	0.37647 (2)	1.696 (9)	C(31A)	−0.0006 (4)	0.4614 (4)	0.2925 (4)	2.5 (2)*
V(1)	0.03063 (3)	0.27877 (3)	0.31588 (3)	1.72 (1)	C(32A)	−0.0570 (4)	0.4759 (4)	0.2161 (5)	2.9 (2)*
V(2)	0.05751 (3)	0.19102 (3)	0.21613 (3)	1.55 (1)	C(33A)	−0.0702 (5)	0.5309 (5)	0.2374 (6)	4.5 (2)*
O(1)	0.0281 (1)	0.1944 (1)	0.3076 (1)	1.61 (5)	C(34A)	−0.0290 (4)	0.5626 (4)	0.2556 (4)	2.1 (2)*
O(2)	0.0510 (1)	0.2745 (1)	0.2201 (1)	1.66 (5)	C(36A)	−0.0453 (5)	0.5002 (5)	0.2813 (6)	3.9 (2)*
O(10)	0.0487 (1)	0.1934 (1)	0.4550 (1)	2.26 (6)	C(40)	0.0325 (2)	0.0682 (2)	0.1807 (2)	1.75 (8)
O(11)	0.0117 (1)	0.2747 (1)	0.4128 (1)	2.14 (6)	C(41)	0.0514 (2)	0.0078 (2)	0.1937 (2)	1.90 (8)
O(20)	0.1148 (1)	0.2851 (1)	0.3453 (1)	2.31 (6)	C(42)	0.0195 (2)	−0.0374 (2)	0.1660 (2)	2.58 (9)
O(21)	0.1664 (1)	0.3284 (1)	0.2667 (2)	2.79 (7)	C(43)	0.0370 (2)	−0.0934 (2)	0.1787 (3)	3.3 (1)
O(30)	0.0258 (1)	0.3637 (1)	0.3212 (2)	2.75 (7)	C(44)	0.0863 (3)	−0.1036 (2)	0.2190 (3)	3.8 (1)
O(31)	−0.0688 (3)	0.3914 (3)	0.3253 (3)	2.8 (1)*	C(45)	0.1182 (2)	−0.0585 (2)	0.2464 (3)	3.6 (1)
O(31A)	−0.0655 (3)	0.3863 (3)	0.3543 (3)	2.3 (1)*	C(46)	0.1005 (2)	−0.0031 (2)	0.2346 (2)	2.65 (9)
O(40)	0.0598 (1)	0.1055 (1)	0.2130 (1)	1.97 (6)	C(50)	0.1690 (2)	0.1686 (2)	0.2963 (2)	1.92 (8)
O(41)	0.0093 (1)	0.0761 (1)	0.3603 (1)	2.18 (6)	C(51)	0.2345 (2)	0.1733 (2)	0.2977 (2)	2.33 (9)
O(50)	0.1424 (1)	0.1899 (1)	0.2464 (1)	1.97 (6)	C(52)	0.2672 (2)	0.1419 (3)	0.3438 (3)	4.2 (1)
O(51)	0.1452 (1)	0.1433 (1)	0.3432 (1)	2.42 (6)	C(53)	0.3286 (2)	0.1455 (3)	0.3446 (3)	5.4 (2)
O(60)	0.0856 (1)	0.1915 (1)	0.1225 (1)	2.02 (6)	C(54)	0.3553 (2)	0.1825 (3)	0.3014 (3)	5.0 (1)
O(61)	0.1393 (1)	0.2708 (1)	0.1104 (1)	2.36 (6)	C(55)	0.3236 (2)	0.2127 (3)	0.2549 (3)	4.3 (1)
O(70)	0.1021 (1)	0.0848 (1)	0.4486 (1)	2.22 (6)	C(56)	0.2621 (2)	0.2085 (2)	0.2530 (3)	3.2 (1)
O(80)	0.1871 (1)	0.3771 (1)	0.1462 (2)	2.94 (7)	C(60)	0.1184 (2)	0.2249 (2)	0.0903 (2)	1.88 (8)
C(10)	0.0241 (2)	0.2409 (2)	0.4596 (2)	2.06 (8)	C(61)	0.1336 (2)	0.2056 (2)	0.0213 (2)	2.20 (9)
C(11)	0.0070 (2)	0.2602 (2)	0.5274 (2)	2.46 (9)	C(62)	0.1748 (2)	0.2357 (2)	−0.0138 (2)	3.6 (1)
C(12)	0.0266 (3)	0.2302 (2)	0.5832 (2)	4.1 (1)	C(63)	0.1890 (3)	0.2183 (3)	−0.0771 (3)	4.6 (1)
C(13)	0.0088 (3)	0.2461 (2)	0.6453 (3)	4.9 (1)	C(64)	0.1614 (3)	0.1716 (2)	−0.1056 (2)	3.7 (1)
C(14)	−0.0294 (3)	0.2917 (3)	0.6515 (3)	4.9 (1)	C(65)	0.1198 (2)	0.1415 (2)	−0.0707 (3)	3.5 (1)
C(15)	−0.0491 (3)	0.3183 (4)	0.5999 (3)	7.0 (2)	C(66)	0.1066 (2)	0.1585 (2)	−0.0067 (2)	2.65 (9)
C(16)	−0.0299 (3)	0.3045 (3)	0.5348 (3)	5.3 (1)	C(71)	0.0686 (2)	0.0647 (2)	0.5039 (2)	3.0 (1)
C(20)	0.1595 (2)	0.3106 (2)	0.3242 (2)	2.32 (9)	C(72)	0.0999 (3)	0.0127 (3)	0.5283 (4)	7.9 (2)
C(21)	0.2087 (2)	0.3203 (2)	0.3735 (2)	2.9 (1)	C(73)	0.1545 (3)	0.0071 (3)	0.4903 (3)	4.6 (1)
C(22)	0.2619 (2)	0.3405 (3)	0.3540 (3)	4.8 (1)	C(74)	0.1399 (2)	0.0393 (2)	0.4275 (3)	3.9 (1)
C(23)	0.3074 (3)	0.3482 (3)	0.4017 (3)	6.6 (2)	C(81)	0.2050 (3)	0.4250 (2)	0.1873 (3)	4.9 (1)
C(24)	0.2977 (3)	0.3372 (3)	0.4671 (3)	5.8 (2)	C(82)	0.2289 (3)	0.4677 (3)	0.1387 (4)	6.5 (2)
C(25)	0.2445 (3)	0.3167 (4)	0.4864 (3)	6.4 (2)	C(83)	0.1989 (4)	0.4549 (3)	0.0745 (4)	8.6 (2)
C(26)	0.1992 (3)	0.3088 (3)	0.4400 (3)	5.3 (1)	C(84)	0.1831 (3)	0.3940 (3)	0.0778 (3)	4.6 (1)
C(30)	−0.0111 (4)	0.3940 (4)	0.3545 (4)	2.0 (1)*	O(90)	0.6952 (5)	0.0988 (5)	0.3870 (5)	8.9 (2)*
C(31)	0.0143 (4)	0.4464 (4)	0.3856 (5)	2.9 (2)*	C(91)	0.7521 (4)	0.1174 (4)	0.4038 (4)	7.9 (2)*
C(32)	−0.0218 (4)	0.4934 (4)	0.3990 (5)	3.3 (2)*	C(92)	0.7917 (3)	0.0837 (3)	0.3638 (4)	7.4 (2)*
C(33)	0.0024 (5)	0.5403 (6)	0.4280 (6)	4.7 (2)*	C(93)	0.7533 (4)	0.0414 (5)	0.3284 (5)	9.3 (2)*
C(34)	0.0620 (5)	0.5431 (6)	0.4450 (6)	4.8 (2)*	C(94)	0.6963 (6)	0.0680 (6)	0.3284 (7)	7.5 (3)*
C(35)	0.0966 (6)	0.4963 (6)	0.4346 (7)	5.3 (3)*	C(95)	0.7035 (9)	0.0684 (9)	0.418 (1)	7.3 (5)*
C(36)	0.0730 (4)	0.4493 (4)	0.4008 (5)	3.4 (2)*	C(96)	0.704 (1)	0.026 (1)	0.372 (1)	10.2 (7)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Important Interatomic Distances (Å) for $[ZnVO(O_2CC_6H_5)_3(C_4H_8O)]_4 \cdot 2C_4H_8O^a$

Zn(1)-V(1)	3.482 (1)	Zn(2)-O(1)	1.978 (2)
-V(1)'	3.495 (1)	-O(10)	2.001 (2)
-V(2)	3.417 (1)	-O(41)	2.029 (2)
Zn(2)-V(1)	3.468 (1)	-O(51)	2.006 (2)
-V(2)	3.425 (1)	-O(70)	2.187 (2)
-V(2)'	3.464 (1)	V(1)-O(1)	1.991 (2)
V(1)-V(1)'	2.976 (1)	-O(2)	2.005 (2)
-V(2)	2.959 (1)	-O(2)'	1.982 (2)
-V(2)'	2.938 (1)	-O(11)	2.019 (2)
V(2)-V(2)'	2.987 (1)	-O(20)	1.998 (2)
Zn(1)-O(2)	2.002 (2)	-O(30)	2.001 (2)
-O(21)	1.995 (2)	V(2)-O(1)	1.984 (2)
-O(31)	1.967 (5)	-O(1)'	1.999 (2)
-O(31A)	2.052 (5)	-O(2)	1.968 (2)
-O(61)	2.002 (2)	-O(40)	2.011 (2)
-O(80)	2.228 (2)	-O(50)	2.013 (2)
		-O(60)	2.014 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

is significantly shorter than in other V(III) compounds, viz. >3.3 Å in oxo-centered trinuclear ones[3a,9] and >3.6 Å in the dimers with axial cyclopentadienyl anions.[10] Whether this relatively short separation is associated with significant metal–metal bonding is a moot point. Clearly, there must be some attractive forces to offset the repulsive forces caused by a close approach of four tripositive metal centers. The bridging ligands are probably not of major importance in this regard, but it is probable that the central oxygen atoms contribute to the stability of the V_4 core. If the distance between vanadium atoms were to increase, the O atoms would have to move closer to the V_3 plane, thus making the O–V–O′ angles more acute. This in turn would result in a deformation of the octahedral coordination around vanadium toward a more strained arrangement. Alternatively the close approach of V atoms can be considered to be a result of attraction of the capping oxygen by the zinc atom. This leads to a pyramidal, instead of planar, V_3O unit, and in order to retain the V–O bonds, the separation between vanadium atoms must decrease. In conclusion, it appears that a major factor providing the stability of the central metal core is the arrangement of two interpenetrating tetrahedra of vanadium and oxygen atoms.

Whether or not direct V–V bonding makes any significant contribution to stability, it seems likely that interactions between the four d^2 V(III) ions will be appreciable and a detailed study of the magnetic susceptibility as a function of temperature would be of interest.

The compound described here is unique in a number of respects, some of which have already been discussed above. To the best of our knowledge, no discrete molecules of such high nuclearity have been reported for carboxylato complexes. Another noteworthy feature associated with this compound is that under similar conditions a regular trinuclear oxo-centered complex of vanadium is obtained with sodium tri-

Table IV. Important Interatomic Angles (deg) for $[ZnVO(O_2CC_6H_5)_3(C_4H_8O)]_4 \cdot 2C_4H_8O$[a]

V(1)-Zn(1)-V(1)′	50.51 (2)	O(1)-V(1)-O(20)	97.11 (9)
-V(2)	50.79 (1)	-O(30)	174.98 (9)
V(1)′-Zn(1)-V(2)	50.31 (1)	O(2)-V(1)-O(2)′	83.15 (9)
V(1)-Zn(2)-V(2)	50.84 (1)	-O(11)	174.32 (9)
-V(2)′	50.16 (1)	-O(20)	92.71 (9)
V(2)-Zn(2)-V(2)′	51.39 (2)	-O(30)	96.7 (1)
V(1)′-V(1)-V(2)	59.35 (2)	O(2)′-V(1)-O(11)	97.60 (9)
-V(2)′	60.03 (2)	-O(20)	175.59 (9)
V(2)-V(1)-V(2)′	60.86 (2)	-O(30)	91.06 (9)
V(1)-V(2)-V(1)′	60.62 (2)	O(11)-V(1)-O(20)	86.67 (9)
-V(2)′	59.23 (2)	-O(30)	88.9 (1)
V(1)′-V(2)-V(2)′	59.91 (2)	O(20)-V(1)-O(30)	87.9 (1)
O(2)-Zn(1)-O(21)	99.24 (9)	O(1)-V(2)-O(1)′	82.66 (9)
-O(31)	95.0 (2)	-O(2)	83.97 (9)
-O(31A)	97.6 (2)	-O(40)	94.48 (9)
-O(61)	98.51 (9)	-O(50)	93.51 (9)
-O(80)	178.03 (9)	-O(60)	177.15 (9)
O(21)-Zn(1)-O(31)	108.8 (2)	O(1)′-V(2)-O(2)	84.07 (9)
-O(31A)	124.5 (2)	-O(40)	93.28 (9)
-O(61)	120.9 (1)	-O(50)	175.94 (9)
-O(80)	80.8 (1)	-O(60)	96.07 (9)
O(31)-Zn(1)-O(61)	125.0 (2)	O(2)-V(2)-O(40)	177.07 (9)
-O(80)	83.1 (2)	-O(50)	94.23 (9)
O(31A)-Zn(1)-O(61)	108.0 (2)	-O(60)	93.36 (9)
-O(80)	80.8 (2)	O(40)-V(2)-O(50)	88.33 (9)
O(61)-Zn(1)-O(80)	83.10 (9)	-O(60)	88.14 (9)
O(1)-Zn(2)-O(10)	98.13 (9)	O(50)-V(2)-O(60)	87.70 (9)
-O(41)	97.33 (9)	Zn(2)-O(1)-V(1)	121.8 (1)
-O(51)	97.44 (9)	-V(2)	119.6 (1)
-O(70)	176.97 (9)	-V(2)′	121.1 (1)
O(10)-Zn(2)-O(41)	118.3 (1)	V(1)-O(1)-V(2)	96.21 (9)
-O(51)	116.3 (1)	-V(2)′	94.86 (9)
-O(70)	84.88 (9)	V(2)-O(1)-V(2)′	97.16 (9)
O(41)-Zn(2)-O(51)	120.2 (1)	Zn(1)-O(2)-V(1)	120.6 (1)
-O(70)	80.93 (9)	-V(1)′	122.6 (1)
O(51)-Zn(2)-O(70)	81.40 (9)	-V(2)	118.7 (1)
O(1)-V(1)-O(2)	82.85 (8)	V(1)-O(2)-V(1)′	96.56 (9)
-O(2)′	83.92 (9)	-V(2)	96.26 (9)
-O(11)	91.62 (9)	V(1)′-O(2)-V(2)	96.12 (9)

[a] Numbers in parentheses are estimated standard deviations in the the least significant digits.

fluoroacetate.[3] The only variation in the latter preparation was the use of CH_2Cl_2 as a component in the solvent mixture. However, as noted, the reaction with trifluoroacetate also affords some as yet unidentified product but its relationship, if any, to the octanuclear benzoate is not clear at this moment.

The oxo-centered tetrahedra of metal ions, V_3ZnO with carboxylate bridged on the edges, of which this molecule is built are, in detail, unprecedented. However, this general type of unit is familiar in the basic carboxylates of beryllium and zinc[12] of general formula $M_4O(O_2CR)_6$. On the whole, however, examples of an oxide ion at the center of a tetrahedron, or other polyhedron, of metal atoms are scarce[13] and the molecule described here is apparently the first example of such a structure with a heteronuclear polyhedron of metal atoms.

Finally, we must address one more issue, namely, the presence of oxygen atoms in the molecule. A similar problem arises in most of the numerous cases where trinuclear oxo-centered or oxo-capped compounds are prepared in nonaqueous, anaerobic media from metal salts and carboxylic acids. Most likely, the oxygen atoms are extracted from the carboxylate ligands, but in this case, as in others, proof of this is lacking. Alternative explanations, such as hydrolysis by the traces of water or adventitious introduction of air, are less likely in view of rapid decomposition of some of those materials upon exposure to air.

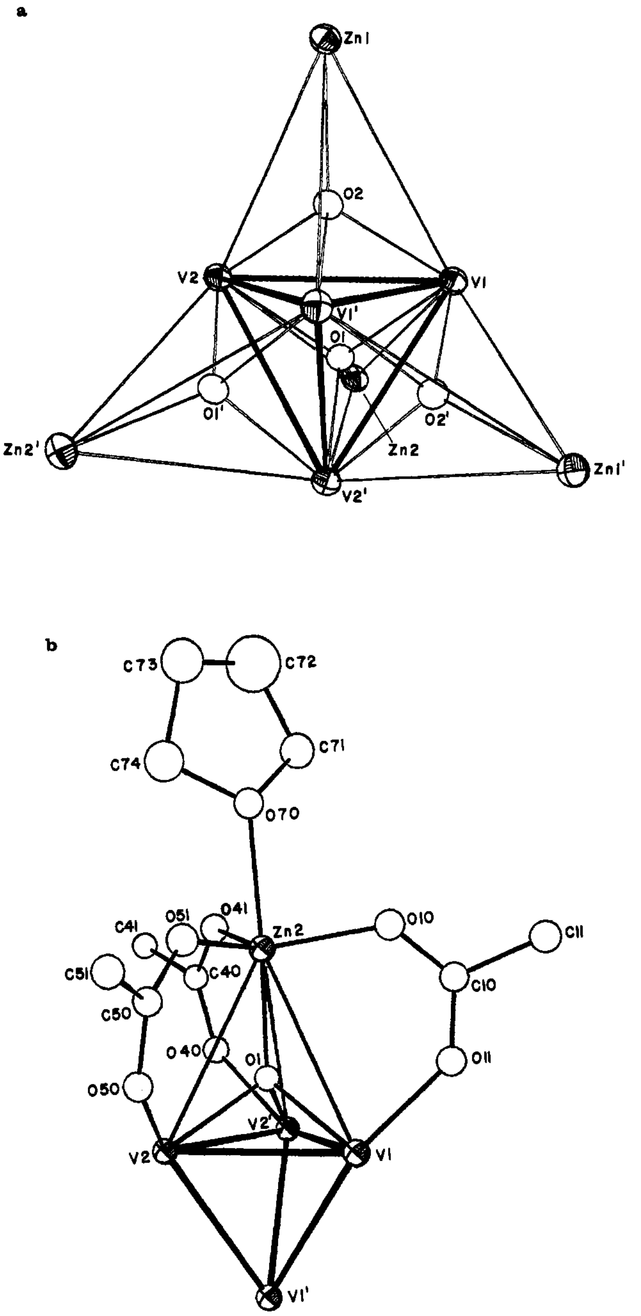

Figure 3. Partial views of the structure: (a) view of the central $[Zn_4V_4O_4]$ core; (b) view of one ZnV_3 unit showing the orientation of benzoate ligands.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal vibration parameters, and bond distances and angles in addition to those given in the text (39 pages). Ordering information is given on any current masthead page.

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