Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843, The Molecular Structure Corporation, College Station, Texas 77840,
and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Four Compounds Containing Oxo-Centered Trivanadium Cores Surrounded by Six μ,η^2-Carboxylato Groups

F. Albert Cotton,*[1a] Michael W. Extine,[1b] Larry R. Falvello,[1a] Diane Beck Lewis,[1a] Gregg E. Lewis,[1a]
Carlos A. Murillo,[1a,c] Willi Schwotzer,[1a] Milagros Tomas,[1a] and Jan M. Troup[1b]

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Four compounds containing the $[V_3O(RCO_2)_6L_3]^{0,+}$ type unit have been prepared and structurally characterized; in two of them the formal distribution of valences is II,III,III and in the other two it is III,III,III. The reaction of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ with CF_3CO_2Na in THF/CH_2Cl_2 produces several products, of which the major one is a black compound, **7**, consisting of $[V_3O(CF_3CO_2)_6(THF)_3]$ molecules and a mixture of solvent molecules of crystallization approximating to $^2/_3$THF + $^1/_3CH_2Cl_2$. Compound **7** crystallizes in space group $P2_1/n$ with $Z = 4$ in a unit cell of the following dimensions: $a = 8.904$ (2) Å; $b = 18.92$ (1) Å; $c = 25.84$ (1) Å; $\beta = 98.78$ (3)°; $V = 4301$ (5) Å^3. The oxo-centered trivanadium molecule is formally a II,III,III species but shows no evidence for valence trapping. The mean dimensions are V···V(av) = 3.364 [10] Å, V–(μ_3-O)(av) = 1.942 [25] Å, V–O(trifluoroacetate)(av) = 2.038 [4] Å, and V–O(THF)(av) = 2.090 [12] Å. The other II,III,III compound, $[V_3O(CH_3CO_2)_6(C_5H_5N)_3]$ (**5**), was prepared by reacting $VCl_2(py)_4$ with LiO_2CCH_3 in THF and cooling to 0 °C. It forms crystals in space group $R32$, and the molecule resides on a position of 32 (D_3) symmetry. The principal mean dimensions are V···V(av) = 3.337 (5) Å, V–(μ_3-O)(av) = 1.927 (3) Å, V–O(acetate) = 2.047 [9] Å, and V–N = 2.210 (14) Å. Again, the II,III,III species shows no evidence for valence trapping. A new III,III,III compound, $[V_3O(O_2CCH_3)_6(THF)_3]_2[V_2O_2Cl_6]\cdot 5CH_2Cl_2$ (**4**), was obtained from the reaction of NaO_2CCH_3 with $VCl_3(THF)_3$ in CH_2Cl_2. The dark green crystals belong to space group $C2/m$ with unit cell dimensions $a = 21.020$ (14) Å, $b = 17.123$ (9) Å, $c = 14.041$ (9) Å, $\beta = 110.71$ (8)°, $V = 4727$ (6) Å^3, and $Z = 2$. The mean values of important distances are V···V = 3.316 [4] Å, V–(μ_3-O) = 1.914 [2] Å, V–O(acetate) = 2.002 [5] Å, and V–O(THF) = 2.063 [9] Å. A new compound, **2**, containing the chloroacetato cation has been prepared and the structure compared with that of the previously reported perchlorate. Compound **2**, $[V_3O(O_2CCClH_2)_6(H_2O)_3](CF_3SO_3)$, crystallizes in space group $P\bar{1}$, with the unit cell dimensions $a = 12.91$ (9) Å, $b = 15.89$ (6) Å, $c = 11.25$ (9) Å, $\alpha = 93.41$ (3)°, $\beta = 115.2$ (4)°, $\gamma = 85.32$ (6)°, $V = 2080$ (10) Å^3, and $Z = 2$. The cation has the following average mean dimensions: V···V = 3.329 [7] Å; V–(μ_3-O) = 1.92 [1] Å; V-O(chloroacetate) = 2.01 [2] Å; V–O(H_2O) = 2.04 [2] Å. A comparison of four III,III,III structures with three II,III,III structures shows that the core dimensions for the former are somewhat smaller, as expected, but only by amounts that are at the threshold of statistical significance. For example, the average V···V distances are 3.322 [6] and 3.353 [8] Å, which differ by 0.031 [10] Å. For any one compound, it would be uncertain from dimensional data for the V_3O unit alone which group it should be assigned to. The structural data for the II,III,III compounds support the view that valence delocalization occurs.

Introduction

Several years ago, we reported[2,3] the preparation and structures of three compounds containing the oxo-centered trivanadium core, V_3O, embraced by six bridging (i.e., μ,η^2) carboxyl anions, along with a set of three ligands, L, occupying the so-called external coordination sites. The general structure of this type of species is shown in Figure 1, and a list of all such vanadium compounds, with the numbers used throughout this paper, is given in Table I. Of the three reported compounds, one had a structure[2] that deviated substantially (and for an identifiable reason) from this highly symmetrical model; we shall not discuss that one further. The other two compounds, $[V_3O(CH_3CO_2)_6(CH_3CO_2H)_2(THF)][VCl_4(CH_3CO_2H)_2]$ (**3**) and $[V_3O(CF_3CO_2)_6(THF)_3]$ (**6**), with structures of the "classical" type,[3] were preceded by only one other structurally characterized example,[4] viz. $[V_3O(CH_2ClCO_2)_6(H_2O_3)]ClO_4\cdot H_2O$ (**1**).

The preparation and study of such compounds of vanadium had not originally been the intended goal of our work, which was undertaken with the hope of obtaining carboxylato-bridged divanadium compounds. However, we have carried the study of the oxo-centered species further for two reasons. First, we continued to hope that proper preparative conditions could be found for obtaining the desired binuclear products. We now believe that this may never be possible, owing to an apparent tendency of vanadium(II) in the presence of excess carboxylic acid to abstract oxygen from the carboxyl group and from the V_3O core. Second, we had a moderate interest in the question of variable valence

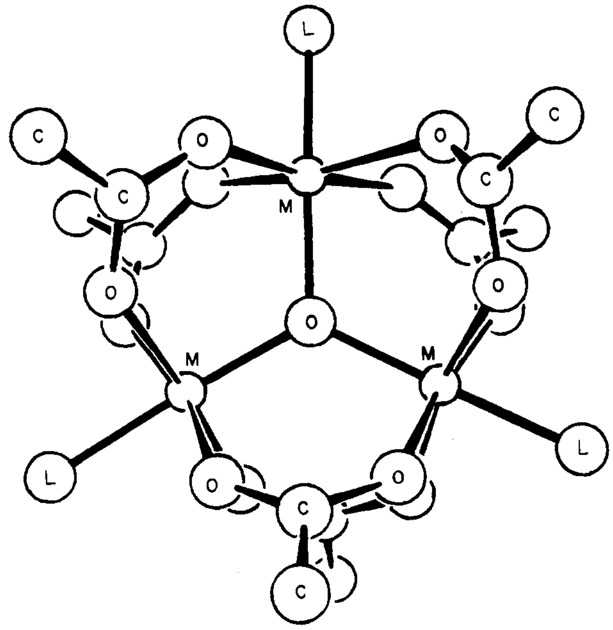

Figure 1. Representation of the general type of structure dealt with in this paper.

of the element vanadium in the $V_3O(RCO_2)_6L_3$ type structure, found for establishing the set of formal valences within a given compound purely from its structure.

and wished to see how many of the formal combinations, viz. II,II,II, II,II,III, II,III,III, and III,III,III, could be obtained and established structurally. Previously only one II,III,III compound and two III,III,III compounds had been described.[3] With respect to the overall study of the variability of metal valence in these compounds, there is the question of whether any criteria can be

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[1] (a) Texas A&M University. (b) The Molecular Structure Corp. (c) University of Costa Rica.

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Table I. Bond Distances (Å) for Compounds of the Type $[V_3O(O_2CR)_6L_3]X$

compd								
no.	R	L_3	X	formal valences	V–V	$V–O_2CR$	$V–\mu_3–O$	$V–O_{eq}$
1	CH_2Cl	$3H_2O$	ClO_4	III,III,III	3.337 [7]	2.01 [1]	1.93 [1]	2.07 [1]
2	CH_2Cl	$3H_2O$	CF_3SO_3	III,III,III	3.329 [7]	2.01 [2]	1.92 [1]	2.04 [2]
3	CH_3	THF, 2HOAc	$VCl_4(HOAc)_2$	III,III,III	3.307 [1]	1.998 [8]	1.910 [4]	2.03 [1]
4	CH_3	3THF	$[V_2O_2Cl_6]^{2-}$	III,III,III	3.316 [4]	2.002 [5]	1.914 [2]	2.063 [9]
5	CH_3	3py		II,III,III	3.337 (5)	2.047 [9]	1.927 (3)	(2.210 (14))
6	CF_3	3THF		II,III,III	3.357 [11]	2.040 [9]	1.94 [2]	2.086 [8]
7	CF_3	3THF		II,III,III	3.364 [10]	2.038 [4]	1.94 [3]	2.09 [1]

Table II. Crystal Data for $[V_3O(O_2CCH_2Cl)_6][CF_3SO_3]\cdot 10.5H_2O$ (**2**), $[V_3O(CH_3COO)_6(THF)_3]_2(V_2O_2Cl_6)\cdot 5CH_2Cl_2$ (**4**), $V_3O(CH_3CO_2)_6(C_5H_5N)_3$ (**5**), and $[V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3]\cdot {}^2/_3THF\cdot {}^1/_3CH_2Cl_2$ (**7**)

	2	**4**	**5**	**7**
formula	$V_3Cl_6SF_3O_{30}C_{13}H_{40}$	$V_8Cl_{16}C_{53}H_{94}O_{34}$	$V_3O_{12}N_3O_{27}H_{33}$	$V_3Cl_{0.67}F_{18}O_{16.67}C_{27}H_{30}$
fw	1131.05	2250.1	744.4	1139.80
space group	$P\bar{1}$	$C2/m$	$R32$	$P2_1/n$
sys absences	none	hkl, $h + k = 2n + 1$	hkl, $-h + k + l \neq 3n$	$0k0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$
a, Å	12.91 (9)	21.020 (14)	17.582 (8)	8.904 (2)
b, Å	15.89 (6)	17.123 (9)	17.582 (8)	18.92 (1)
c, Å	11.25 (9)	14.041 (9)	10.590 (5)	25.84 (1)
α, deg	93.41 (3)	90	90.0	90.0
β, deg	115.2 (4)	110.71 (8)	90.0	98.78 (3)
γ, deg	85.32 (6)	90	120.0	90.0
V, Å^3	2080 (10)	4727 (6)	2835 (4)	4301 (5)
Z	2	2	3	4
d_{calcd}, g/cm^3	1.806	1.58	1.308	1.760
cryst size, mm	0.5 × 0.5 × 0.3	0.82 × 0.39 × 0.28	0.04 × 0.2 × 0.2	0.35 × 0.30 × 0.30
μ(Mo Kα), cm^{-1}	11.788	13.2	7.55	8.727
data colln instrum	$P\bar{1}$	Nicolet P3/F	CAD-4	CAD-4
radiation (monochromated in incident beam)	Mo Kα^d	Mo Kα^d	Mo Kα^d	Mo Kα^d
orientation reflcns: no.; range (2θ), deg	15; $18 < 2\theta < 25$	23; $17 < 2\theta < 30$	25; 10–25	25; 20–40
temp, °C	ambient	22 ± 2	−110	−112 ± 1
scan method	$\theta/2\theta$	ω scans	ω–2θ	ω–2θ
data colln range (2θ), deg	$4 < 2\theta < 45$	4–50	6–46; $+h,+k,+l$	$0 < 2\theta < 45$; $+h+k\pm l$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5557	3560, 2255	338	3489
no. of params refined	514	256	72	541
trans factors: max, min	0.9989, 0.9757	obsd 1.00, 0.57	...	
R^a	0.0581	0.0855	0.072	0.082
$R_w{}^b$	0.0606	0.1204	0.079	0.102
quality-of-fit indicator^c	2.759	1.09	1.81	2.70
largest shift/esd, final cycle	0.15	0.20	0.04	0.46
largest peak, e/Å^3	1.121	0.91	0.34	0.99

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. For **2**, $w = 1/[\sigma^2|F_o| + 0.001|F_o|^2]$; for **4**, $w = 1/[\sigma^2|F_o| + 0.01|F_o|^2]$. For **5** and **7**, $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$. $^d \lambda_\alpha = 0.71073$ Å.

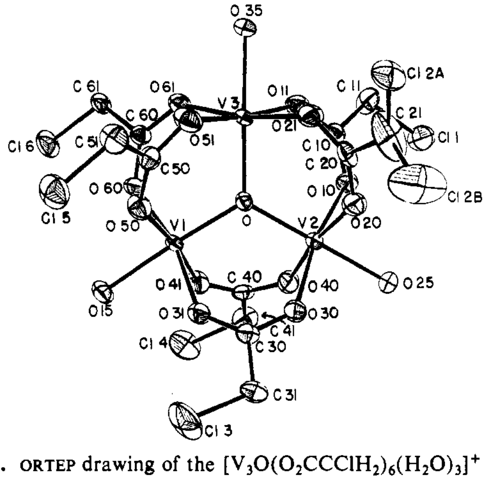

Figure 2. ORTEP drawing of the $[V_3O(O_2CCClH_2)_6(H_2O)_3]^+$ ion in **2**. Each atom is represented by its ellipsoid of thermal displacement drawn at the 40% probability level.

We have now prepared three more new oxo-centered trivanadium compounds, **4**, **5**, and **7**, and determined their structures. In addition, because of a need to make quantitative structural comparisons with the $[V_3O(CH_2ClCO_2)_6(H_2O)_3]^+$ ion, we have prepared another compound, **2**, that contains this cation (along with the $CF_3SO_3^-$ ion instead of the ClO_4^- ion) and determined its structure. We report on all four compounds here.

Experimental Section

I. Preparative Procedures. (a) General Procedures. All operations were performed under an argon atmosphere by using standard Schlenk type techniques.

(b) $[V_3O(O_2CCClH_2)_6(H_2O)_3](CF_3SO_3)$ (2). To an aqueous solution of $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$[5] (0.50 g, 1.45 mmol) was added NaO_2CCH_2Cl (0.34 g, 2.90 mmol) as an aqueous solution. The resulting red/green solution was slowly evaporated in vacuum to afford a large quantity of well-formed crystals.

(c) $[V_3O(CH_3CO_2)_6(THF)_3][V_2O_2Cl_6]\cdot 5CH_2Cl_2$ (4). Sodium acetate (0.74 mg 9.0 mmol) was added to a solution of $VCl_3(THF)_3$ (1.12 g, 3.0 mmol) in 30 mL of CH_2Cl_2. This mixture was stirred overnight and then filtered through Celite. The volume was reduced in vacuum to about 15 mL, hexane (7 mL) was added, and the mixture was maintained for 24 h in an ice chest (−10 °C). Dark green crystals (0.48 g; 58% yield), some of which were directly suitable for crystallography, were obtained.

(d) $V_3O(CH_3CO_2)_6(C_5H_5N)_3$ (5). The starting material, dichlorotetrakis(pyridine)vanadium(II) was prepared according to a published procedure.[6] To a mixture of $VCl_2(C_5H_5N)_4$ (0.53 g, 1.1 mmol) and lithium acetate (0.19 g, 2.3 mmol) was added THF (15 mL). The reaction mixture was stirred at room temperature for 24 h and then filtered. The dark purple-red solution was cooled to 0 °C. After several days, red-purple, air-sensitive crystals separated from the solution. Yield: 0.50 g, 54%. A crystal suitable for X-ray work was selected from this homogeneous product.

(e) $V_3O(CF_3CO_2)_6(THF)_3\cdot {}^2/_3THF\cdot {}^1/_3CH_2Cl_2$ (7). The compound

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(6) Cotton, F. A.; Murillo, C. A. *Ing. Cienc. Quim.* **1985**, *9*, 5.

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound **2**[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.88494 (7)	0.24279 (5)	0.37339 (7)	1.55 (2)	O(11)	1.0155 (3)	0.1188 (2)	0.0868 (4)	2.7 (1)
V(2)	1.14309 (7)	0.22840 (5)	0.37449 (8)	1.64 (2)	O(11L)	0.180 (2)	0.6018 (9)	0.182 (2)	9.6 (7)
V(3)	0.91045 (7)	0.21791 (5)	0.09003 (7)	1.67 (2)	O(15)	0.7913 (3)	0.2559 (3)	0.4830 (4)	2.7 (1)
Cl(1)	1.3137 (1)	−0.0004 (1)	0.1997 (2)	4.22 (5)	O(20)	1.1618 (3)	0.3139 (3)	0.2613 (4)	2.9 (1)
Cl(2A)	1.0856 (4)	0.4325 (3)	−0.0469 (4)	3.8 (1)	O(21)	1.0143 (3)	0.2973 (3)	0.0677 (4)	3.0 (1)
Cl(2B)	0.2075 (5)	0.4770 (3)	0.1658 (4)	9.5 (2)	O(25)	1.3166 (3)	0.2279 (2)	0.4738 (4)	2.4 (1)
Cl(3)	1.0088 (2)	0.4811 (1)	0.6797 (2)	5.89 (7)	O(30)	1.1443 (3)	0.3255 (2)	0.4994 (4)	2.5 (1)
Cl(4)	1.0307 (2)	0.0340 (1)	0.7115 (2)	4.55 (6)	O(31)	0.9735 (3)	0.3343 (2)	0.5007 (4)	2.6 (1)
Cl(5)	0.6085 (2)	0.4753 (1)	0.1779 (2)	3.96 (5)	O(35)	0.8407 (3)	0.2055 (3)	−0.1084 (3)	2.8 (1)
Cl(6)	0.5737 (1)	0.0585 (1)	0.1904 (2)	3.54 (4)	O(40)	1.1510 (3)	0.1439 (2)	0.5047 (4)	2.5 (1)
S	0.7152 (1)	0.78634 (9)	0.0769 (1)	2.97 (4)	O(41)	0.9774 (3)	0.1528 (2)	0.5013 (4)	2.5 (1)
F(1)	0.5111 (4)	0.7318 (3)	−0.0531 (7)	8.0 (2)	O(50)	0.7807 (3)	0.3343 (2)	0.2576 (4)	2.6 (1)
F(2)	0.5937 (5)	0.6952 (3)	0.1468 (6)	7.8 (2)	O(51)	0.7987 (4)	0.3173 (3)	0.0694 (4)	3.0 (1)
F(3)	0.6444 (5)	0.6347 (3)	0.0070 (6)	6.7 (2)	O(60)	0.7741 (3)	0.1569 (2)	0.2663 (3)	2.4 (1)
O	0.9796 (3)	0.2296 (2)	0.2806 (3)	1.58 (8)	O(61)	0.7908 (3)	0.1407 (3)	0.0767 (4)	2.7 (1)
O(1L)	0.5683 (3)	0.8581 (3)	0.3012 (4)	3.3 (1)	C	0.6117 (6)	0.7084 (4)	0.0415 (8)	4.2 (2)
O(1)	0.8149 (4)	0.7509 (4)	0.1808 (5)	5.0 (2)	C(10)	1.1169 (4)	0.0984 (3)	0.1585 (5)	1.9 (1)
O(2)	0.6639 (4)	0.8598 (3)	0.1148 (5)	4.0 (1)	C(11)	1.1678 (5)	0.0262 (4)	0.1019 (6)	3.4 (2)
O(2L)	0.3788 (4)	0.7745 (3)	0.2759 (4)	3.9 (1)	C(20)	1.1030 (5)	0.3307 (3)	0.1440 (5)	2.2 (1)
O(3)	0.7246 (4)	0.7915 (3)	−0.0446 (4)	4.4 (1)	C(21)	1.1431 (8)	0.3980 (5)	0.087 (1)	5.8 (3)
O(3L)	0.3642 (4)	0.8412 (3)	0.5060 (5)	4.0 (1)	C(30)	1.0711 (4)	0.3567 (3)	0.5376 (5)	2.0 (1)
O(4L)	1.3945 (6)	0.0144 (4)	0.5131 (5)	6.8 (2)	C(31)	1.1151 (5)	0.4267 (4)	0.6405 (6)	3.0 (2)
O(5L)	0.6644 (5)	0.5739 (4)	0.4883 (6)	6.2 (2)	C(40)	1.0788 (4)	0.1222 (3)	0.5395 (5)	2.0 (1)
O(6L)	0.6824 (8)	0.4040 (4)	0.519 (1)	9.9 (4)	C(41)	1.1227 (5)	0.0504 (4)	0.6356 (6)	2.9 (2)
O(7L)	0.4369 (7)	0.6039 (5)	0.302 (1)	10.2 (3)	C(50)	0.7577 (4)	0.3536 (3)	0.1428 (5)	2.1 (1)
O(8L)	0.4252 (4)	0.2230 (4)	0.3172 (5)	4.7 (1)	C(51)	0.6753 (5)	0.4283 (4)	0.0800 (6)	3.2 (2)
O(9L)	0.4520 (8)	0.3948 (6)	0.346 (1)	11.0 (4)	C(60)	0.7446 (4)	0.1278 (3)	0.1518 (5)	1.9 (1)
O(10L)	0.0538 (4)	0.7371 (4)	0.2454 (4)	4.8 (2)	C(61)	0.6451 (5)	0.0713 (4)	0.0899 (5)	2.5 (1)
O(10)	1.1759 (3)	0.1312 (3)	0.2684 (4)	2.8 (1)					

[a] *B* values for 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 IV. Important Distances and Angles in Compound **2**

	Distances, Å		
V(1)–V(2)	3.316 (1)	V(3)–O(11)	2.003 (4)
V(1)–V(3)	3.338 (1)	V(3)–O(21)	2.012 (5)
V(2)–V(3)	3.334 (1)	V(3)–O(51)	2.004 (4)
V(1)–O(15)	2.054 (5)	V(3)–O(61)	2.000 (5)
V(2)–O(25)	2.032 (3)	S–C	1.799 (8)
V(3)–O(35)	2.023 (3)	S–O(1)	1.421 (5)
V(1)–O	1.909 (4)	S–O(2)	1.428 (5)
V(2)–O	1.915 (3)	S–O(3)	1.430 (6)
V(3)–O	1.943 (3)	C–F(1)	1.322 (8)
V(1)–O(31)	2.025 (4)	C–F(2)	1.330 (13)
V(1)–O(41)	2.010 (4)	C–F(3)	1.306 (9)
V(1)–O(50)	2.008 (4)		
–O(60)	2.005 (4)		
V(2)–O(10)	2.023 (4)		
–O(20)	2.011 (5)		
–O(30)	2.020 (4)		
–O(40)	2.011 (4)		
	Angles, deg		
O–V(1)–O(15)	176.7 (1)	O–V(3)–O(51)	92.8 (2)
–O(31)	96.1 (2)	O–V(3)–O(61)	96.1 (2)
–O(41)	92.9 (2)	O–V(3)–O(11)	94.1 (1)
–O(50)	94.0 (2)	O–V(3)–O(21)	94.1 (2)
–O(60)	96.4 (2)	O–V(3)–O(35)	179.2 (2)
O–V(2)–O(10)	95.5 (1)	V(1)–O–V(2)	120.3 (2)
–O(20)	94.8 (2)	–V(3)	120.1 (2)
–O(25)	179.7 (2)	V(2)–O–V(3)	119.6 (2)
–O(30)	95.8 (2)		
–O(40)	94.2 (2)		

$[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$[7] (2.66 g, 1.5 mmol) and sodium trifluoroacetate (2.72 g, 20 mmol) were placed in 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 then filtered to remove precipitated sodium chloride. When the volume of the filtrate was reduced to ca. 30 mL and the filtrate cooled at −10 °C, black crystals of the title complex were obtained as the major product (ca. 70% yield) along with orange crystals of an as yet unidentified compound. In addition, slow evaporation of the mother liquor under argon or in moist air yields green $[V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3]$[3] or blue $[Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2]$,[8] respectively. A crystal suitable for X-ray work

Table V. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[V_3O(CH_3COO)_6(THF)_3]_2(V_2O_2Cl_6)\cdot 5CH_2Cl_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.5952 (1)	0.000	0.2984 (2)	3.47 (5)
V(2)	0.44943 (7)	0.09719 (8)	0.2222 (1)	3.27 (3)
V(3)	0.4155 (1)	0.500	0.0104 (2)	5.36 (7)
Cl(1)	0.3369 (2)	0.4040 (2)	−0.0609 (3)	9.0 (1)
Cl(2)	0.500	0.4093 (3)	0.000	7.7 (1)
O(1)	0.4979 (4)	0.000	0.2480 (6)	3.2 (2)
O(2)	0.7006 (4)	0.000	0.3514 (7)	4.5 (2)
O(3)	0.3953 (3)	0.1999 (3)	0.1935 (5)	4.3 (2)
O(4)	0.6047 (3)	0.0820 (4)	0.4047 (5)	4.5 (2)
O(5)	0.5082 (3)	0.1470 (4)	0.3543 (5)	4.5 (2)
O(6)	0.6046 (3)	0.0815 (4)	0.2028 (5)	4.5 (1)
O(7)	0.5071 (3)	0.1474 (4)	0.1530 (5)	4.3 (1)
O(8)	0.3835 (3)	0.0635 (4)	0.2886 (5)	4.6 (2)
O(9)	0.3828 (3)	0.0651 (4)	0.0877 (5)	4.3 (1)
O(12)	0.4235 (8)	0.500	0.1255 (9)	8.3 (4)
C(1)	0.7432 (6)	−0.0708 (7)	0.373 (1)	7.8 (4)
C(2)	0.8138 (7)	−0.0398 (9)	0.399 (2)	12.1 (6)
C(3)	0.3212 (6)	0.2055 (7)	0.157 (1)	7.2 (4)
C(4)	0.3049 (8)	0.2897 (8)	0.167 (2)	10.2 (5)
C(5)	0.3722 (8)	0.3303 (7)	0.220 (1)	8.4 (4)
C(6)	0.4256 (6)	0.2784 (6)	0.2076 (9)	5.8 (3)
C(7)	0.5677 (5)	0.1358 (5)	0.4131 (6)	3.7 (2)
C(8)	0.5963 (6)	0.1904 (6)	0.5044 (7)	5.1 (3)
C(9)	0.5653 (5)	0.1371 (5)	0.1534 (7)	4.1 (2)
C(10)	0.5928 (5)	0.1896 (5)	0.0929 (6)	4.5 (2)
C(11)	0.3622 (6)	0.000	0.3057 (9)	3.7 (3)
C(12)	0.3046 (7)	0.000	0.346 (1)	5.6 (4)
C(13)	0.3605 (7)	0.000	0.0491 (9)	3.8 (3)
C(14)	0.3010 (8)	0.000	−0.054 (1)	5.1 (4)
C(15)	0.641 (2)	0.349 (2)	0.270 (3)	4.9 (8)*
C(15A)	0.602 (2)	0.332 (2)	0.289 (2)	13.6 (9)*
Cl(3)	0.6979 (4)	0.2956 (4)	0.3564 (5)	15.0 (2)*
Cl(4)	0.5787 (7)	0.3880 (7)	0.342 (1)	13.5 (4)*
Cl(4A)	0.604 (1)	0.416 (1)	0.298 (2)	26 (1)*
C(16)	0.498 (3)	0.500	0.393 (5)	13 (2)*
Cl(5)	0.500	0.418 (1)	0.500	29.2 (8)*

[a] Starred values denote isotropically refined atoms. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

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(7) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913.
(8) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 1825.

Table VI. Important Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Compound **4** ($[V_3O(CH_3COO)_6(THF)_3]_2(V_2O_2Cl_6)\cdot5CH_2Cl_2$)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
V(1)	V(2)	3.312 (2)	V(2)	O(9)	1.985 (6)	O(8)	C(11)	1.230 (9)
V(1)	O(1)	1.912 (8)	V(3)	Cl(1)	2.293 (5)	O(9)	C(13)	1.253 (8)
V(1)	O(2)	2.071 (9)	V(3)	Cl(2)	2.403 (4)	C(1)	C(2)	1.50 (2)
V(1)	O(4)	2.005 (6)	V(3)	O(12)	1.564 (13)	C(2)	C(2′)	1.36 (3)
V(1)	O(6)	1.993 (6)	O(2)	C(1)	1.472 (13)	C(3)	C(4)	1.50 (2)
V(2)	V(2′)	3.325 (3)	O(3)	C(3)	1.460 (13)	C(4)	C(5)	1.51 (2)
V(2)	O(1)	1.916 (4)	O(3)	C(6)	1.469 (12)	C(5)	C(6)	1.49 (2)
V(2)	O(3)	2.054 (6)	O(4)	C(7)	1.237 (11)	C(7)	C(8)	1.525 (12)
V(2)	O(5)	2.014 (6)	O(5)	C(7)	1.243 (11)	C(9)	C(10)	1.488 (13)
V(2)	O(7)	1.999 (7)	O(6)	C(9)	1.288 (11)	C(11)	C(12)	1.51 (2)
V(2)	O(8)	2.013 (7)	O(7)	C(9)	1.236 (12)	C(13)	C(14)	1.54 (2)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
V(2)	V(1)	V(2′)	60.27 (6)	V(2′)	V(2)	O(8)	73.3 (2)	C(1)	O(2)	C(1′)	111 (1)
V(2)	V(1)	O(1)	30.14 (3)	V(2′)	V(2)	O(9)	73.9 (2)	V(2)	O(3)	C(3)	124.9 (6)
V(2)	V(1)	O(2)	149.85 (3)	O(1)	V(2)	O(3)	178.6 (3)	V(2)	O(3)	C(6)	124.9 (6)
V(2)	V(1)	O(4)	73.9 (2)	O(1)	V(2)	O(5)	94.8 (3)	C(3)	O(3)	C(6)	110.1 (8)
V(2)	V(1)	O(4′)	115.2 (2)	O(1)	V(2)	O(7)	95.2 (3)	V(1)	O(4)	C(7)	133.8 (6)
V(2)	V(1)	O(6)	74.6 (2)	O(1)	V(2)	O(8)	94.1 (3)	V(2)	O(5)	C(7)	133.4 (6)
V(2)	V(1)	O(6′)	115.9 (2)	O(1)	V(2)	O(9)	95.0 (3)	V(1)	O(6)	C(9)	132.9 (7)
O(1)	V(1)	O(2)	179.4 (4)	O(3)	V(2)	O(5)	86.2 (3)	V(2)	O(7)	C(9)	135.1 (6)
O(1)	V(1)	O(4)	94.8 (3)	O(3)	V(2)	O(7)	85.8 (3)	V(2)	O(8)	C(11)	134.6 (7)
O(1)	V(1)	O(6)	95.8 (3)	O(3)	V(2)	O(8)	84.9 (3)	V(2)	O(9)	C(13)	133.3 (7)
O(2)	V(1)	O(4)	85.6 (3)	O(3)	V(2)	O(9)	84.1 (3)	O(2)	C(1)	C(2)	104 (1)
O(2)	V(1)	O(6)	83.8 (3)	O(5)	V(2)	O(7)	89.2 (3)	C(1)	C(2)	C(2′)	110.8 (8)
O(4)	V(1)	O(4′)	88.7 (4)	O(5)	V(2)	O(8)	89.6 (3)	O(3)	C(3)	C(4)	106 (1)
O(4)	V(1)	O(6)	90.2 (3)	O(5)	V(2)	O(9)	170.3 (3)	C(3)	C(4)	C(5)	106 (1)
O(4)	V(1)	O(6′)	169.4 (3)	O(7)	V(2)	O(8)	170.6 (3)	C(4)	C(5)	C(6)	106 (1)
O(6)	V(1)	O(6′)	88.8 (4)	O(7)	V(2)	O(9)	90.1 (3)	O(3)	C(6)	C(5)	105 (1)
V(1)	V(2)	V(2′)	59.86 (3)	O(8)	V(2)	O(9)	89.5 (3)	O(4)	C(7)	O(5)	124.7 (8)
V(1)	V(2)	O(1)	30.1 (2)	Cl(1)	V(3)	Cl(1′)	91.6 (2)	O(4)	C(7)	C(8)	117.6 (8)
V(1)	V(2)	O(3)	151.3 (2)	Cl(1)	V(3)	Cl(2)	86.8 (1)	O(5)	C(7)	C(8)	117.7 (9)
V(1)	V(2)	O(5)	73.9 (2)	Cl(1)	V(3)	Cl(2′)	150.5 (2)	O(6)	C(9)	O(7)	123.5 (9)
V(1)	V(2)	O(7)	73.8 (2)	Cl(1)	V(3)	O(12)	104.2 (4)	O(6)	C(9)	C(10)	117 (1)
V(1)	V(2)	O(8)	114.7 (2)	Cl(2)	V(3)	Cl(2′)	80.5 (2)	O(7)	C(9)	C(10)	119.9 (9)
V(1)	V(2)	O(9)	115.2 (2)	Cl(2)	V(3)	O(12)	104.7 (5)	O(8)	C(11)	O(8′)	124 (1)
V(2′)	V(2)	O(1)	29.8 (2)	V(3)	Cl(2)	V(3′)	99.5 (2)	O(8)	C(11)	C(12)	118.0 (6)
V(2′)	V(2)	O(3)	148.8 (2)	V(1)	O(1)	V(2)	119.8 (2)	O(9)	C(13)	O(9′)	125 (1)
V(2′)	V(2)	O(5)	115.0 (2)	V(2)	O(1)	V(2′)	120.4 (4)	O(9)	C(13)	C(14)	117.4 (6)
V(2′)	V(2)	O(7)	115.5 (2)	V(1)	O(2)	C(1)	124.7 (6)				

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

Table VII. Table of Positional Parameters and Their Estimated Standard Deviations for Compound **5** ($V_3O(O_2CCH_3)_6(py)_3$)[a]

atom	*x*	*y*	*z*	*B*, Å^2
V	0.1096 (2)	0.000	0.000	3.06 (8)
O(1)	0.000	0.000	0.000	1.7 (3)
O(2)	0.1676 (5)	0.0965 (5)	0.132 (1)	4.0 (2)
O(3)	0.0762 (6)	−0.0907 (7)	0.1428 (9)	4.7 (3)
N(1)	0.2353 (8)	0.000	0.000	3.4 (5)
C(1)	0.1547 (8)	0.1544 (8)	0.173 (1)	3.8 (4)
C(2)	0.216 (1)	0.218 (1)	0.280 (2)	6.8 (5)
C(3)	0.312 (1)	0.074 (1)	0.012 (2)	5.5 (5)
C(4)	0.393 (1)	0.076 (1)	0.013 (2)	5.3 (5)
C(5)	0.391 (2)	0.000	0.000	6.5 (8)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

was selected from the homogeneous mass of black crystals.

II. X-ray Crystallography. (a) General Procedures. Experimental and computational procedures were those used routinely in this laboratory and described elsewhere.[9,10] For each compound the pertinent crystallographic parameters and details relating to data collection are summarized in Table II. Important additional details pertaining to individual compounds will now be presented.

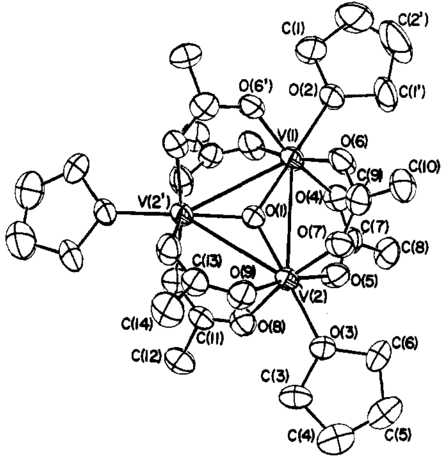

Figure 3. ORTEP drawing of the $[V_3O(O_2CCH_3)_6(THF)_3]^+$ ion in **4**. Each atom is represented by its ellipsoid of thermal displacement drawn at the 50% probability level. A crystallographic mirror plane includes atom V(1) and bisects the line between V(2) and V(2′).

(b) Compound 2. A well-formed crystal of approximate dimensions 0.4 × 0.4 × 0.3 mm was mounted in a glass capillary with epoxy cement. The structure was refined in the centrosymmetric space group *P*1̄. All

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(9) (a) All calculations were done by a VAX-11/780, with software from SHELX76 and the Enraf-Nonius package VAXSDP. (b) Empirical absorption correction: North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351. (c) Intensity-distribution analysis: Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210. (d) Least-squares weighting scheme; Grant, D. F.; Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 374.

(10) Deviations given in square brackets are calculated as

$$[\,] = [\sum_{i=1}^{n}\Delta_i^2/n(n-1)]^{1/2}$$

in which Δ_i is the deviation of the *i*th value from the mean of the set of *n* values.

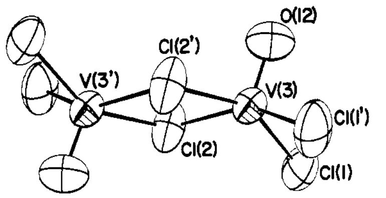

Figure 4. Structure and labeling scheme for the $[V_2O_2Cl_6]^{2-}$ anion in **4**. Atoms are represented by their 50% probability ellipsoids. A crystallographic 2-fold axis lies along the line joining Cl(2) and Cl(2′), while V(3), V(3′), O(12), and O(12′) lie in a crystallographic mirror plane.

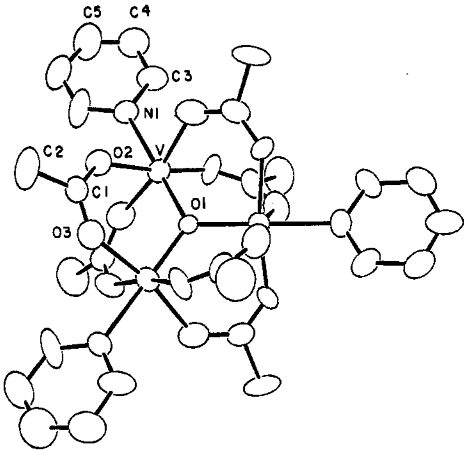

Figure 5. ORTEP drawing of the $V_3O(O_2CCH_3)_6(py)_3$ molecule in **5**. The ellipsoids represent atoms at the 50% probability level.

non-hydrogen atoms were located by using alternating cycles of least-squares refinements and difference Fourier syntheses. One of the six chlorine atoms was found to be disordered over two sites and was modeled with a 2:3 ratio of site occupancies for Cl(2a):Cl(2b). Eleven water molecules were found in the unit cell. However, O(11) gave a reasonable refinement only at one-half site occupancy. All 57 atoms were refined first with isotropic and then with anisotropic displacement parameters.

(c) Compound 4. The choice of space group $C2/m$ was justified by the successful refinement, which proceeded smoothly for the vanadium-containing cation and anion. The CH_2Cl_2 molecules of solvation, however, were systematically disordered, and considerable effort was required to devise and refine a satisfactory model. The following summary should suffice, but readers desiring more detailed information may consult two drawings that are presented in the supplementary material. One CH_2Cl_2 site has its C and Cl atoms on general positions, and the model employs C(15), C(15A), Cl(3), Cl(4) and Cl(4A), none of which are symmetry-related. A total of eight CH_2Cl_2 molecules per unit cell are found on this site. The second CH_2Cl_2 site, which contributes two CH_2Cl_2 molecules per cell, is a site of crystallographic $2/m$ symmetry. This leads to the overall composition of the crystal given in Table II. It is by no means clear, however, that the composition reported represents the only model that could have been refined. Indeed, the composition may not even be static, since crystals of this material undergo physical decomposition—apparently by loss of CH_2Cl_2—with time.

(d) $V_3O(CH_3CO_2)_6(C_5H_5N)_3$ (5). A dark red tablet, purple by transmitted light, was mounted in an argon atmosphere on the tip of a glass fiber and immediately transferred into the cold nitrogen stream of a low-temperature unit of a CAD-4 diffractometer. There was no indication, either in a visual inspection or in the behavior of standard reflections, that significant decomposition occurred during the time the crystal was in use. Preliminary examination showed that the crystal had trigonal symmetry and belonged to the Laue class $\bar{3}m$. The only systematic absence, hkl with $-h + k + l = 3n \pm 1$, limited the space groups to $R\bar{3}m$, $R3m$, and $R32$. Since the cell volume indicated that $Z = 3$, the trinuclear unit would be required to have $\bar{3}m$, $3m$, or 32 symmetry, respectively, for each of the above space groups. As the solution and refinement of the structure progressed it was seen that the arrangement of the pyridine rings was consistent with 32 site symmetry and an absence of disorder, thus identifying the space group as $R32$.

(e) Compound 7. Data for this compound were collected at −112 ± 1 °C. The unit cell was found to be monoclinic, and the systematic absences uniquely fixed the space group as $P2_1/n$. Because of the small absorption coefficient, no absorption corrections were made. An overall linear and isotropic decay in intensities of 30% took place, and the data were corrected accordingly. The coordinates of the three crystallographically distinct vanadium atoms were obtained by direct methods (MULTAN program), and the rest of the structure was developed in a series of difference Fourier maps and refinement cycles.

Table VIII. Important Distances and Angles in Compound **5** $(V_3O(O_2CCH_3)_6(py)_3)$

	Distances, Å		
V–V′	3.337 (5)	V–O(3)	2.059 (9)
V–O(1)	1.927 (3)	V–N(1)	2.210 (14)
V–O(2)	2.035 (8)		
	Angles, deg		
V–V–V	60.00[a]	N(1)–V–O(2)	85.2 (2)
O(1)–V–N(1)	180.00[a]	–O(3)	84.1 (3)
–O(2)	94.8 (2)		
–O(3)	95.9 (3)		

[a] By symmetry.

The fluorine atoms of three trifluoroacetate groups were found to be subject to 2-fold disorder and were refined by using a 2:1 model. Minor problems arose during the refinement of the molecules of solvation. A difference Fourier synthesis revealed the presence of a methylene chloride molecule. After inclusion of these atoms in the refinement, a difference Fourier synthesis showed quite clearly the presence of a THF molecule with one carbon atom in common with the methylene chloride molecule. Attempts to include these atoms in the refinement led to chemically unreasonable results. The positions of all seven solvent atoms were then fixed and their thermal parameters were treated isotropically by using a 2:1 (THF:methylene chloride) model. The overall composition reported represents the best result which could be achieved with the data at hand. We do not, however, assert that this is only acceptable model for this disordered region of the crystal. It is not even clear that the composition of the crystal was static throughout the course of data collection, since the observed decay was likely a result of solvent loss.

Results

Compound 2, $[V_3O(O_2CCClH_2)_6(H_2O)_3](CF_3SO_3)$. The structure of the trinuclear cation is shown, along with the atom labeling scheme, in Figure 2. The positional and isotropic equivalent displacement parameters are listed in Table III, and the important interatomic distances and angles are listed in Table IV for the compound. There are statistically significant differences among the V⋯V distances in the cation, especially between V(1)⋯V(2) and the others, which differ from each other by an amount that is barely significant. Still, the difference of 0.020 Å between V(1)⋯V(2) and the average of the other two is presumably due only to packing forces, and we have therefore averaged the three with equal weights in Table I. There is no disorder in this crystal, nor any other reason for uncertainty about its composition. Therefore, the assignment of a charge of +1 to the trinuclear cation is unambiguous, and hence a III,III,III assignment of formal valences to the vanadium atoms is straightforward. The mean dimensions of the trinuclear cation do not differ significantly in compounds **1** and **2**.

The triflate anion, $CF_3SO_3^-$, showed up very clearly, and it refined well, giving the following mean dimensions: C–F, 1.320 [7] Å; C–S, 1.799 (8) Å; S–O, 1.426 [3] Å; F–C–F, 106.8 [5]°; O–S–O, 114.7 [4]°.

Compound 4, $[V_3O(O_2CCH_3)_6(THF)_3]_2[V_2O_2Cl_6]\cdot 5CH_2Cl_2$. The positional and isotropic-equivalent displacement parameters are listed in Table V. The trinuclear cation resides on a crystallographic mirror plane and has the structure shown in Figure 3. The important distances and angles in both the cation and the $[V_2O_2Cl_6]^{2-}$ ion are listed in Table VI. The average values for the cation, based on D_{3h} symmetry, are given in Table I.

The binuclear anion, for which we know of no prior report, is shown in Figure 4. It resides on a site of crystallographic $2/m$ (C_{2h}) symmetry. The V⋯V distance, 3.668 (6) Å, indicates that no metal–metal bond exists. The assigned charge of 2− means that each vanadium atom is formally V^{IV}. Since each vanadium atom is in a distorted-square-pyramidal environment, with a short (1.564 (13) Å) V–O bond, only V^{IV} or V^{V} would be reasonable possibilities. To choose the latter would make the $V_2O_2Cl_6$ unit a neutral molecule, which seems very unlikely. Furthermore, if this were the case, the trinuclear oxo species would be a neutral

Table IX. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 7 ($V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3\cdot{}^2/_3THF\cdot{}^1/_3CH_2Cl_2$)[a,b]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.4685 (2)	0.23243 (9)	0.91783 (7)	3.17 (4)	C(91)	0.248 (2)	0.3750 (7)	0.7215 (6)	7.4 (4)
V(2)	0.5791 (2)	0.10424 (9)	0.84230 (7)	2.62 (4)	C(92)	0.193 (2)	0.388 (1)	0.6649 (7)	14.0 (5)
V(3)	0.4192 (2)	0.25131 (9)	0.78610 (7)	3.17 (4)	C(93)	0.256 (2)	0.3424 (8)	0.6310 (6)	9.8 (5)
O(1)	0.4899 (7)	0.1940 (3)	0.8484 (2)	2.7 (1)	C(94)	0.341 (2)	0.2854 (6)	0.6646 (4)	5.5 (3)
O(10)	0.6831 (8)	0.2042 (4)	0.9527 (3)	4.0 (2)	Cl(S1)	0.456	0.143	0.575	11*
O(11)	0.7536 (8)	0.1208 (3)	0.9007 (3)	3.3 (2)	Cl(S2)	0.255	0.032	0.534	10*
O(20)	0.3858 (8)	0.1395 (3)	0.9441 (3)	3.5 (2)	F(11A)	0.942 (1)	0.0865 (5)	0.9921 (4)	5.2 (2)*
O(21)	0.4597 (8)	0.0544 (3)	0.8924 (3)	3.4 (2)	F(11B)	0.925 (2)	0.115 (1)	1.0111 (8)	5.8 (5)*
O(30)	0.7121 (8)	0.1353 (3)	0.7899 (3)	3.4 (2)	F(12A)	1.039 (1)	0.1489 (5)	0.9444 (4)	5.0 (2)*
O(31)	0.6070 (8)	0.2346 (4)	0.7519 (3)	3.6 (2)	F(12B)	0.973 (2)	0.218 (1)	0.9955 (8)	5.2 (5)*
O(40)	0.4190 (8)	0.0694 (3)	0.7834 (3)	3.3 (2)	F(13A)	0.939 (1)	0.1892 (7)	1.0177 (5)	8.2 (3)*
O(41)	0.3118 (8)	0.1686 (3)	0.7449 (3)	3.5 (2)	F(13B)	1.038 (2)	0.177 (1)	0.9601 (7)	5.1 (4)*
O(50)	0.5517 (8)	0.3303 (4)	0.9030 (3)	4.1 (2)	F(21)	0.2681 (7)	0.0439 (3)	0.9994 (2)	4.6 (2)
O(51)	0.5172 (9)	0.3434 (4)	0.8157 (3)	4.3 (2)	F(22)	0.1758 (7)	0.0074 (4)	0.9229 (3)	4.8 (2)
O(60)	0.2501 (8)	0.2661 (4)	0.8965 (3)	4.1 (2)	F(23)	0.3787 (7)	−0.0387 (3)	0.9622 (3)	4.6 (2)
O(61)	0.2192 (8)	0.2784 (4)	0.8092 (3)	4.3 (2)	F(31A)	0.968 (1)	0.1663 (6)	0.7535 (4)	6.0 (3)*
O(70)	0.4436 (9)	0.2738 (4)	0.9917 (3)	4.7 (2)	F(31B)	0.777 (3)	0.228 (1)	0.6795 (8)	5.9 (5)*
O(80)	0.6771 (8)	0.0065 (4)	0.8347 (3)	3.3 (2)	F(32A)	0.798 (1)	0.1364 (6)	0.6872 (4)	5.8 (3)*
O(90)	0.3411 (9)	0.3096 (4)	0.7183 (3)	4.7 (2)	F(32B)	0.937 (3)	0.209 (1)	0.736 (1)	8.3 (7)*
C(10)	0.773 (1)	0.1605 (6)	0.9391 (4)	3.3 (2)	F(33A)	0.864 (1)	0.2466 (6)	0.7092 (4)	6.5 (3)*
C(11)	0.924 (2)	0.1531 (7)	0.9733 (4)	5.1 (3)	F(33B)	0.851 (2)	0.122 (1)	0.7036 (8)	6.2 (5)*
C(20)	0.393 (1)	0.0786 (6)	0.9282 (4)	3.1 (2)	F(41)	0.1539 (9)	0.0944 (4)	0.6717 (3)	6.6 (2)
C(21)	0.303 (1)	0.0221 (6)	0.9536 (4)	3.4 (3)	F(42)	0.293 (1)	0.0034 (4)	0.6951 (3)	7.7 (2)
C(30)	0.704 (1)	0.1850 (5)	0.7589 (4)	2.9 (2)	F(43)	0.1154 (9)	0.0311 (4)	0.7364 (3)	7.4 (2)
C(31)	0.827 (2)	0.1832 (6)	0.7212 (5)	6.0 (4)	F(51)	0.7532 (9)	0.4370 (4)	0.9044 (3)	7.5 (2)
C(40)	0.330 (1)	0.1040 (5)	0.7508 (4)	3.1 (2)	F(52)	0.5343 (9)	0.4796 (3)	0.8847 (3)	7.1 (2)
C(41)	0.223 (2)	0.0574 (6)	0.7121 (5)	5.2 (3)	F(53)	0.666 (1)	0.4634 (4)	0.8254 (3)	8.2 (2)
C(50)	0.559 (1)	0.3617 (5)	0.8613 (4)	3.1 (2)	F(61A)	0.016 (2)	0.3524 (7)	0.8930 (5)	9.4 (4)*
C(51)	0.628 (1)	0.4368 (6)	0.8677 (5)	4.3 (3)	F(61B)	−0.083 (4)	0.281 (2)	0.827 (1)	12 (1)*
C(60)	0.179 (1)	0.2830 (5)	0.8527 (5)	3.6 (3)	F(62A)	−0.038 (1)	0.3472 (6)	0.8137 (4)	6.1 (3)*
C(61)	0.012 (2)	0.3088 (7)	0.8567 (5)	6.7 (3)	F(62B)	−0.016 (2)	0.3155 (9)	0.9043 (6)	3.6 (4)*
C(71)	0.374 (2)	0.3451 (8)	0.9958 (6)	9.0 (5)	F(63A)	−0.083 (1)	0.2556 (6)	0.8535 (4)	6.2 (3)*
C(72)	0.372 (2)	0.3523 (8)	1.0540 (6)	10.0 (5)	F(63B)	0.011 (2)	0.376 (1)	0.8398 (8)	5.4 (5)*
C(73)	0.413 (3)	0.287 (1)	1.0775 (6)	13.5 (7)	O(S)	0.468	0.097	0.612	21*
C(74)	0.460 (3)	0.2395 (9)	1.0359 (5)	12.2 (7)	C(S1)	0.375	0.155	0.575	10*
C(81)	0.743 (2)	−0.0381 (6)	0.8796 (4)	4.9 (3)	C(S2)	0.358	0.116	0.524	16*
C(82)	0.802 (2)	−0.1028 (7)	0.8568 (5)	6.5 (4)	C(S3)	0.391	0.038	0.536	19*
C(83)	0.802 (2)	−0.0889 (7)	0.7993 (5)	7.7 (4)	C(S4)	0.443	0.033	0.582	24*
C(84)	0.703 (2)	−0.0248 (6)	0.7841 (4)	5.3 (3)					

[a] Starred values denote isotropically refined atoms. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

molecule, similar to those in compounds **6** and **7**. However, it differs from them markedly in being pale green (**6** and **7** are dark green to black) and in having a mean V···V distance that is shorter than those in **6** and **7** by an average of 0.044 [8] Å, which, at more than 5 times its esd is indicative of a real difference.

The $[V_2O_2Cl_6]^{2-}$ ion consists essentially of two square-pyramidal VCl_4O^- units sharing a basal edge. With V—Cl$_t$ = 2.293 (5) Å, V—Cl$_b$ = 2.403 (4) Å, and V═O = 1.564 (13) Å, this structure is indicative of a pair of VO^{2+} units coordinated, and linked, by Cl^- ions. The V═O distance is very similar to those in a considerable number of square-pyramidal VO^{2+} complexes, where the range is approximately 1.55–1.61 Å.

Compound 5, $V_3O(O_2CCH_3)_6(C_5H_5N)_3$. The atomic positional parameters and isotropic equivalent displacement parameters are listed in Table VII, and the important distances and angles are given in Table VIII. A drawing of the molecule is presented in Figure 5. Crystallographic 32 (D_3) symmetry is imposed on the molecule, and the inner region, consisting of the V_3O core and the 15 coordinated oxygen and nitrogen atoms, does not deviate significantly from D_{3h} symmetry.

Compound 7, $[V_3O(O_2CCF_3)_6(THF)_3]\cdot{}^2/_3THF\cdot{}^1/_3CH_2Cl_2$. The positional and isotropic-equivalent displacement parameters are listed in Table IX. The trinuclear molecule is shown in Figure 6, and the important distances and angles are given in Table X. With four molecules in a unit cell in space group $P2_1/n$, the entire molecule is the asymmetric unit (together with some disordered molecules of solvent) and no crystallographic symmetry is imposed.

Summary. The structural results for all four of the new compounds, **2**, **4**, **5** and **7**, averaged according to the D_{3d} symmetry are listed in Table I, along with the results from the literature for the three previously reported compounds, **1**, **3**, and **6**.

Discussion

All of the structural work to date on $V_3O(O_2CR)_6L_3$ species, which is summarized in Table I, has produced only those with formal oxidation numbers II,III,III and III,III,III; although one compound with a deviant structure and a IV,IV,IV set of oxidation numbers has also been found,[2] it is not pertinent to the present discussion. It is interesting that even when V^{II} starting materials were used, we have not identified any II,II,II or II,II,III products. We believe that there is a strong tendency, presumably thermodynamic (as opposed to purely kinetic), on the part of V^{II} in the presence of carboxylic acids (or carboxylate ions) to react in a manner that can be expressed formally by eq 1.

$$3V^{II} + RCO_2H \rightarrow \text{“}V_3O^{6+}\text{”} + \text{“RCHO”} \qquad (1)$$

In effect, oxygen atom transfer from the carboxyl function provides the central oxygen atom in the V_3O-containing product and simultaneously oxidizes two-thirds of the V^{II} atoms to V^{III}. By starting with V^{III} compounds, one can proceed directly to the V_3O^{7+} core, although there are other ways to obtain this type of product and other oxidative processes (possibly attributable to O_2 that is unintentionally present) also occur.

In each of the three II,III,III compounds, the structural data are indicative of charge delocalization in the formally II,III,III, V_3O^{6+} unit. In other words, the three vanadium atoms are to be regarded as equivalent. Such a leveling out of charge could be attributed to the existence of a π-orbital system comprised of the

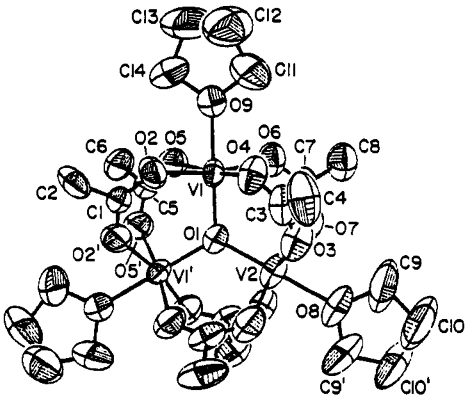

Figure 6. ORTEP drawing of the $V_3O(O_2CCF_3)_6(THF)_3$ molecule in **7**. The ellipsoids represent atoms at the 40% probability level. Fluorine atoms are omitted for clarity.

oxygen atom p orbital perpendicular to the V_3O plane and one d orbital from each vanadium atom. These orbitals can be combined to form a bonding orbital and an antibonding orbital, each containing both oxygen and metal contributions and each totally symmetric with respect to the 3-fold rotation axis, and a doubly degenerate orbital pair of exclusively metal provenance. With two electrons occupying the bonding orbital and one in the doubly degenerate orbital, the metal atoms would each have effectively the oxidation state $2^2/_3$.

In one of the three II,III,III compounds, **5**, the molecule resides on a position of crystallographic 32 (D_3) symmetry. While in principle this does not rule out the possibility of a valence-trapped species in the form of an isosceles triangle being disordered from site to site over three orientations, there is nothing in the appearance of the structure (such as unusual thermal displacement ellipsoids) to support such a speculation. We prefer to accept the more "obvious" interpretation, namely that each molecule actually has D_3 symmetry, subject perhaps to a minor Jahn–Teller perturbation.

The other two II,III,III compounds **6** and **7**, are not crystallographically required to have 3-fold symmetry and, in fact they show small deviations. The nature of these deviations actually appears to support the view that the metal atoms are essentially equivalent and that the distortions have some perturbational origin, such as packing forces or possibly a Jahn–Teller effect. If valence trapping were actually taking place, we would expect the V_3O units to have the form of isosceles triangles with *one short* and *two long* V···V distances, since one V atom (V^{II}) would be larger than the other two (V^{III}). The experimental fact, in both cases, is that there are *two short* distances and *one long* distance, the differences, in each case, being about 0.02 Å. The observations are opposite to what would have been predicted by the trapped-valence model.

A final point to be addressed concerns the very small dimensional differences between the II,III,III and III,III,III species. Assuming, for the reasons given above, valence delocalization in the former, comparisons are appropriately to be made between dimensions averaged according to D_{3h} symmetry. Such averaged dimensions are listed in Table I. The class to class differences are very small and scarcely significant in a statistical sense, although in the right direction, namely, such that the II,III,III species are generally larger than the III,III,III species. For the V···V distances, the average values are 3.353 [8] and 3.322 [6] Å; they differ by 0.031 [10] Å, so that the difference is just at the 3σ level. From another point of view, the ranges are 3.364 [10]–3.337(5) Å for the II,III,III group and 3.337 [7]–3.307[1] Å for the III,III,III group. The two ranges meet at 3.337 Å.

The V–(μ_3-O) distances are trigonometrically related to the V···V distances; thus they provide a different but not independent way to compare the two sets. The average V–(μ_3-O) distances in the two sets are 1.94 [2] and 1.92 [1] Å, which do not differ significantly. Again, the two ranges are not separated. Comparisons of the other two types of averaged dimensions are of little value because the ligands vary.

Table X. Important Interatomic Distances and Bond Angles for Compound 7 ($V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3\cdot{}^2/_3THF\cdot{}^1/_3CH_2Cl_2$)[a]

Distances, Å			
V(1)–V(2)	3.354 (2)	V(2)–O(11)	2.019 (5)
–V(3)	3.383 (2)	–O(21)	2.028 (4)
–O(1)	1.971 (4)	–O(30)	2.018 (5)
–O(10)	2.055 (5)	–O(40)	2.030 (5)
–O(20)	2.060 (5)	–O(80)	2.067 (4)
–O(50)	2.052 (5)	V(3)–O(1)	1.963 (4)
–O(60)	2.040 (5)	–O(31)	2.031 (5)
–O(70)	2.106 (5)	–O(41)	2.046 (4)
V(2)–V(3)	3.354 (2)	–O(51)	2.044 (5)
–O(1)	1.891 (4)	V(3)–O(61)	2.028 (5)
		–O(90)	2.097 (5)

Angles, deg			
V(2)–V(1)–V(3)	59.71 (3)	O(10)–V(1)–O(70)	85.3 (2)
O(1)–V(1)–O(10)	95.2 (2)	O(20)–V(1)–O(50)	171.4 (2)
–O(20)	94.2 (2)	–O(60)	89.0 (2)
–O(50)	94.3 (2)	–O(70)	85.8 (2)
–O(60)	95.2 (2)	O(50)–V(1)–O(60)	91.4 (2)
–O(70)	179.5 (2)	–O(70)	85.7 (2)
O(10)–V(1)–O(20)	89.4 (2)	O(60)–V(1)–O(70)	84.3 (2)
–O(50)	88.8 (2)	V(1)–V(2)–V(3)	60.58 (3)
–O(60)	169.6 (2)	O(1)–V(2)–O(11)	94.8 (2)
O(1)–V(2)–O(21)	95.5 (2)	O(41)–V(3)–O(51)	170.3 (2)
–O(30)	95.2 (2)	–O(61)	89.1 (2)
–O(40)	95.7 (2)	–O(90)	84.2 (2)
–O(80)	179.3 (2)	O(51)–V(3)–O(61)	91.1 (2)
O(11)–V(2)–O(21)	90.8 (2)	–O(90)	86.1 (2)
–O(30)	89.6 (2)	O(61)–V(3)–O(90)	85.3 (2)
–O(40)	169.5 (2)	V(1)–O(1)–V(2)	120.5 (2)
–O(80)	85.5 (2)	–V(3)	118.6 (2)
O(21)–V(2)–O(30)	169.2 (2)	V(2)–O(1)–V(3)	120.9 (2)
–O(40)	87.2 (2)	V(1)–O(10)–C(10)	130.2 (5)
–O(80)	85.1 (2)	V(2)–O(11)–C(10)	133.8 (5)
O(30)–V(2)–O(40)	90.5 (2)	V(1)–O(20)–C(20)	130.6 (5)
–O(80)	84.1 (2)	V(2)–O(21)–C(20)	130.7 (4)
O(40)–V(2)–O(80)	84.1 (2)	–O(30)–C(30)	132.6 (5)
V(1)–V(3)–V(2)	59.71 (3)	V(3)–O(31)–C(30)	129.8 (4)
O(1)–V(3)–O(31)	95.0 (2)	V(2)–O(40)–C(40)	129.4 (4)
–O(41)	94.0 (2)	V(3)–O(41)–C(40)	130.5 (5)
–O(51)	95.7 (2)	V(1)–O(50)–C(50)	131.5 (5)
–O(61)	94.8 (2)	V(3)–O(51)–C(50)	130.3 (5)
–O(90)	178.2 (2)	V(1)–O(60)–C(60)	130.7 (5)
O(31)–V(3)–O(41)	90.3 (2)	V(3)–O(61)–C(60)	132.4 (5)
–O(51)	87.9 (2)	V(1)–O(70)–C(71)	120.1 (6)
–O(61)	170.1 (2)	–C(74)	126.6 (6)
–O(90)	84.8 (2)	V(2)–O(80)–C(81)	124.0 (4)
V(2)–O(80)–C(84)	124.3 (4)		
V(3)–O(90)–C(91)	120.3 (6)		
–C(94)	125.5 (4)		

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

It must be concluded that the attempt to classify any one compound from dimensional data alone as to whether it is II,III,III or III,III,III would be risky, unless it were to be at an extreme value, for example, with a V···V value of 3.300 or 3.360 Å.

We find it surprising that there is so little dimensional difference between the two classes. On the basis that the V^{2+} and V^{3+} radii might be expected to differ by at least 0.20 Å, a difference of ca. one-third of that in the V–(μ_3-O) distances, viz. ca. 0.07Å, might have been expected.

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Registry No. **2**, 103500-03-4; **4**, 103500-07-8; **5**, 103500-08-9; **7**, 103500-10-3; $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$, 91238-34-5; $VCl_3(THF)_3$, 19559-06-9; $VCl_2(C_5H_5N)_4$, 15225-42-0; $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, 89172-48-5; lithium acetate, 546-89-4; sodium trifluoroacetate, 2923-18-4.

Supplementary Material Available: Tables of complete bond distances, bond angles, and anisotropic displacement parameters for the structures

3512 *Inorg. Chem.* **1986**, *25*, 3512–3514

of **2**, **4**, **5**, and **7**, tables of rms amplitudes of thermal vibration for **2**, **4**, and **5**, and figures showing the special position and general equivalent position region for **4** (23 pages); tables of structure factors (58 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306-3006

Thermodynamics of Complexation of Lanthanides by 3-Fluoro-, 4-Fluoro-, and 3-Nitrobenzoic Acids

Gregory R. Choppin* and Lauri H. J. Lajunen†

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The thermodynamic parameters (log β_{101}, ΔH_{101}, and ΔS_{101}) for the formation of the LnL^{2+} complexes between lanthanide cations and 3-fluoro-, 4-fluoro-, and 3-nitrobenzoate anions (L^-) were determined by potentiometric and calorimetric titrations in 0.10 M ($NaClO_4$) ionic strength aqueous solution at 25 °C. The stabilities of the present complexes agreed with the relationship for monocarboxylate complexation (e.g. log β_{101} vs. log K_{011}).

Introduction

The complexation of trivalent lanthanide cations has been studied with a relatively large number of aliphatic monocarboxylic acid ligands. The stability constants show a linear correlation with the acidity constants of the ligands. The enthalpy and entropy of complexation are positive and largely compensatory, reflecting the major effect that dehydration has in the overall complexation reaction. Recently, complexation by benzoate ligand has been reported,[1] and the same trends in β_{101}, ΔH_{101}, and ΔS_{101} have been observed. The subscripts refer to the coefficients of the reaction

$$p\mathrm{Ln}^{3+} + q\mathrm{H}^+ + r\mathrm{L}^- = \mathrm{Ln}_p\mathrm{H}_q\mathrm{L}_r \quad \beta_{pqr}, \text{ etc.}$$

In this paper we report the results of complexation studies of lanthanides by three additional aromatic monocarboxylate ligands. Our primary goal was to extend the data base for such systems and to compare these data with corresponding values of lanthanide–aliphatic monocarboxylate interaction.

Experimental Section

Reagents. Stock solutions of lanthanide perchlorates were prepared and analyzed as described previously.[1] Commercially available 3-fluoro-, 4-fluoro-, and 3-nitrobenzoic acids (Aldrich) were used without further purification. The concentrations of aqueous solutions of the ligand acids were determined by titration with a standard sodium hydroxide solution. The buffer solutions of the ligands were prepared by dissolving the acids in known amounts of 1 M NaOH and adjusting the [HL]/[L^-] ratios with standardized $HClO_4$, followed by dilution to the desired concentrations (0.02–0.04 M). A stock solution of perchloric acid was prepared by dilution of concentrated perchloric acid (Baker) with deionized water and analysis by titration with NaOH solution. The other chemicals were reagent grade. The metal and ligand solutions used in the titrations were adjusted to 0.10 M ionic strength with $NaClO_4$.

Procedures. In potentiometric measurements a Corning Model 130 pH meter was used with a combination electrode. The potentiometer allowed pH readings to ±0.001 pH unit accuracy. The titrations were performed in the pH region between 2 and 4, where the liquid-junction potential due to the free hydrogen ions of the test solution is significant. Therefore, the –log [H^+] values after each titrant addition were determined from a plot of –log [H^+] (calculated) vs. pH (experimental). This calibration plot was developed by titration of 0.10 M $NaClO_4$ solution with standardized $HClO_4$ solution.

Because of the limited solubilities of the ligand acids (especially 4-fluorobenzoic acid), the stability constants were evaluated by titration of mixtures of lanthanide perchlorates and sodium salts of the ligand anions with standardized (about 0.1 M) $HClO_4$ solution. The stability constants of the 3-fluoro- and 3-nitrobenzoate complexes were determined by other titrations of lanthanide perchlorate solutions with buffered ligand solutions. In all titrations, the total metal concentrations, C_M, were varied between 0.008 and 0.02 M. In the first type of titrations, the C_L/C_M ratios (C_L = the total concentration of the ligand) varied between 0.5 and 2. In the second type of titrations, the total ligand concentrations in the titrant were 0.02–0.04 M, and about two-thirds of the ligand acids was neutralized with NaOH.

The protonation constants were determined by titration of the ligand acid solutions with CO_2-free NaOH solution.

Calorimetric titrations were performed on a Peltier-cooled calorimeter with use of titration techniques described elsewhere.[2,3] For a particular experiment, 50 mL of a lanthanide perchlorate solution ($0.008 < C_M < 0.018$ M) was titrated with 0.5-mL aliquots of the neutralized ligand solution (C_L = 0.025, 0.04, and 0.04 M for 4-fluoro-, 3-fluoro-, and 3-nitrobenzoic acids, respectively). The heats of dilution of the ligands and lanthanide solutions were also determined as described earlier.[1]

Under the experimental conditions the effect of the heats of protonation should be minimal. Nevertheless, they were included in the calculations. For the protonation heats of 3-fluoro- and 3-nitrobenzoic acids the values –0.92 and –1.55 kJ/mol respectively were used[4] while for 4-fluorobenzoic acid the estimated value of –0.85 kJ/mol was used.

The protonation constants, stability constants, and ΔH_{101} values were calculated with Simplex algorhythm programs written by Dr. William B. Cacheris.

Results and Discussion

Typical sets of potentiometric and calorimetric data are listed in Tables I–III. The "calcd" columns are the values calculated for each titration point with the final constants of Table V. The protonation constants are given in Table IV, and the thermodynamic parameters (log β_{101}, $-\Delta G_{101}$, ΔH_{101}, and ΔS_{101}) are presented in Table V. The standard deviations in individual titrations for log K_{011}, log β_{101}, and ΔH_{101} were estimated to be 0.001–0.005, 0.005–0.020, and 0.03–0.10, respectively. However, the errors given in Tables IV and V are based on the agreement in repetitive titrations. Both potentiometric and calorimetric measurements have some evidence of the formation of the second complex, LnL_2^+, but no values of log β_{102} or ΔH_{102} are reported as the maximum $\bar{n}$ values were too small to allow a valid estimate. The protonation constants agree well with the literature values[4] when the difference in the ionic strengths is taken into account.

Figure 1 shows the relationship between the value of log β_{101} for a number of Sm(III) complexes with monocarboxylate ligands and the acidity, pK_a, of the ligand acid. The values for the Sm(III)–benzoate system are taken from ref 1 and the remaining data from ref 5. The values have been adjusted when necessary

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† On leave from the Department of Chemistry, University of Oulu, SF-90570 Oulu, Finland.

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