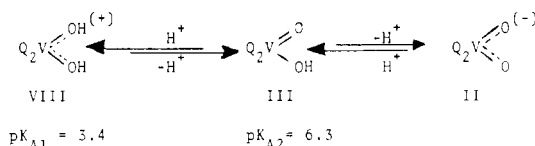


a further result making liable the comparison with an organic acid.

The weak-acid nature of III can be inferred from the basic hydrolysis of its salts in aqueous solution. Any attempt to determine the acid strength of this species is affected by two main difficulties, that is, the very low solubility of III in water, the possible equilibrium involving the loss of Q ligand by the metal,³² and the acid-base equilibrium of 8-quinolinol. These facts must be taken into account when the pK_A value determined as described in the experimental Section are considered. The procedure adopted¹⁷ requires the determination of the acid solubility at different pHs. With this method, two pK_A values have been obtained: $pK_{A1} = 3.4$ and $pK_{A2} = 6.3$. The first of them is very probably due to protonated III. The most plausible basic sites are, as suggested, the V=O oxygen¹⁶ or the nitrogen atoms of the oxine ligands.³¹ Following this hypothesis, we can write the acid-base equilibria for III as



The species having the pK_A of 6.3 is very likely the inorganic acid III. The acid strength along with the chemical properties of III is highly reminiscent of an organic carboxylic acid.

Acknowledgment. We thank the CNR (Rome) for financial support.

Registry No. I, 70748-61-7; II, *n*-butylammonium salt, 82281-76-3; II, calcium salt, 82281-77-4; II, tetraphenylphosphonium salt, 82281-78-5; II, potassium salt, 29966-90-3; III, 41922-39-8; IV, 82281-79-6; V (R = Me), 82335-35-1; V (R = Et), 41922-40-1; V (R = *i*-Pr), 40031-92-3; VI, 82281-80-9; VII, 82281-81-0; VO(acac)₂, 3153-26-2.

Supplementary Material Available: Thermal parameters (Tables III and IV) and listings of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

(32) Yuchi, A.; Yamada, S.; Tanaka, M. *Bull. Chem. Soc. Jpn.* 1979, 52, 1643-7. Yuchi, A.; Muranaka, H.; Yamada, S.; Tanaka, M. *Ibid.* 1980, 53, 1560-3.

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New Trinuclear, Oxo-Centered, Basic Carboxylate Compounds of Transition Metals. 3. Syntheses and X-ray Studies of the Trivanadium(III,III,III) and Trivanadium(II,III,III) Compounds $[\text{V}_3(\mu_3\text{-O})(\text{CH}_3\text{CO}_2)_6(\text{CH}_3\text{COOH})_2(\text{THF})]^+[\text{VCl}_4(\text{CH}_3\text{COOH})_2]^-$ and $\text{V}_3(\mu_3\text{-O})(\text{CF}_3\text{CO}_2)_6(\text{THF})_3$ with "Classical" Triangular Structures

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Two new oxo-centered vanadium carboxylate trimers have been prepared and characterized by X-ray crystallography. These are $[\text{V}_3(\mu_3\text{-O})(\text{CH}_3\text{CO}_2)_6(\text{CH}_3\text{COOH})_2(\text{THF})]^+[\text{VCl}_4(\text{CH}_3\text{COOH})_2]^-$ (**1**) and $\text{V}_3(\mu_3\text{-O})(\text{CF}_3\text{CO}_2)_6(\text{THF})_3$ (**2**). The former, synthesized from $\text{VCl}_3 \cdot 3\text{THF}$ and acetic acid, crystallizes in space group $C2/c$ with $Z = 4$ and unit cell dimensions of $a = 12.132$ (3) Å, $b = 15.458$ (4) Å, $c = 22.905$ (4) Å, $\beta = 96.80$ (2)°, and $V = 4266$ (3) Å³. **1** is ionic with all the vanadium atoms in the formal oxidation state III. The important dimensions in the cation are V-V = 3.307 (2) Å and V-($\mu_3\text{-O}$) = 1.910 (6) Å. The anion has regular octahedral geometry with an average V-Cl distance of 2.336 (11) Å and V-O distance of 2.089 (8) Å. Compound **2**, one of several products obtained from the reaction between $\text{VCl}_3 \cdot 2\text{THF}$ and sodium trifluoroacetate, crystallizes in space group $P2_1/m$ with $Z = 2$ and unit cell dimensions $a = 9.032$ (2) Å, $b = 18.066$ (5) Å, $c = 12.682$ (4) Å, $\beta = 101.41$ (3)°, and $V = 2028$ (2) Å³. **2** is a neutral compound in which the metal atoms are formally in oxidation states of II, III, and III, but approximate D_{3h} symmetry in this molecule suggests that the three vanadium atoms are electronically equivalent. In **2** the V-V distances average 3.357 (11) Å and the crystallographically distinct V-($\mu_3\text{-O}$) distances are 1.90 (2) and 1.953 (8) Å.

Introduction

In this paper, the third of a series,^{1,2} we report the preparation and structural characterization of two more compounds having the type of structure shown in Figure 1. Such compounds belong to a class called trinuclear, oxo-centered, basic carboxylates. In part 1¹ of this series the knowledge of this field prior to our own contemporary additions thereto was briefly reviewed.

Our own recent studies have been concerned with compounds of chromium¹ (for which we reported the first examples of II,III,III compounds and compared them with the previously known III,III,III type) and vanadium.² We present here two more compounds containing the latter element. Our earlier paper dealing with vanadium reported a rather anomalous or "deviant" structure whereas in this paper we describe two "classical" compounds, namely, compounds having the oxo-centered structure depicted in Figure 1 in an essentially regular

form. These new compounds are the first ones of this type containing the element vanadium and they comprise both the III,III,III and the II,III,III sets of formal metal atom valences. As in earlier cases, a key question in connection with the mixed-valence species is whether it will show valence trapping or a symmetrical structure with equivalent metal atoms.

Experimental Section

All chemical operations were conducted under an atmosphere of dry argon with use of standard Schlenk techniques. Dichloromethane was dried over P_2O_5 , THF over sodium-potassium amalgam, and acetic acid with acetic anhydride. Each solvent was purged with argon, distilled immediately before use, and transferred by syringe.

Synthesis and Crystallization of $[\text{V}_3(\mu_3\text{-O})(\text{CH}_3\text{CO}_2)_6(\text{CH}_3\text{COOH})_2(\text{THF})]^+[\text{VCl}_4(\text{CH}_3\text{COOH})_2]^-$ (1**).** Vanadium(III) chloride as $\text{VCl}_3 \cdot 3\text{THF}$ ³ (1.12 g, 3 mmol) was placed at the bottom of an air-free 2 × 12 cm Schlenk tube. Acetic acid (15 mL) was carefully placed over the solid with a minimum of turbulence and the mixture set aside for 1 week. After this time a large crop (ca. 0.5 g) of light green crystals had formed; they were isolated by filtration

(1) Part 1: Cotton, F. A.; Wang, W. *Inorg. Chem.* 1982, 21, 2675.

(2) Part 2: Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* 1982, 21, 3127.

(3) Kurras, E. *Naturwissenschaften* 1959, 46, 171.

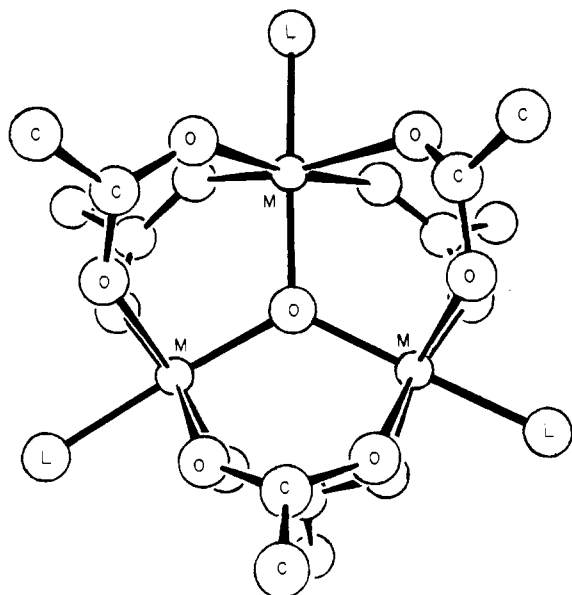


Figure 1. General trinuclear, oxo-centered, basic metal carboxylate structure, of formula $M_3O(RCO_2)_6L_3$.

and proved adequate for an X-ray crystallographic study.

Synthesis and Crystallization of $V_3(\mu_3-O)(CF_3CO_2)_6(THF)_3$ (2). Vanadium(II) chloride as $VCl_2 \cdot 2THF$ (2.66 g, 10 mmol) and sodium trifluoroacetate (2.72 g, 20 mmol) were loaded into an air-free, three-neck flask. Dichloromethane (60 mL) and THF (20 mL) were added, and the mixture was stirred overnight. The resulting red-green dichroic solution was filtered to remove the precipitated sodium chloride. When the volume of the filtrate was reduced to ca. 30 mL and the solution was cooled at $-10^\circ C$ overnight, orange and/or black crystals of, as yet, unidentified compounds were formed. The mother liquor was removed and set aside at room temperature under an argon atmosphere whereupon dark green crystals (ca. 0.3 g) formed over a period of 1 h. These crystals were found to be suitable for X-ray structural analysis.

X-ray Structure Determinations. Compound 1. A well-formed, regularly shaped crystal of dimensions $0.3 \times 0.3 \times 0.35$ mm was sealed in an air-free glass capillary with degassed epoxy cement. The crystal was transferred to an Enraf-Nonius CAD-4 automated diffractometer where a least-squares analysis of the setting angles of 25 reflections ($16^\circ \leq 2\theta \leq 26^\circ$), automatically located and centered, provided accurate unit cell parameters (Table I). A monoclinic cell, later shown by systematic absences and successful refinement to belong to the space group $C2/c$, was used. The intensity data were collected at room temperature with use of graphite-monochromated Mo $K\alpha$ radiation in the range $0^\circ \leq 2\theta \leq 45^\circ$. A total of 2940 unique reflections were measured, of which 1424 had intensity, I , exceeding $3\sigma(I)$ and were considered observed. The data were corrected for Lorentz and polarization effects. With $\mu = 11.47 \text{ cm}^{-1}$ no absorption correction was deemed necessary.

The atomic coordinates for the three unique vanadium atoms were obtained with use of the direct methods program MULTAN⁵ and refined in four cycles of least-squares refinement to give discrepancy indices

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.431$$

$$R_2 = (\sum |F_o| - |F_c|)^2 / \sum |F_o|^{1/2} = 0.507$$

The remaining non-hydrogen atoms of the cation and the two crystallographically distinct chlorine atoms of the anion were located from subsequent difference Fourier maps and were well-behaved during the refinement. Minor problems arose during the refinement of the coordinated acid ligands in both the cation and the anion. To deal first with the latter, we found O(10), C(11), and C(12) to be well-

Table I. Crystallographic Data and Data Collection Procedures

	$V_4Cl_4O_{22}C_{24}H_{42}$ (1)	$V_3F_{18}O_{16}C_{24}H_{24}$ (2)
mol wt	1028.17	1063.25
space group	$C2/c$	$P2_1/m$
a , Å	12.132 (3)	9.032 (2)
b , Å	15.458 (4)	18.066 (5)
c , Å	22.905 (4)	12.682 (4)
V , Å ³	4266 (3)	2028 (2)
β , deg	96.80 (2)	101.41 (3)
Z	4	2
ρ_c , g/cm ³	1.601	1.741
μ (Mo $K\alpha$), cm ⁻¹	11.473	7.951
cryst size, mm	$0.3 \times 0.3 \times 0.35$	$0.2 \times 0.2 \times 0.25$
diffractometer	Enraf-Nonius CAD-4	
radiation	graphite-monochromated Mo $K\alpha$ ($\lambda_\alpha = 0.71073 \text{ Å}$)	
collection range, deg	$+h, +k, \pm l$; $0 \leq 2\theta \leq 45$	$+h, +k, \pm l$; $0 \leq 2\theta \leq 45$
scan width	$0.95 + 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$
max counting time, s	90	75
X-ray exposure time, h	66	36
% cryst dec	14	0
no. of unique data	2940	2765
no. of data with $I \geq 3\sigma(I)$	1424	1547 ^c
ρ	0.05	0.05
no. of variables	238	289
R_1	0.069	0.060
R_2	0.085	0.072
esd	2.21	1.939
largest shift ^a	0.21	0.90
largest peak ^b	0.65	1.14

^a Largest Δ_i/σ_i ratio in final refinement cycle. ^b Largest peak in a final difference Fourier in $e/\text{Å}^3$. ^c $I \geq 2\sigma(I)$.

behaved. After inclusion of these atoms in the refinement, a difference Fourier synthesis showed quite clearly the OH group bound to C(11) with C(11)–O(11) at 1.31 Å, O(11)–H(11) at 0.93 Å, and C(11)–O(11)–H(11) at 118° . Attempted refinement of O(11) and H(11) either by themselves or as one unit resulted in a too short C(11)–O(11) distance and distortion of the geometry at C(11). One possible cause of this problem is a disordering of the acetic acid methyl and hydroxyl groups. In any event, O(11) and H(11) were then fixed at the positions obtained from the difference map; the thermal parameter of O(11) was treated isotropically, and B_{150} for H(11) was repeatedly set equal to that of O(11). There was also a difficulty in handling O(8) and C(8). Here, the refinement led to improbable C(7)–O(8) and C(7)–C(8) distances, such that an attempt was made to interchange the identities of C(8) and O(8). This did not significantly improve the distances but led to unreasonable thermal parameters. Hence, the original refinement, albeit with quite unreliable C–O and C–C distances, was retained. Refinement of the structure was then continued to convergence at $R_1 = 0.069$ and $R_2 = 0.085$.

Compound 2. Crystals of this substance were mounted in a manner similar to those of compound 1 and studied on an Enraf-Nonius CAD-4 diffractometer. Unit cell parameters were obtained as above and are listed in Table I. Systematic absences in $0k0$ for $k \neq 2n$ indicated the space group $P2_1/m$ (second setting). Intensity data were collected as before. From a total of 2765 unique data 1547 had $I > 2\sigma(I)$ and were considered observed. Standard Lorentz and polarization corrections were made, but with $\mu = 7.95 \text{ cm}^{-1}$ no absorption correction was deemed necessary.

The structure was solved by routine methods. A three-dimensional Patterson map yielded the positions of the two independent vanadium atoms, and least-squares refinement of these positions produced agreement factors of $R_1 = 0.479$ and $R_2 = 0.534$. A difference Fourier synthesis produced positions for the remaining non-hydrogen atoms, and convergence of refinement with an isotropic model led to values of $R_1 = 0.170$ and $R_2 = 0.221$. The inclusion of anisotropic thermal parameters for all atoms produced the final figures of merit given in Table I.

Final positional parameters for 1 and 2 are given in Tables II and III, respectively. Tables of thermal parameters and observed and calculated structure factors are available as supplementary material.

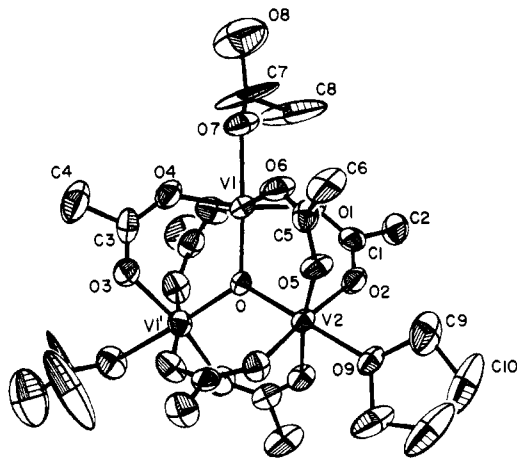
(4) Hall, V. M.; Schmulbach, D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.

(5) The crystallographic programs for the structural solutions 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 II. Positional Parameters and Their Estimated Standard Deviations for $[V_3(\mu_3-O)(CH_3CO_2)_6(CH_3COOH)_2(THF)]^+ [VCl_4(CH_3COOH)_2]^- (1)^a$

atom	x	y	z
V(1)	0.3784 (2)	0.2170 (1)	0.2090 (1)
V(2)	0.5000 (0)	0.4024 (2)	0.2500 (0)
V(3)	0.2500 (0)	0.2500 (0)	0.5000 (0)
Cl(1)	0.2188 (4)	0.2178 (3)	0.5967 (2)
Cl(2)	0.3128 (4)	0.3876 (3)	0.5288 (2)
O	0.5000 (0)	0.2783 (6)	0.2500 (0)
O(1)	0.6194 (6)	0.2839 (5)	0.3664 (4)
O(2)	0.5396 (6)	0.4089 (5)	0.3380 (4)
O(3)	0.5256 (6)	0.1319 (5)	0.3260 (4)
O(4)	0.3596 (7)	0.1367 (5)	0.2753 (4)
O(5)	0.6568 (5)	0.4134 (5)	0.2367 (4)
O(6)	0.2596 (6)	0.2933 (5)	0.2343 (4)
O(7)	0.7504 (7)	0.3559 (6)	0.6624 (4)
O(8)	0.6328 (12)	0.4443 (9)	0.5995 (6)
O(9)	0.5000 (0)	0.5339 (6)	0.2500 (0)
O(10)	0.4129 (8)	0.2037 (7)	0.5131 (6)
C(1)	0.5809 (9)	0.3590 (8)	0.3769 (6)
C(2)	0.5803 (12)	0.3848 (9)	0.4411 (6)
C(3)	0.4270 (11)	0.1112 (8)	0.3177 (6)
C(4)	0.3792 (13)	0.0521 (10)	0.3636 (7)
C(5)	0.2402 (10)	0.1330 (8)	0.7458 (6)
C(6)	0.3519 (9)	0.0959 (9)	0.7283 (8)
C(7)	0.7666 (15)	0.1050 (12)	0.3817 (7)
C(8)	0.7349 (16)	0.1592 (15)	0.4252 (9)
C(9)	0.4141 (12)	0.4127 (9)	0.7155 (8)
C(10)	0.4670 (17)	0.3223 (9)	0.7209 (9)
C(11)	0.4756 (13)	0.1680 (13)	0.5526 (16)
C(12)	0.5906 (15)	0.1463 (14)	0.5407 (14)
O(11) ^b	0.4160 (0)	-0.1035 (0)	0.0684 (0)
H(11) ^b	0.3594 (0)	-0.0820 (0)	0.0410 (0)

^a Estimated standard deviations in the least significant digits are shown in parentheses. ^b These atoms were refined isotropically with $B = 28.8 \text{ \AA}^2$.

**Figure 2.** $[V_3(\mu_3-O)(CH_3CO_2)_6(CH_3COOH)_2(THF)]^+$ cation, computer drawn with use of the ORTEP program. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

Results and Discussion

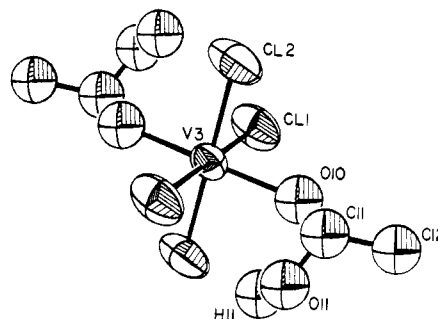
Compound 1. This compound crystallizes in the space group $C2/c$ with $Z = 4$. It consists of trinuclear cations that reside on crystallographic twofold symmetry axes and mononuclear anions that reside on crystallographic inversion centers. The cation and anion are shown in Figures 2 and 3, respectively, where the atom-labeling scheme is defined. The important interatomic distances and angles are listed in Table IV.

We have formulated the cation and anion as $[V_3O(CH_3CO_2)_6(CH_3CO_2H)_2(THF)]^+$ and $[VCl_4(CH_3CO_2H)_2]^-$, respectively. This means that all vanadium atoms are in oxidation state III. There are at least nine other possible formulations for this compound depending on whether the va-

Table III. Positional Parameters and Their Estimated Standard Deviations for $V_3(\mu_3-O)(CF_3CO_2)_6(THF)_3 (2)^a$

atom	x	y	z
V(1)	0.0659 (1)	0.15678 (7)	0.2970 (1)
V(2)	-0.1492 (2)	0.25000 (0)	0.0953 (1)
F(1)	0.5602 (7)	0.3046 (4)	0.4571 (7)
F(2)	0.5918 (10)	0.2500 (0)	0.3401 (10)
F(3)	0.1863 (9)	0.4756 (4)	0.0077 (5)
F(4)	0.0608 (9)	0.4124 (6)	0.8896 (5)
F(5)	0.2615 (7)	0.3762 (5)	0.9716 (5)
F(6)	-0.1038 (11)	0.2500 (0)	0.6249 (6)
F(7)	0.0967 (9)	0.3077 (4)	0.6573 (4)
F(8)	0.3443 (8)	0.5022 (5)	0.7572 (7)
F(9)	0.5071 (7)	0.4127 (4)	0.2277 (6)
F(10)	0.4333 (7)	0.5389 (4)	0.9021 (5)
O(1)	-0.0079 (7)	0.2500 (0)	0.2280 (5)
O(2)	0.2869 (5)	0.3105 (3)	0.3421 (4)
O(3)	-0.0366 (6)	0.1734 (4)	0.0263 (4)
O(4)	0.1190 (6)	0.1148 (4)	0.1587 (4)
O(5)	0.0349 (6)	0.1887 (3)	0.4469 (4)
O(6)	-0.1393 (6)	0.1042 (3)	0.2672 (4)
O(7)	-0.2829 (6)	0.1709 (4)	0.1371 (4)
O(8)	-0.3003 (9)	0.2500 (0)	-0.0505 (6)
O(9)	0.1430 (6)	0.0559 (3)	0.3689 (4)
C(1)	0.3467 (10)	0.2500 (0)	0.3587 (8)
C(2)	0.5070 (12)	0.2500 (0)	0.4131 (13)
C(3)	0.0672 (9)	0.1301 (5)	0.0650 (6)
C(4)	0.1438 (11)	0.0932 (6)	-0.0179 (8)
C(5)	0.0358 (11)	0.2500 (0)	0.4895 (8)
C(6)	0.0356 (15)	0.2500 (0)	0.6069 (9)
C(7)	-0.2568 (8)	0.1190 (5)	0.1994 (6)
C(8)	-0.3821 (11)	0.0636 (6)	0.1942 (7)
C(9)	-0.3606 (15)	0.3149 (9)	-0.1100 (8)
C(10)	-0.4677 (15)	0.2898 (8)	-0.2062 (8)
C(11)	0.1248 (19)	-0.0162 (6)	0.3169 (10)
C(12)	0.2492 (19)	-0.0637 (7)	0.3762 (10)
C(13)	0.2799 (19)	-0.0349 (7)	0.4772 (12)
C(14)	0.2447 (15)	0.0487 (7)	0.4743 (9)

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

**Figure 3.** $[VCl_4(CH_3COOH)_2]^-$ anion. The acetic acid atoms are shown as arbitrarily small spheres for clarity.

nadium atom is assumed to be in oxidation state III, IV, or V and whether the nonbridging $CH_3CO_2(H)$ ligands in the cation and/or the anion are $CH_3CO_2^-$ ions or CH_3CO_2H molecules. While conclusive evidence for the formulation we propose is not available, we are convinced it is the only one that is plausible when the method of preparation and various features of the structure are taken into account.

The method of preparation strongly favors the retention of oxidation state III for all or nearly all vanadium atoms and favors the presence of CH_3CO_2H molecules rather than $CH_3CO_2^-$ ions are ligands. V-Cl distances in the anion, which average $2.336 (11) \text{ \AA}$, are very close to those found in both $Cs_2[VCl_2(H_2O)_4]Cl_3$ and $[VCl_2(H_2O)_4]Cl \cdot 2H_2O$, which are $2.361 (2) \text{ \AA}$ in each case.⁶ Moreover, the composition $[V-$

(6) (a) Donovan, W. F.; Smith, P. W. *J. Chem. Soc., Dalton Trans.* **1975**, 894. (b) Donovan, W. F.; Podmore, L. P.; Smith, P. W. *Ibid.* **1976**, 1741.

Table IV. Bond Distances (Å) and Bond Angles (Deg) in $[V_3(\mu_3-O)(CH_3COO)_2(THF)(CH_3COO)_6]^{2-}$ $[VCl_4(CH_3COO)_2]^- (1)^a$

Distances			
V(1)-V(1)'	3.305 (3)	O(3)-C(3)	1.231 (3)
-V(2)	3.308 (2)	O(4)-C(3)	1.26 (1)
-O	1.906 (3)	O(5)-C(5)	1.24 (1)
-O(1)	2.016 (6)	O(6)-C(5)	1.23 (2)
-O(3)	1.987 (5)	O(7)-C(7)	1.18 (4)
-O(4)	1.996 (7)	O(8)-C(7)	1.46 (2)
-O(6)	2.00 (1)	O(9)-C(9)	1.48 (3)
-O(7)	2.10 (1)	O(10)-C(11)	1.24 (3)
V(2)-O	1.917 (7)	O(11)-C(11)	1.31 (2)
-O(2)	2.018 (7)	-H(11)	0.93 (0)
-O(5)	1.969 (9)	C(1)-C(2)	1.52 (1)
-O(9)	2.03 (1)	C(3)-C(4)	1.56 (2)
V(3)-Cl(1)	2.344 (7)	C(5)-C(6)	1.57 (3)
-Cl(2)	2.328 (6)	C(7)-C(8)	1.39 (7)
-O(10)	2.089 (8)	C(9)-C(10)	1.54 (3)
O(1)-C(1)	1.285 (6)	C(10)-C(10)'	1.47 (5)
O(2)-C(1)	1.240 (8)	C(11)-C(12)	1.49 (3)

Angles			
V(1)-V(1)-V(2)	60.03 (3)	O(10)-V(3)-O(10)'	180.0 (9)
O-V(1)-O(1)	94.5 (2)	V(1)-O-V(1)'	120.3 (3)
-O(3)	94.1 (2)	-V(2)	119.9 (2)
-O(4)	94.9 (2)	V(1)-O(1)-C(1)	131.8 (5)
-O(6)	96.0 (3)	V(2)-O(2)-C(1)	135.8 (5)
-O(7)	176.9 (4)	V(1)-O(3)-C(3)	135.7 (5)
O(1)-V(1)-O(3)	85.8 (2)	V(1)-O(4)-C(3)	131.3 (5)
-O(4)	170.3 (2)	V(2)-O(5)-C(5)	135 (1)
-O(6)	91.7 (3)	V(1)-O(6)-C(5)	133.3 (8)
-O(7)	85.7 (3)	V(1)-O(7)-C(7)	139 (1)
O(3)-V(1)-O(4)	91.2 (2)	V(2)-O(9)-C(9)	124 (1)
-O(6)	169.7 (3)	C(9)-O(9)-C(9)'	112 (2)
-O(7)	82.8 (3)	V(3)-O(10)-C(11)	138 (2)
O(4)-V(1)-O(6)	89.7 (3)	C(11)-O(11)-H(11)	118 (2)
-O(7)	84.7 (3)	O(1)-C(1)-O(2)	123.5 (7)
O(6)-V(1)-O(7)	87.1 (4)	-C(2)	117.4 (5)
V(1)-V(2)-V(1)'	59.94 (6)	O(2)-C(1)-C(2)	119.0 (4)
O-V(2)-O(2)	92.9 (2)	O(3)-C(3)-O(4)	124.7 (8)
-O(5)	95.0 (3)	-C(4)	118.8 (7)
-O(9)	179.97 (4)	O(4)-C(3)-C(4)	116.5 (5)
O(2)-V(2)-O(2)'	174.3 (4)	O(5)-C(5)-O(6)	124 (1)
-O(5)	91.7 (3)	-C(6)	117 (2)
-O(9)	87.1 (2)	O(6)-C(5)-C(6)	118 (1)
O(5)-V(2)-O(5)'	170.1 (6)	O(7)-C(7)-O(8)	125 (2)
-O(9)	85.0 (3)	-C(8)	106 (3)
Cl(1)-V(3)-Cl(1)'	180.0 (3)	O(8)-C(7)-C(8)	113 (4)
-Cl(2)	90.6 (2)	O(9)-C(9)-C(10)	102 (1)
-Cl(2)'	89.4 (2)	C(9)-C(10)-C(10)'	104 (2)
-O(10)	92.7 (4)	O(10)-C(11)-O(11)	103 (1)
-O(10)'	87.3 (4)	-C(12)	118 (3)
Cl(2)-V(3)-Cl(2)'	180.0 (5)	O(11)-C(11)-C(12)	116 (1)
-O(10)	90.0 (3)		
-O(10)'	90.0 (3)		

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

$Cl_4(CH_3CO_2H)_2]^-$ is far more probable for V^{III} than is $[VCl_4(CH_3CO_2)_2]^-$ for V^V , which has a profound tendency to give oxo ions, VO^{3+} , while $[VCl_4(CH_3CO_2)_2]^{3-}$ for V^{III} would require oxidation state IV or V in the trinuclear cation.

The structural characteristics of the cation are quite compatible with the assumption that it has three M^{III} ions and three neutral ligands in the external positions. It may naturally be compared with the $[Cr_3O(CH_3CO_2)_6(H_2O)_3]^+$ ion whose structure was reported some years ago.⁷ In that species, where the Cr^{III} ions should be ca. 0.02–0.04 Å smaller than the V^{III} ion, the $M\cdots M$, $M-(\mu_3-O)$, and $M-O(\text{acetate})$ distances are 3.274 [7], 1.89 [2], and 1.98 [2] Å, respectively, while in the V_3 cation under discussion, the corresponding values are 3.307 [2], 1.910 [6], and 2.00 [2] Å.

The V_3O portion of the cation is planar, the μ_3 oxygen atom

Table V. Bond Distances (Å) and Bond Angles (Deg) in $V_3(\mu_3-O)(CF_3COO)_6(THF)_3 (2)^a$

Distances			
V(1)-V(1)'	3.368 (2)	F(9)-C(8)	1.24 (1)
-V(2)	3.345 (1)	F(10)-C(8)	1.30 (1)
-O(1)	1.953 (8)	O(2)-C(1)	1.219 (9)
-O(2)	2.052 (5)	O(3)-C(3)	1.25 (2)
-O(4)	2.053 (9)	O(4)-C(3)	1.22 (2)
-O(5)	2.058 (6)	O(5)-C(5)	1.232 (9)
-O(6)	2.050 (9)	O(6)-C(7)	1.26 (1)
-O(9)	2.094 (7)	O(7)-C(7)	1.22 (1)
V(2)-O(1)	1.90 (2)	O(8)-C(9)	1.442 (8)
-O(3)	2.017 (8)	O(9)-C(11)	1.46 (1)
-O(7)	2.009 (6)	-C(14)	1.470 (8)
-O(8)	2.070 (9)	C(1)-C(2)	1.48 (2)
F(1)-C(2)	1.187 (8)	C(3)-C(4)	1.52 (2)
F(2)-C(2)	1.31 (2)	C(5)-C(6)	1.49 (2)
F(3)-C(4)	1.32 (1)	C(7)-C(8)	1.50 (2)
F(4)-C(4)	1.27 (1)	C(9)-C(10)	1.47 (1)
F(5)-C(4)	1.23 (1)	C(10)-C(10)'	1.44 (2)
F(6)-C(6)	1.32 (1)	C(11)-C(12)	1.49 (1)
F(7)-C(6)	1.289 (7)	C(12)-C(13)	1.36 (1)
F(8)-C(8)	1.28 (1)	C(13)-C(14)	1.54 (2)

Angles			
V(1)-V(1)-V(2)	59.77 (2)	C(11)-O(9)-C(14)	109.1 (7)
O(1)-V(1)-O(2)	96.0 (3)	O(2)-C(1)-O(2)'	128 (1)
-O(4)	93.0 (7)	O(2)-C(1)-C(2)	116.2 (6)
-O(5)	94.3 (6)	F(1)-C(2)-F(1)'	112 (1)
-O(6)	95.8 (4)	-F(2)	95.3 (9)
-O(9)	179.1 (4)	-C(1)	119.3 (8)
O(2)-V(1)-O(4)	88.0 (4)	F(2)-C(2)-C(1)	109 (1)
-O(5)	88.0 (3)	O(3)-C(3)-O(4)	130 (1)
-O(6)	168.3 (4)	-C(4)	114 (1)
-O(9)	84.7 (2)	O(4)-C(3)-C(4)	116 (1)
O(4)-V(1)-O(5)	172.0 (5)	F(3)-C(4)-F(4)	104.0 (8)
-O(6)	91.6 (4)	-F(5)	103.5 (9)
-O(9)	86.4 (5)	-C(3)	113.0 (9)
O(5)-V(1)-O(6)	91.0 (4)	F(4)-C(4)-F(5)	107.6 (9)
-O(9)	86.3 (3)	-C(3)	114 (1)
O(6)-V(1)-O(9)	83.6 (4)	F(5)-C(4)-C(3)	113.6 (9)
V(1)-V(2)-V(1)'	60.46 (4)	O(5)-C(5)-O(5)'	128 (1)
O(1)-V(2)-O(3)	94.4 (4)	-C(6)	115.9 (6)
-O(7)	95.7 (4)	F(6)-C(6)-F(7)	104.1 (7)
-O(8)	179.1 (5)	-C(5)	111.2 (8)
O(3)-V(2)-O(3)'	86.7 (5)	F(7)-C(6)-F(7)'	108.1 (9)
O(3)-V(2)-O(7)	90.4 (3)	-C(5)	114.2 (7)
-O(7)'	169.7 (4)	O(6)-C(7)-O(7)	130 (1)
O(3)-V(2)-O(8)	85.0 (3)	-C(8)	115 (1)
O(7)-V(2)-O(7)'	90.7 (4)	O(7)-C(7)-C(8)	115.9 (8)
-O(8)	84.9 (3)	F(8)-C(8)-F(9)	107.0 (9)
V(1)-O(1)-V(1)'	119.1 (8)	-F(10)	100 (1)
-V(2)	120.4 (4)	-C(7)	115.4 (8)
V(1)-O(2)-C(1)	132.8 (8)	F(9)-C(8)-F(10)	106.3 (8)
V(2)-O(3)-C(3)	131.7 (9)	-C(7)	114 (1)
V(1)-O(4)-C(3)	130 (1)	F(10)-C(8)-C(7)	113 (1)
V(1)-O(5)-C(5)	131.8 (8)	O(8)-C(9)-C(10)	107.5 (6)
V(1)-O(6)-C(7)	129.7 (9)	C(9)-C(10)-C(10)'	108.0 (4)
V(2)-O(7)-C(7)	132.0 (8)	O(9)-C(11)-C(12)	106.3 (9)
V(2)-O(8)-C(9)	125.6 (4)	C(11)-C(12)-C(13)	104.3 (7)
C(9)-O(8)-C(9)'	108.9 (8)	C(12)-C(13)-C(14)	110.5 (6)
V(1)-O(9)-C(11)	125.7 (5)	O(9)-C(14)-C(13)	101.4 (7)
-C(14)	124.6 (6)		

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

deviating by only 0.002 Å from the plane defined by the three vanadium atoms. Apart from the fact that the outer ligands are not all the same, two being CH_3CO_2H and one a THF molecule, the trinuclear cation has essentially threefold symmetry. Thus, the difference between the two crystallographically distinct $V\cdots V$ separations is 0.003 Å with an esd of 0.004 Å. The two crystallographically nonequivalent $V-(\mu_3-O)$ distances differ by 0.011 (7) Å, which is statistically negligible but in a direction compatible with the fact that the longer $V-(\mu_3-O)$ distance is trans to the shorter external $V-O$ distance, to THF.

Table VI. Structurally Characterized Trinuclear Oxo-Centered Basic Carboxylate Structures

compd	formal valences of metal atoms	M...M, Å	M-(μ_3 -O), Å	comments	ref
$[V_3O(CF_3CO_2)_6(THF)_3]$	II,III,III	3.357 [11]	1.90-1.95	no valence trapping	<i>b</i>
$[V_3O(CH_3CO_2)_6(CH_3CO_2H)_2(THF)] [VCl_4(CH_3CO_2H)_2]$	III,III,III	3.307 [2]	1.910 (6)		<i>b</i>
$[V_3O_3(C_6H_5CO_2)_6(THF)]$	IV,IV,IV	3.520 [2]	1.626 (6)	anomalous structure	2
		3.572 [2]	2.344 (7)		
		4.050 [2]	2.452 (6)		
$[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 6H_2O$	III,III,III	3.274 [7] ^a	1.89 [2]		7
$Cr_3O(CHF_2CO_2)_6(C_5H_5N)_3$	II,III,III	3.356 (1)	1.938 (1)	<i>c</i>	1
$Cr_3O(CHF_2CO_2)_6(4-CNC_5H_4N)_3$	II,III,III	3.336 (1)	1.926 (1)	<i>c</i>	1
$Mn_3O(CH_3CO_2)_6(C_5H_5N)_3$	II,III,III	3.363 (1)	1.941 (1)	<i>c</i>	9
$Mn_3O(CH_3CO_2)_6(3-ClC_5H_4N)_3$	II,III,III	<i>d</i>	1.863 (4)	valence trapping	10
			1.864 (4)		
			2.034 (4)		
$[Ru_3O(CH_3CO_2)_6(PPh_3)_3]$	II,III,III	3.329 (3)	1.92 [2]		11
$[Fe_3O(CMe_3CO_2)_6(MeOH)_3]Cl$	III,III,III	3.27 ^e	1.905 [3]	<i>c</i>	12

^a Not given in reference. See ref 1 for the three independent values. ^b This work. ^c Threefold crystallographic symmetry. ^d Not reported. ^e No esd reported.

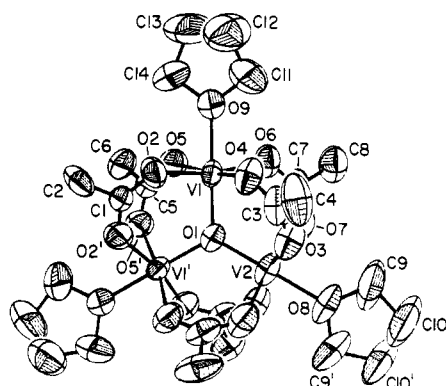


Figure 4. $V_3(\mu_3-O)(CF_3CO_2)_6(THF)_3$ molecule, computer drawn with use of the ORTEP program. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density. Fluorine atoms are omitted for clarity.

Compound 2. In this case we are dealing with neutral molecules, $V_3O(CF_3CO_2)_6(THF)_3$, and there is no ambiguity about the oxidation state of the vanadium. Formally, this is a II,III,III species. Each molecule resides on a crystallographic mirror plane that passes through O(8), V(2), O(1), C(1), C(2), C(5), and C(6). The structure is depicted in Figure 4, and the important interatomic distances and angles are listed in Table V.

The molecule has approximately D_{3h} symmetry provided we ignore the CF_3 rotational orientations and the conformations of the THF rings. There are, however, small deviations from D_{3h} symmetry which are real in a statistical sense. Thus the independent V...V distances differ by 0.023 (2) Å and the V-(μ_3 -O) distances differ by 0.053 (13) Å. The V-O(CF_3 -CO₂) distances at V(1) average 2.052 [5] Å while those at V(2) average 2.013 [7] Å. The V-O(THF) distances also differ, but by an amount that may not be real in a statistical sense, viz., 0.024 (12) Å.

Whether these small differences have any chemical significance in relation to the electronic structure of the molecule or whether they are merely distortions created by packing forces is an important question but not an easy one to answer with certainty. It could first be asked why a species with an inherent preference for threefold symmetry would not have adopted a mode of crystallization that permits it to retain such symmetry. Several of the previously studied oxo-centered trinuclear molecules have crystallized in trigonal or hexagonal space groups, but others have not and in general high-symmetry molecules are found often enough in low-symmetry crystal environments that such an occurrence would not be surprising in this case.

If the molecule does not have an inherent tendency to deviate from threefold symmetry, there is only one evident cause, namely, a tendency toward trapping of the II, III, and III valence states. However, the pattern of the distortions does not conform to that expected for such a phenomenon. The unique vanadium atom, in oxidation state II, should have a greater radius than the other two, which would be in oxidation state III. It would also be expected that a V^{II} species with three t_{2g} electrons and a lower charge than V^{III} would have a smaller tendency than V^{III} to participate in π bonding to the μ_3 -O atom. The inequalities itemized earlier are all in the opposite sense, showing V(2), the structurally unique vanadium atom, to behave as if smaller than the other two, V(1) and V(1)'. However, the size of the V_3O core of this molecule is significantly larger than that in compound 1 (e.g., by 0.050 Å in the mean V...V distance) just as the Cr_3O cores in the II,III,III compounds were larger (e.g., by 0.060-0.080 Å) than that in the III,III,III Cr_3O case.

General Comments. For reasons presented in detail above, we are confident that the compounds reported here contain oxo-centered trivanadium carboxylates with III,III,III and II,III,III formal valences in 1 and 2, respectively, and that there is no evidence for valence trapping in the latter. The small distortions from threefold symmetry are most likely attributable to unsymmetrical packing forces, although a Jahn-Teller effect in the necessarily degenerate electronic ground state of the odd-electron system cannot be entirely ruled out. However, in view of the well-known failure of incomplete t_{2g} configurations to produce significant structural effects in octahedral complexes generally, we would not favor this idea.

Since the last time accurate structural data were tabulated⁸ for the oxo-centered trinuclear basic carboxylate species, the number of examples has about doubled and it thus appears worthwhile to present a new table of structural results. Accordingly, Table VI lists the available results. On the basis of all of these data several observations seem warranted. First, this class of compounds is potentially a large one and of general importance for the transition elements. Second, the element vanadium now appears to be particularly prone to form such species, even though their existence for this element has not heretofore been documented. Third, the question of what

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factors are important in determining the character (i.e., valence trapped or delocalized) of mixed-valence species is still unresolved.

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Supplementary Material Available: Tables of observed and calculated structure factors and thermal vibration parameters for both compounds (20 pages). Ordering information is given on any current masthead page.

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Synthesis, Interconversions, and Structural Characterization of the $[(\text{S}_4)_2\text{MoS}]^{2-}$, $[(\text{S}_4)_2\text{MoO}]^{2-}$, $(\text{Mo}_2\text{S}_{10})^{2-}$, and $(\text{Mo}_2\text{S}_{12})^{2-}$ Anions

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The MoS_4^{2-} anion reacts with elemental sulfur and "active" sulfur reagents such as organic trisulfides or ammonium sulfides to afford binary molybdenum sulfides. The successful isolation of these sulfides, which appear to be components of a complex equilibrium system, depends on the solvent system and the nature of the counterions present in solution. With $(\text{C}_2\text{H}_5)_4\text{N}^+$ as the counterion the $[(\text{S}_4)_2\text{MoS}]^{2-}$ anion, I, can be isolated from either CH_3CN or DMF solutions. The hydrolysis of I in DMF or CH_3CN affords the $[(\text{S}_4)_2\text{MoO}]^{2-}$ anion, II. In the presence of the $(\text{C}_6\text{H}_5)_4\text{P}^+$ cation the $(\text{Mo}_2\text{S}_{10})^{2-}$ (III) and $(\text{Mo}_2\text{S}_{12})^{2-}$ (IV) anions can be isolated from DMF solutions as mixed-anion $(\text{C}_6\text{H}_5)_4\text{P}^+$ salts. Both I and II crystallize in the orthorhombic space group *Ibca* with eight molecules in the unit cell. The cell dimensions are $a = 15.594$ (3) Å, $b = 13.264$ (4) Å, and $c = 27.577$ (5) Å for I and $a = 15.470$ (1) Å, $b = 13.224$ (2) Å, and $c = 27.425$ (3) Å for II. In the structure of III/IV, both anions occupy the same position in the crystal lattice, with III being the major component (72%). III/IV crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules per unit cell. The cell dimensions are $a = 22.288$ (4) Å, $b = 11.724$ (4) Å, $c = 10.512$ (2) Å, $\alpha = 78.06$ (4)°, $\beta = 86.00$ (3)°, and $\gamma = 76.10$ (3)°. Intensity data for all three structures were collected with a four-circle computer-controlled diffractometer by the θ - 2θ scan technique. For I and II, all non-hydrogen atoms were refined with anisotropic thermal parameters. For III/IV, the S_2^{2-} ligand of $\text{Mo}_2\text{S}_{10}^{2-}$ and the S_4^{2-} ligand of $\text{Mo}_2\text{S}_{12}^{2-}$, as well as the DMF molecule of crystallization, were refined with isotropic thermal parameters. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Refinement by a full-matrix least-squares procedure, of 145 parameters on 2146 data for I, 145 parameters on 1175 data for II, and 585 parameters on 7022 data for III/IV, gave final *R* values of 0.025, 0.047, and 0.065, respectively. In I and II, the Mo(IV) ion is coordinated by two bidentate S_4^{2-} chelates and a terminal sulfur or oxygen atom in a distorted-square-pyramidal arrangement. The molybdenum is situated above the basal sulfur plane by 0.72 Å for I and 0.76 Å for II. The $\text{Mo}_2\text{S}_{10}^{2-}$ and $\text{Mo}_2\text{S}_{12}^{2-}$ anions have in common the $(\text{Mo}_2\text{S}_4)^{2+}$ core as well as the tetrasulfide ligand attached to Mo(1). Mo(2) is coordinated by either a persulfido group in III or a tetrasulfido unit in compound IV. The core contains two $(\text{Mo}^{\text{V}}=\text{S})^{3+}$ units bridged asymmetrically by two sulfide ligands in the syn configuration, with a Mo-Mo distance of 2.846 (1) Å. In all three structures, an alternation of the S-S bond lengths in the S_4^{2-} chelate rings is observed, and the Mo-S₄ ring is in the "puckered" or envelope configuration. The coordinated sulfur atoms of the S_4^{2-} ligand are asymmetrically bound to the molybdenum. The MoS_4 ring conformation and the consequent effects on Mo-S bonding are attributed to intraligand sulfur lone-pair repulsions.

Introduction

Interest in molybdenum-sulfur coordination chemistry derives primarily from recent advances in the chemistry of molybdoenzymes¹ and from the apparent importance of molybdenum-sulfur coordination in hydrodesulfurization reactions.² The coordination of molybdenum by sulfur atoms in the molybdenum-containing enzymes has been demonstrated by molybdenum K-edge X-ray absorption fine structure (EXAFS) analyses. In nitrogenase, the EXAFS analyses³ are consistent with a molybdenum surrounded by four sulfur atoms at ~ 2.35 Å and two or three iron atoms at ~ 2.7 Å. In sulfite oxidase⁴ and xanthine oxidase,⁵ analyses of the EXAFS data

also indicate the presence of three or four sulfur atoms around the molybdenum atoms. On the basis of Mo-S bond length considerations the sulfur ligands have been characterized tentatively as either terminal sulfido groups or protein-bound cysteinyl or methioninyl sulfur atoms.

The hydrodesulfurization reaction involved in the catalytic hydrogenolysis of organosulfur compounds is an important process in the purification of petroleum products. The heterogeneous catalysts often used in this process contain "sulfided" molybdenum and cobalt salts supported on alumina. It has been proposed⁶⁻⁸ that a molybdenum sulfide surface is the catalytic site for this hydrogenolysis reaction.

The basic coordination chemistry of molybdenum with sulfur ligands also has received considerable attention in recent years.¹ The intricacies of the Mo-S coordination chemistry are aptly illustrated in the chemical and crystallographic studies of the binary molybdenum thioanions. In various such Mo-S anions the sulfide (S^{2-}), persulfide (S_2^{2-}), and tetrasulfide (S_4^{2-}) ligands appear as ligands in complex anions such as $[\text{Mo}_2$ -

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