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New Trinuclear, Oxo-Centered, Basic Carboxylate Compounds of Transition Metals. 2.[1] Synthesis and X-ray Structure of $V_3(O)_3(THF)(C_6H_5CO_2)_6$, a Compound with a Deviant Structure

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The preparation and first structural characterization of a trinuclear vanadium carboxylate, namely, $V_3(O)_3(THF)(C_6H_5CO_2)_6$, is reported. A single-crystal X-ray diffraction study has shown that the molecule contains an unusual planar V_3O trimetal moiety with two distinct types of vanadium coordination spheres even though each metal atom is present in the same formal oxidation state, IV. Instead of a centered oxygen atom equivalently bonded to all three vanadium atoms, the central oxygen atom is much closer (1.626 (6) Å) to one vanadium atom, forming a vanadyl group, than to the other two (2.344 (7), 2.452 (6) Å). Each of the others forms an exo V═O double bond (average 1.575 (6) Å). There are, as usual, six bridging carboxylate groups, and the exo position of the first V atom is filled by a THF molecule (V—O = 2.186 (6) Å). The title complex forms crystals belonging to the monoclinic space group $P2_1/n$ with unit cell dimensions a = 13.722 (4) Å, b = 21.443 (3) Å, c = 15.758 (2) Å, β = 93.30 (2)°, and Z = 4.

Introduction

This is the second in a series of papers in which we describe the synthesis and structural characterization of oxo-centered metal carboxylate trimers of the early transition series. In part 1[1] and in earlier work[1,2] the basic structural unit of these molecules when the metals are present in the +3 or an averaged $+2^2/_3$ oxidation state has been recognized as consisting of an exactly or approximately equilateral triangle of metal atoms with an oxygen atom at the center, six edge-bridging carboxylato groups, and three equatorial ligands. With vanadium, however, there has been no firm structural data to show whether such species exist since no suitably crystalline compounds have been obtained.[3-5] This difficulty has been attributed in some cases to the supposedly polymeric nature of the compounds, but that is entirely speculative.

Vanadium(III) and -(IV) carboxylates have previously been prepared from precursors such as vanadium(V) oxide trichloride,[6] vanadium(IV) oxide dichloride,[7] vanadium(IV) or -(V) oxides[8] anhydrous vanadium trichloride,[9] and vanadium diboride,[5] and as studies of their physical properties have been largely concerned with their unusual magnetic behavior, confusion has arisen as to the exact empirical formulas and molecular structures of these complexes. Many contradictory statements exist in the literature.

We have discovered that the use of the tris(tetrahydrofuranate) of vanadium(III) chloride[10] (and, as we shall demonstrate in a subsequent paper, $VCl_2{\cdot}2THF$[11] as well) affords a simple, efficient route to crystalline samples of a variety of trimeric vanadium carboxylate compounds whose oxidation states and overall formulas are dependent on both reaction conditions and crystallization procedures. In this report we describe the synthesis and X-ray crystallographic study of $V_3(O)_3(THF)(C_6H_5CO_2)_6$, an unprecedented and anomalous M_3O (M = transition metal) carboxylate complex in which the central oxygen atom is tightly bound to one vanadium atom while forming weaker, bridging interactions with the other two.

Table I. Crystallographic Data and Syntex P$\bar{1}$ Data Collection Parameters

formula	$V_3O_{16}C_{48}H_{38}$	β, deg	93.30 (2)
M_r	999.6	V, Å^3	4629 (3)
space group	$P2_1/n$	Z	4
a, Å	13.722 (4)	ρ_c, g/cm^3	1.434
b, Å	21.443 (3)	cryst size, mm	0.35 × 0.35 × 0.5
c, Å	15.758 (2)	μ(Mo Kα), cm^{-1}	6.401

radiation	graphite-monochromated Mo Kα
scan type	θ–2θ
collection range	$+h,+k,\pm l$; $0 < 2\theta \leqslant 50°$
max counting time, s	80
X-ray exposure time, h	270
no. of unique data	5131
no. of data, $I > 3\sigma(I)$	3133
p	0.07
no. of variables	566
cryst dec	0
R_1	0.064
R_2	0.082
esd	1.625
largest shift[a]	0.33
largest peak[b]	0.66

[a] Largest Δ_i/σ_i ratio in final refinement cycle. [b] Largest peak in a final difference Fourier, e/Å^3.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon except where otherwise specified. Dichloromethane was dried over P_2O_5, distilled immediately before use, and transferred by syringe.

Synthesis and Crystal Preparation of the Title Complex. $VCl_3{\cdot}3THF$[10] (1.12 g, 3 mmol) was dissolved in 50 mL of dichloromethane. To this solution 1.30 g (9 mmol) of sodium benzoate was added over a 0.5-h period. The mixture was stirred overnight and subsequently filtered through Celite. The resulting dark green solution was slowly evaporated under a stream of dry air, affording dark green crystals in ca. 30% yield.

Collection and Reduction of X-ray Data. A rectangular crystal measuring approximately 0.35 × 0.35 × 0.5 mm was immersed in degassed mineral oil, transferred to a thin-walled glass capillary, fixed in position with epoxy cement, and placed on a Syntex P$\bar{1}$ four-circle, automated diffractometer. Least-squares refinement of 15 intense reflections in the range 20° < 2θ < 30° gave an orientation matrix for calculation of setting angles and cell parameters. A monoclinic cell, later shown by systematic absences and successful refinement to belong to the space group $P2_1/n$, was used. The cell parameters are presented in Table I. Intensity data were collected for two

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Table IIA. Positional Parameters and Their Estimated Standard Deviations for $V_3(O)_3(THF)(C_6H_5COO)_6$ [a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
V(1)	0.7321 (1)	0.20078 (8)	0.7949 (1)	C(31)	0.5716 (7)	0.0171 (5)	0.8057 (6)
V(2)	0.7878 (1)	0.04249 (8)	0.7637 (1)	C(32)	0.5221 (7)	−0.0275 (5)	0.8634 (6)
V(3)	0.5323 (1)	0.12377 (9)	0.6838 (1)	C(33)	0.5702 (9)	−0.0821 (5)	0.8912 (7)
O(1)	0.6168 (4)	0.2241 (3)	0.8573 (4)	C(34)	0.5217 (10)	−0.1228 (6)	0.9450 (8)
O(1′)	0.4974 (5)	0.1866 (3)	0.7713 (4)	C(35)	0.4292 (9)	−0.1068 (6)	0.9702 (8)
O(2)	0.7905 (5)	0.1695 (3)	0.9041 (4)	C(36)	0.3842 (9)	−0.0517 (6)	0.9443 (8)
O(2′)	0.8087 (5)	0.0672 (3)	0.8860 (4)	C(37)	0.4286 (8)	−0.0131 (6)	0.8883 (7)
O(3)	0.6604 (5)	0.0052 (3)	0.7943 (5)	C(41)	0.6842 (7)	0.0520 (4)	0.5894 (6)
O(3′)	0.5221 (5)	0.0606 (3)	0.7738 (4)	C(42)	0.6968 (8)	0.0441 (5)	0.4952 (6)
O(4)	0.7569 (5)	0.0426 (3)	0.6386 (4)	C(43)	0.7947 (9)	0.0305 (5)	0.4702 (8)
O(4′)	0.6007 (5)	0.0666 (4)	0.6109 (4)	C(44)	0.8099 (12)	0.0305 (7)	0.3810 (8)
O(5)	0.8977 (5)	0.0999 (3)	0.7378 (5)	C(45)	0.7270 (13)	0.0377 (7)	0.3259 (9)
O(5′)	0.8636 (4)	0.2012 (3)	0.7466 (4)	C(46)	0.6340 (12)	0.0490 (8)	0.3514 (9)
O(6)	0.5876 (5)	0.1923 (3)	0.6167 (4)	C(47)	0.6193 (9)	0.0515 (7)	0.4381 (7)
O(6′)	0.6853 (4)	0.2545 (3)	0.6982 (4)	C(51)	0.9186 (6)	0.1565 (5)	0.7299 (6)
O(7)	0.7847 (6)	0.2902 (3)	0.8459 (4)	C(52)	1.0194 (7)	0.1723 (5)	0.7025 (6)
O(8)	0.8488 (5)	−0.0202 (3)	0.7671 (4)	C(53)	1.0442 (8)	0.2342 (5)	0.6937 (8)
O(9)	0.4281 (5)	0.1187 (4)	0.6380 (5)	C(54)	1.1413 (8)	0.2469 (6)	0.6688 (8)
O(10)	0.6944 (4)	0.1341 (3)	0.7565 (4)	C(55)	1.2073 (8)	0.1999 (6)	0.6573 (8)
C(11)	0.5278 (7)	0.2185 (4)	0.8336 (6)	C(56)	1.1811 (8)	0.1384 (6)	0.6684 (8)
C(12)	0.4516 (7)	0.2493 (5)	0.8826 (6)	C(57)	1.0829 (7)	0.1237 (6)	0.6911 (7)
C(13)	0.3547 (7)	0.2394 (6)	0.8594 (8)	C(61)	0.6330 (7)	0.2426 (5)	0.6315 (6)
C(14)	0.2817 (9)	0.2706 (6)	0.9020 (9)	C(62)	0.6271 (7)	0.2917 (5)	0.5643 (6)
C(15)	0.3092 (9)	0.3083 (6)	0.9706 (8)	C(63)	0.6809 (11)	0.3447 (6)	0.5753 (9)
C(16)	0.4072 (10)	0.3190 (6)	0.9944 (8)	C(64)	0.6776 (12)	0.3894 (6)	0.5072 (10)
C(17)	0.4816 (9)	0.2891 (5)	0.9493 (7)	C(65)	0.6187 (11)	0.3803 (6)	0.4353 (9)
C(21)	0.8166 (6)	0.1159 (5)	0.9308 (6)	C(66)	0.5639 (10)	0.3272 (6)	0.4270 (7)
C(22)	0.8568 (6)	0.1101 (5)	1.0195 (6)	C(67)	0.5662 (8)	0.2804 (6)	0.4909 (6)
C(23)	0.8492 (8)	0.1597 (6)	1.0762 (6)	C(71)	0.792 (1)	0.3055 (9)	0.937 (1)
C(24)	0.8894 (8)	0.1566 (6)	1.1587 (7)	C(72)	0.808 (1)	0.3761 (10)	0.937 (1)
C(25)	0.9381 (9)	0.1024 (6)	1.1852 (8)	C(73)	0.872 (2)	0.3852 (10)	0.867 (1)
C(26)	0.9445 (10)	0.0528 (6)	1.1290 (8)	C(74)	0.827 (1)	0.3386 (10)	0.799 (1)
C(27)	0.9028 (8)	0.0565 (5)	1.0458 (7)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

overlapping spheres of reflections (θ = 15–25° and 0–16°) with use of graphite-monochromated Mo Kα radiation and a θ–2θ scan rate varying from 1.5 to 12°/min, depending upon the intensity of the reflection. Background measurements were made at both limits of each scan. After the twice-collected reflections were averaged with use of the program PAINT,[12] 3133 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. The standard reflections measured repeatedly every 100 data points showed no significant decline in intensity. With μ = 6.40 cm^{-1} no absorption correction was deemed necessary.

Structure Solution and Refinement.[12] The Patterson map was quite complex as expected with three unique vanadium atoms per asymmetric unit, and the direct-methods program MULTAN was used to determine the three independent metal atom positions. Three cycles of isotropic least-squares refinement then gave values of R_1 = 0.42 and R_2 = 0.51, where the R_i are defined as

$$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$$
$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$$

Subsequent least-squares cycles and difference Fourier maps located all 62 remaining non-hydrogen atoms. Isotropic refinement of these gave discrepancy indices of R_1 = 0.092 and R_2 = 0.119, and subsequently when all atoms except the THF carbon atoms were subjected to anisotropic refinement, convergence was reached at R_1 = 0.064 and R_2 = 0.082. The error in an observation of unit weight was 1.625, and the largest shift/error ratio in the final cycle was 0.33. A final difference synthesis showed random fluctations not exceeding ±0.66 e/Å^3. No attempt was made to include hydrogen atoms.

Final positional parameters of non-hydrogen atoms are given in Table IIA. The thermal parameters are listed in Table IIB, which is available as supplementary material. Values of F_o vs. F_c for the 3133 observed data are also available as supplementary material.

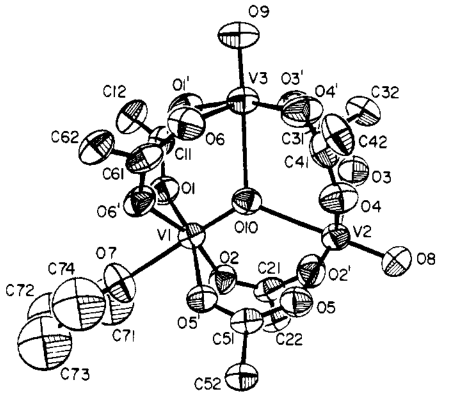

Figure 1. $V_3(O)_3(THF)(C_6H_5COO)_6$ molecule, computer-drawn with the ORTEP program. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density. Phenyl groups are omitted for clarity.

Results

The crystal structure consists of a packing of discrete $V_3(O)_3(THF)(C_6H_5CO_2)_6$ molecules. The entire molecule constitutes the asymmetric unit and is not subject to any crystallographically imposed symmetry. The molecule is depicted in Figure 1, where the atom-numbering scheme used in all tables is defined. The bond distances and angles are listed in Table III, and a least-squares plane defined by V(1), V(2), V(3), O(7), O(8), O(9), and O(10) is given in Table IV.

The molecule has virtual C_{2v} symmetry, with the C_2 axis defined by the bonds O(7)–V(1) and V(1)–O(10) and continuing through a point bisecting an imaginary line between C(31) and C(41). Approximate mirror planes are defined by the least-squares plane mentioned above and by that drawn through O(7), V(1), O(10), C(31), C(32), C(41), and C(42)

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[12] The crystallographic programs for the structural solution and refinement, those of the Enraf-Nonius structure determination package, were used on a PDP 11/45 computer at B. A. Frenz and Associates, College Station, TX.

Table III. Bond Distances (Å) and Bond Angles (Deg) in $V_3(O)_3(THF)(C_6H_5COO)_6$[a]

V(1)-V(2)	3.520 (2)	V(1)-O(7)	2.186 (6)	V(2)-O(4)	1.991 (6)	V(3)-O(3')	1.972 (6)
-V(3)	3.572 (2)	-O(10)	1.626 (6)	-O(5)	2.007 (5)	-O(4')	1.957 (6)
-O(1)	1.975 (6)	V(2)-V(3)	4.050 (2)	-O(8)	1.582 (5)	-O(6)	1.986 (6)
-O(2)	1.973 (7)	-O(2')	2.004 (6)	-O(10)	2.344 (7)	-O(9)	1.568 (6)
-O(5')	1.998 (6)	-O(3)	2.007 (6)	V(3)-O(1')	2.005 (6)	-O(10)	2.452 (6)
-O(6')	1.988 (6)						
O(1)-C(11)	1.262 (9)	O(5')-C(51)	1.26 (1)	C(14)-C(15)	1.39 (1)	C(25)-C(26)	1.39 (2)
O(1')-C(11)	1.25 (1)	O(6)-C(61)	1.26 (1)	C(15)-C(16)	1.39 (1)	C(26)-C(27)	1.40 (1)
O(2)-C(21)	1.27 (1)	O(6')-C(61)	1.26 (1)	C(16)-C(17)	1.43 (1)	C(31)-C(32)	1.51 (1)
O(2')-C(21)	1.26 (1)	O(7)-C(71)	1.48 (2)	C(21)-C(22)	1.48 (1)	C(32)-C(33)	1.40 (2)
O(3)-C(31)	1.27 (1)	-C(74)	1.42 (2)	C(22)-C(23)	1.40 (2)	C(32)-C(37)	1.40 (1)
O(3')-C(31)	1.24 (1)	C(11)-C(12)	1.49 (2)	C(22)-C(27)	1.37 (2)	C(33)-C(34)	1.41 (2)
O(4)-C(41)	1.25 (2)	C(12)-C(13)	1.38 (2)	C(23)-C(24)	1.38 (2)	C(34)-C(35)	1.39 (2)
O(4')-C(41)	1.25 (2)	-C(17)	1.40 (2)	C(24)-C(25)	1.39 (2)	C(35)-C(36)	1.39 (1)
O(5)-C(51)	1.26 (1)	C(13)-C(14)	1.41 (2)				
C(36)-C(37)	1.38 (1)	C(46)-C(47)	1.39 (2)	C(55)-C(56)	1.38 (2)	C(64)-C(65)	1.37 (2)
C(41)-C(42)	1.51 (2)	C(51)-C(52)	1.51 (2)	C(56)-C(57)	1.45 (2)	C(65)-C(66)	1.37 (2)
C(42)-C(43)	1.45 (1)	C(52)-C(53)	1.38 (2)	C(61)-C(62)	1.49 (2)	C(66)-C(67)	1.42 (2)
C(42)-C(47)	1.36 (1)	C(52)-C(57)	1.38 (2)	C(62)-C(63)	1.36 (2)	C(71)-C(72)	1.53 (3)
C(43)-C(44)	1.43 (1)	C(53)-C(54)	1.44 (2)	C(62)-C(67)	1.41 (2)	C(72)-C(73)	1.46 (3)
C(44)-C(45)	1.40 (1)	C(54)-C(55)	1.37 (3)	C(63)-C(64)	1.44 (2)	C(73)-C(74)	1.57 (3)
C(45)-C(46)	1.38 (2)						
V(2)-V(1)-V(3)	69.65 (4)	O(1')-V(3)-O(4')	165.1 (2)	O(1')-C(11)-C(12)	116.0 (9)	C(41)-C(42)-C(43)	116.6 (9)
O(1)-V(1)-O(2)	87.1 (3)	-O(6)	89.0 (3)	C(11)-C(12)-C(13)	119 (1)	-C(47)	120 (1)
-O(5')	162.9 (3)	-O(9)	96.6 (3)	-C(17)	118 (1)	C(43)-C(42)-C(47)	123.0 (9)
-O(6')	90.1 (2)	-O(10)	82.2 (2)	C(13)-C(12)-C(17)	122 (1)	C(42)-C(43)-C(44)	117.1 (7)
-O(7)	81.5 (2)	O(3')-V(3)-O(4')	92.8 (3)	C(12)-C(13)-C(14)	120 (1)	C(43)-C(44)-C(45)	116.8 (8)
-O(10)	99.2 (3)	-O(6)	159.4 (3)	C(13)-C(14)-C(15)	118.7 (8)	C(44)-C(45)-C(46)	124.7 (9)
O(2)-V(1)-O(5')	90.2 (3)	-O(9)	100.5 (3)	C(14)-C(15)-C(16)	121.5 (8)	C(45)-C(46)-C(47)	119 (1)
-O(6')	164.3 (3)	-O(10)	80.0 (2)	C(15)-C(16)-C(17)	119.9 (9)	C(42)-C(47)-C(46)	119 (1)
-O(7)	82.5 (2)	O(4')-V(3)-O(6)	86.6 (3)	C(12)-C(17)-C(16)	117.3 (9)	O(5)-C(51)-O(5')	124.9 (9)
-O(10)	97.5 (3)	-O(9)	98.1 (3)	O(2)-C(21)-O(2')	123.5 (7)	-C(52)	118 (1)
O(5')-V(1)-O(6')	88.0 (3)	-O(10)	83.0 (2)	-C(22)	118.2 (8)	O(5')-C(51)-C(52)	117 (1)
-O(7)	81.4 (2)	O(6)-V(3)-O(9)	100.0 (3)	O(2')-C(21)-C(22)	118.4 (8)	C(51)-C(52)-C(53)	119 (1)
-O(10)	97.9 (3)	-O(10)	79.5 (2)	C(21)-C(22)-C(23)	120.3 (9)	-C(57)	118 (1)
O(6')-V(1)-O(7)	81.9 (2)	O(9)-V(3)-O(10)	178.7 (3)	-C(27)	119.8 (9)	C(53)-C(52)-C(57)	124 (1)
-O(10)	98.2 (3)	V(1)-O(1)-C(11)	128.2 (6)	C(23)-C(22)-C(27)	119.9 (9)	C(52)-C(53)-C(54)	117 (1)
O(7)-V(1)-O(10)	179.2 (3)	V(3)-O(1')-C(11)	145.7 (6)	C(22)-C(23)-C(24)	121.6 (9)	C(53)-C(54)-C(55)	122 (1)
V(1)-V(2)-V(3)	55.78 (4)	V(1)-O(2)-C(21)	133.6 (6)	C(23)-C(24)-C(25)	119 (1)	C(54)-C(55)-C(56)	120 (1)
O(2')-V(2)-O(3)	87.3 (2)	V(2)-O(2')-C(21)	139.4 (5)	C(24)-C(25)-C(26)	120 (1)	C(55)-C(56)-C(57)	119 (1)
-O(4)	164.2 (2)	V(2)-O(3)-C(31)	144.2 (6)	C(25)-C(26)-C(27)	121.1 (9)	C(52)-C(57)-C(56)	118 (1)
-O(5)	88.1 (2)	V(3)-O(3')-C(31)	138.3 (6)	C(22)-C(27)-C(26)	119.1 (9)	O(6)-C(61)-O(6')	125.2 (9)
-O(8)	98.4 (3)	V(2)-O(4)-C(41)	137.3 (7)	O(3)-C(31)-O(3')	127.0 (8)	-C(62)	118 (1)
-O(10)	82.7 (2)	V(3)-O(4')-C(41)	142.4 (8)	-C(32)	115.3 (8)	O(6')-C(61)-C(62)	116.9 (9)
O(3)-V(2)-O(4)	95.8 (2)	V(2)-O(5)-C(51)	142.3 (6)	O(3')-C(31)-C(32)	117.7 (8)	C(61)-C(62)-C(63)	119 (1)
-O(5)	165.7 (3)	V(1)-O(5')-C(51)	130.0 (7)	C(31)-C(32)-C(33)	119.8 (8)	-C(67)	118 (1)
-O(8)	96.9 (3)	V(3)-O(6)-C(61)	137.3 (6)	-C(37)	118.8 (9)	C(63)-C(62)-C(67)	123 (1)
-O(10)	82.2 (2)	V(1)-O(6')-C(61)	131.6 (6)	C(33)-C(32)-C(37)	121.4 (9)	C(62)-C(63)-C(64)	118 (1)
O(4)-V(2)-O(5)	85.3 (2)	V(1)-O(7)-C(71)	123.8 (8)	C(32)-C(33)-C(34)	118 (1)	C(63)-C(64)-C(65)	121 (1)
-O(8)	96.7 (3)	-C(74)	125.8 (9)	C(33)-C(34)-C(35)	119 (1)	C(64)-C(65)-C(66)	120 (1)
-O(10)	82.3 (2)	C(71)-O(71)-C(74)	110 (1)	C(34)-C(35)-C(36)	121.6 (8)	C(65)-C(66)-C(67)	122 (1)
O(5)-V(2)-O(8)	97.2 (3)	V(1)-O(10)-V(2)	123.9 (3)	C(35)-C(36)-C(37)	119.7 (9)	C(62)-C(67)-C(66)	117 (1)
-O(10)	83.8 (2)	-V(3)	120.9 (3)	C(32)-C(37)-C(36)	120 (1)	O(7)-C(71)-C(72)	103 (1)
O(8)-V(2)-O(10)	178.6 (2)	V(2)-O(10)-V(3)	115.2 (2)	O(4)-C(41)-O(4')	126 (1)	C(71)-C(72)-C(73)	103 (1)
V(1)-V(3)-V(2)	54.57 (4)	O(1)-C(11)-O(1')	123.9 (8)	-C(42)	117 (1)	C(72)-C(73)-C(74)	102 (1)
O(1')-V(3)-O(3')	86.4 (2)	-C(12)	120.1 (9)	O(4')-C(41)-C(42)	117 (1)	O(7)-C(74)-C(73)	105 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table IV. Least-Squares Plane Illustrating the Near Planarity of the $V_3(O)_3O(THF)$ Moiety in the Title Complex

$A = 0.4323; B = 0.2271; C = -0.8727; D = -5.8925$[a]

atom	dev, Å	atom	dev, Å	atom	dev, Å
V(1)	−0.013	O(7)	0.009	O(9)	0.015
V(2)	−0.009	O(8)	−0.014	O(10)	0.014
V(3)	−0.002				

[a] The equation of the plane is of the form $Ax + By + Cz - D = 0$.

perpendicular to the plane in Figure 1.

Discussion

In light of our long-term goal of investigating the interactions between transition-metal atoms[13] and our current studies involving early transition series trimeric complexes[14] we became interested in a series of publications that appeared in the late 1960s and early 1970s.[2-9] At that time Greenwood et al.[5] reported the synthesis of complexes analyzed as $V_2(O_2CR)_6$ by reaction of vanadium diboride and carboxylic acids in dry air at temperatures exceeding 100 °C. They proposed a dinuclear structure with four bridging and two terminal carboxylate groups, and a metal–metal interaction, on the basis of magnetic susceptibility studies. Several other groups[6,7] reacted vanadium(III), -(IV), and -(V) oxides or oxychlorides with carboxylic acids and formulated both ionic

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[13] For a recent review see: Cotton, F. A. *Adv. Chem. Ser.* **1981**, *No. 155*, 1.

[14] Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

and neutral vanadium(IV) products. The former were thought to occur as the symmetrical oxygen-bridged trimers, as mentioned in the Introduction, whereas the latter were proposed to be linear polymers with repeating $VO(O_2CR)_2$ units and syn–syn carboxylate bridges.[3,4] The relatively low yields and extremely long reaction periods for Greenwood's syntheses led us to search for simpler and more efficient routes to these and other vanadium carboxylates.

Reaction of $VCl_3 \cdot 3THF$ and 3 equiv of sodium benzoate in dichloromethane proceeds smoothly in a matter of hours at room temperature, producing a green solution as expected for the $V_2(O_2CR)_6$ complexes.[5] Evaporation of this solution in dry air, since Greenwood reported that his products were moisture but not air sensitive, resulted in the formation of dark green crystals. However, their empirical formula has been shown by X-ray crystallography not to be that of $V_2(O_2CC_6H_5)_6$ but rather to be $V_3(O)_3(THF)(C_6H_5CO_2)_6$. The substance is thus trinuclear and contains vanadium atoms formally in the oxidation state IV.

The crystallographic study of this compound has revealed an unprecedented structure, the appreciation of which is facilitated by a comparison with other structurally characterized triangular transition-metal carboxylates. In $V_3(O)_3(THF)(C_6H_5CO_2)_6$ each of the three vanadium atoms has a near-perfect octahedral environment and the set of three forms an approximate isosceles triangle [V(1)–V(2) = 3.520 (2) Å; V(1)–V(3) = 3.572 (2) Å; V(2)–V(3) = 4.050 (2) Å] with the V(2)–V(3) distance far greater than any previously observed for planar M_3O systems, M–M distances between 3.28 and 3.35 Å having previously been reported.[2] The Mn^{II}–Mn^{III}–Mn^{III} molecule $Mn_3O(OOCCH_3)_6(3\text{-}ClC_5H_4N)_3$[15] with crystallographically distinct manganese atoms is, to our knowledge, the only other reported nonsymmetrical, planar M_3O triangle.

This structure possesses all of the three components characteristic of the trinuclear, basic, oxo-centered transition-metal carboxylates: (1) the oxygen atom in the plane of the metal triangle; (2) the six bridging carboxyl groups; (3) an equatorial ligand on each metal atom. However, there are gross deviations from the symmetrical (ideally D_{3h}) structure normally found. The central oxygen atom is very close, 1.626 (6) Å, to V(1) but relatively far from the other two, viz., 2.344 (7) Å from V(2) and 2.452 (6) Å from V(3). The set of equatorial ligands consists of two oxygen atoms at very short distances, 1.582 (5) Å to V(2) and 1.568 (6) Å to V(3), and one THF oxygen atom at a distance of 2.186 (6) Å from V(1). Thus, this structure can be described in relation to the D_{3h} prototypal structure by saying that it has a massive distortion toward C_{2v} symmetry.

It is possible, however, to analyze the structure of $V_3(O)_3(THF)(C_6H_5CO_2)_6$ in a different way, namely, as a trimeric oxovanadium(IV) structure containing the unprecedented feature of a bridging oxovanadium(IV) group. The two VO groups formed by V(2) and V(3) can be considered as "normal" vanadyl groups. The V–O distances in these are toward the lower end of the range (ca. 1.56–1.62 Å) in which these usually occur,[15] and the rest of the coordination sphere is also typical, namely, a square array of cis ligand atoms and a weak bond in the trans position. For the V(1)–O(10) group, however, the V–O distance is at or slightly beyond the upper end of the normal range and the bond in the trans position to the THF oxygen, while it is the longest bond to this vanadium atom, is nonetheless relatively short for such a bond. In addition, O(10) is weakly, but very significantly, serving as a donor to both V(2) and V(3) with O···V distances of 2.344 (7) and 2.452 (6) Å, respectively. Doubtless, these three features, the relatively short V(1)–O(THF) distance, the relatively long V(1)–O(10) distance, and the donor function of O(10), are all synergistically interrelated.

The manifest tendency of this compound to have more the character of an oxovanadium(IV) trimer and less the character of a normal oxo-centered trinuclear complex is presumably derived from the high oxidation state of the metal atoms. In all previous oxo-centered trinuclear complexes the mean oxidation state of the metal atoms has been III or lower. With the formal oxidation state of IV there is a strong driving force toward strong covalent bonding that can reduce the effective positive charge on the metal atoms, and the formation of oxovanadium(IV) units is the result.

The only distorted oxo-centered trinuclear complex previously reported is $Mn_3O(CH_3COO)_6(3\text{-}ClC_6H_4N)_3$, where the Mn^{II}–O(central) and Mn^{III}–O(central) bond lengths are distinguishable, viz., 2.034 (4) and 1.864 (4) Å (average), respectively.[16] The underlying cause of this distortion, however, is quite different. It is because the metal atoms can actually assume different oxidation states, and these have inherently different stereochemical properties.

One final consideration requires comment. It will be recalled that the title compound was prepared with a vanadium(III) starting material, whereas we have attributed its anomalous—and unique—structure to the fact that it contains all of its metal atoms in the oxidation state IV. One can envisage the reactions previously thought to produce $VO(O_2CR)_2$ polymers may in the presence of donors such as THF result in formation of trimers akin to the title complex. It should also be noted that, while we have no evidence of any intermediate species in the reported synthesis, it is likely that a vanadium(III) species is formed initially, since the reaction is performed under anaerobic conditions, and that this subsequently undergoes oxidation, probably during crystallization. If this be the case, it is likely that Greenwood's $V_2(O_2CR)_6$ complexes, or trinuclear $V_3L_3(O_2CR)_6$ species containing metal–metal interactions, may exist, and consequently we are continuing our work in this direction.

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Registry No. $V_3(O)_3(THF)(C_6H_5CO_2)_6$, 81830-71-9.

Supplementary Material Available: Tables of observed and calculated structure factors and thermal parameters (Table IIB) (22 pages). Ordering information is given on any current masthead page.

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(15) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 715.

(16) Baikie, A. R. E.; Hursthouse, M. B.; New, L.; Thornton, P.; White, R. G. *J. Chem. Soc., Chem. Commun.* **1980**, 684.