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New Trinuclear, Oxo-Centered, Basic Carboxylate Compounds of Transition Metals. 1. Trichromium(II,III,III) Compounds

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The preparation and structural characterization of two compounds of general formula $Cr_3(\mu_3\text{-}O)(O_2CCF_2H)_6L_3\cdot$(solvent) is reported, viz., compound **1** with L = pyridine and solvent = $(C_2H_5)_2O$ and compound **2** in which L = 4-cyanopyridine and solvent = toluene. These are the first compounds containing a planar-triangular Cr_3O moiety in a neutral rather than cationic $Cr_3O(O_2CR)_6L_3$ unit. Formally the chromium atoms are in oxidation states of II, III, and III, but the structures have 3-fold symmetry, which indicates that the three metal atoms are electronically equivalent as a result of electron delocalization. Some important intramolecular distances, given in each case in angstroms for compounds **1** and **2** in that order, are as follows: Cr⋯Cr, 3.356 (2), 3.336 (1); Cr–(μ_3-O), 1.938 (1), 1.926 (1); Cr–N, 2.158 (7), 2.155 (5); Cr–O(carboxyl), 2.034 [7], 2.028 [4]. The crystallographic parameters are as follows. Compound **1**: space group *R*32; a = 18.149 (4) Å; c = 10.675 (3) Å; Z = 3; refined to R_1 = 0.069 and R_2 = 0.081. Compound **2**: space group *R*$\bar{3}$*c*; a = 16.422 (2) Å; c = 60.227 (8) Å; Z = 12; refined to R_1 = 0.080 and R_2 = 0.097.

Introduction

In this and several papers to follow we shall present new results on trinuclear complexes of the structural type shown in Figure 1. The essential components of this structure are the equilateral triangle of metal atoms with an oxygen atom at the center, the six edge-bridging carboxyl groups, and the three equatorial ligands, L. The ideal structure has D_{3h} symmetry and may also be described approximately as three octahedra sharing a common vertex, which is the central oxygen atom. It is to be emphasized that species with this structure are not metal atom cluster compounds. With the μ_3-O atom lying in the plane of the M_3 triangle, the M–(μ_3-O) bonds, even though they are rather short, require the metal atoms to be so far from one another ($\gtrsim 3.3$ Å) that for M^{II} and/or M^{III} atoms no significant M–M bonding is possible.

Although several compounds of this type have been known for more than half a century, it is only since about 1969 that structural information has become available through X-ray crystallography, first, in approximate form, for $[Fe_3O(O_2C\text{-}CH_3)_6(H_2O)_3]ClO_4$[1] and $[Mn_3O(O_2CCH_3)_6(CH_3CO_2)_{2/2}\text{-}(CH_3COOH)]$.[2] In 1970 the first accurate structure was reported for $[Cr_3O(O_2CCH_3)_6(H_2O)_3]Cl\cdot6H_2O$.[3] In each of these compounds all three metal atoms are formally M^{III}, so that their structural equivalence is not unexpected. In 1972 the first example of a compound having L other than H_2O and metal atoms in formal oxidation states II, III, and III was reported,[4] namely, $Ru_3O(O_2CCH_3)_6(PPh_3)_3$. Here there was the possibility that the different oxidation states might be trapped, but the structure appears to have genuine 3-fold symmetry. Since then three more II, III, III structures have been reported, namely, for $M_3O(O_2CCH_3)_6(py)_3$ with M = Mn[5] and Fe[6] and for $Mn_3O(O_2CCH_3)_6[3\text{-}Cl(py)]_3$.[7] In the

first two, there appears to be full 3-fold symmetry, but in the last one there is, undoubtedly, a trapping of the valences.

Of all these compounds, the chromium compound has been most thoroughly studied both magnetically[8] and spectroscopically,[9] although the two manganese compounds have been subjected to detailed magnetic study.[10] All of the data for the chromium compound were satisfactorily explained by a model in which there is weak coupling between localized d^3 configurations, presumably through the central μ_3-O atom.

We have recently isolated two compounds of the type under consideration in which there are chromium atoms with formal oxidation numbers II, III, and III. We have investigated their structures to determine the effect of having mixed oxidation states (or, from another point of view, introducing one more electron into the III, III, III system), particularly to see if any valence trapping might occur. These two new compounds contain O_2CCF_2H groups and have either pyridine (**1**) or 4-cyanopyridine (**2**) as equatorial ligands.

## Experimental Section

Reactions and manipulations involving oxidation-sensitive chromium(II) solutions and compounds were carried out under atmospheres of nitrogen or, in the case of selecting and mounting crystals for X-ray studies, under a layer of heavy, degassed mineral oil. The compounds studied are also moisture sensitive, and appropriate precautions were taken to exclude water from the reaction systems.

To a suspension of 1.3 g (2.8 mmol) of $(NH_4)_4[Cr_2(CO_3)_4(H_2O)_3]$[11] in 50 mL of diethyl ether was added 1.0 mL (16 mmol) of CF_2HC-OOH. The mixture was refluxed for 2 h to convert the slurry of the yellow carbonate complex to a purple solution. The solvent was then stripped from the solution, and the residue was dried for 16 h under

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(6) See Table III in: Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.
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(11) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 2004.
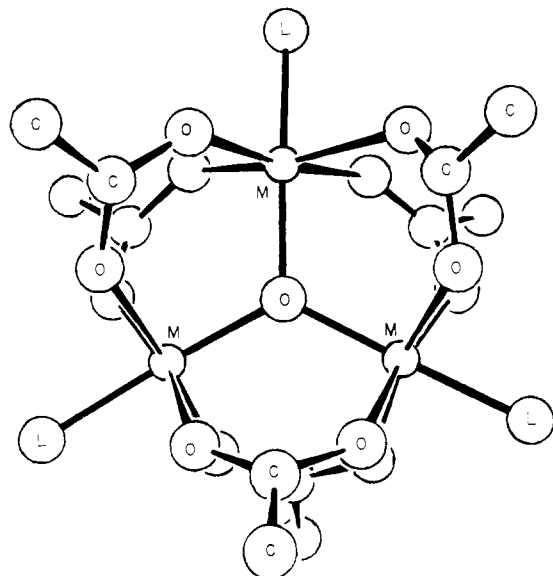
Figure 1. General structure of trinuclear oxo-centered basic carboxyl compounds of transition metals. The ideal structure has D_{3h} symmetry.

Table I. Crystallographic Parameters

	1	2
space group	$R32$	$R\bar{3}c$
a, Å	18.149 (4)	16.422 (2)
b, Å	18.149 (4)	16.422 (2)
c, Å	10.675 (3)	60.227 (8)
α, deg	(90)	(90)
β, deg	(90)	(90)
γ, deg	(120)	(120)
V, Å^3	3045 (2)	14 065 (6)
d_{calcd}, g cm^{-3}	1.723	1.624
Z	3	12
fw	1053.57	1146.62
cryst size, mm	0.3 × 0.3 × 0.7	0.4 × 0.4 × 0.4
μ(Mo Kα), cm^{-1}	8.876	7.760
range 2θ, deg	0–50	0–50
no. of unique data	1300	5805
no. of data, $F_o^2 > 3\sigma(F_o^2)$	902	2768
no. of variables	103	200
R_1[a]	0.069	0.080
R_2[b]	0.081	0.097
esd	2.205	1.802
largest peak, e Å^{-3}	0.541	0.544

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [b] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 4F_o^2/\sigma(F_o^2)^2$.

vacuum to ensure the removal of excess difluoroacetic acid. Very fine deep purple crystals (1.55 g) formed. This product (compound X) is believed to be $Cr_2(O_2CCF_2H)_4 \cdot 2(C_2H_5)_2O$. On the basis of this formula the yield is close to 100% (0.28 mmol).

$Cr_3O(O_2CCF_2H)_6(C_5H_5N)_3 \cdot (C_2H_5)_2O$ (1). Compound X (0.55 g, 1 mmol) was dissolved in 20 mL of THF. The solution was filtered into a Schlenk tube and covered with 15 mL of hexane. A solution of 1.6 mL (20 mmol) of pyridine in 20 mL of hexane was carefully added to the hexane layer. The tube was allowed to stand undisturbed so as to permit slow diffusion of pyridine into the chromium(II) difluoroacetate solution. After 3 days, the THF layer contained large single crystals (dimensions up to 0.7 mm) of the olive green product. After 1 week, 0.28 g (40% yield) of product may be obtained.

$Cr_3O(O_2CCF_2H)_6(4-CNC_5H_4N)_3 \cdot CH_3C_6H_5$ (2). Compound X and 0.21 g (2 mmol) of 4-cyanopyridine were placed in a round-bottomed flask and dissolved in 20 mL of dry, degassed toluene, and the mixture was allowed to stir for 8 h. The light orange solution was filtered into a Schlenk tube and carefully covered with 15 mL of hexane. After 3 days, the toluene layer contained large blue–green dichroic single crystals (dimensions up to 0.4 mm). After 1 week, 0.22 g (31% yield) of product may be obtained.

X-ray Structure Determinations. For each compound the experimental procedure was essentially the same. Pertinent data and

Table II. Positional Parameters and Their Estimated Standard Deviations for Compound 1[a]

atom	x	y	z
Cr	0.0000 (0)	0.10677 (9)	0.0000 (0)
O	0.0000 (0)	0.0000 (0)	0.0000 (0)
O(1)	−0.0871 (3)	0.0732 (3)	−0.1372 (6)
O(2)	−0.1619 (4)	−0.0679 (3)	−0.1329 (7)
N	0.0000 (0)	0.2257 (5)	0.0000 (0)
C(1)	−0.1481 (5)	0.0000 (0)	−0.1691 (9)
C(3)	−0.0735 (4)	0.2249 (4)	0.0000 (0)
C(4)	−0.0754 (5)	0.3013 (6)	0.0000 (0)
C(5)	0.0000 (0)	0.3779 (8)	0.0000 (0)
O(11)	0.0000 (0)	0.0700 (28)	0.5000 (0)
C(12)	0.0000 (0)	0.0000 (0)	0.3908 (37)
C(11)	0.0000 (0)	−0.0657 (38)	0.5000 (0)
F(2)	−0.236 (1)	−0.053 (1)	−0.352 (1)
F(1)[b]	−0.1826 (12)	0.0718 (11)	−0.320 (2)
F(1A)[b]	−0.2874 (16)	−0.0428 (16)	−0.212 (3)
F(2A)[b]	−0.1464 (10)	0.0683 (10)	−0.364 (2)
F(1B)[b]	−0.2684 (9)	−0.0598 (8)	−0.296 (2)
F(2B)[b]	−0.2365 (13)	0.0494 (14)	−0.208 (2)
C(2)[b]	−0.2101 (8)	0.0000 (0)	−0.271 (1)

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

parameters are listed in Table I. In each case a crystal of suitable size and appearance was coated with epoxy cement, attached to a glass fiber, and mounted on an Enraf-Nonius CAD-4F automated diffractometer. The general procedures used with this instrument have been described previously.[12] For each crystal, indexing on 25 intense centered reflections in the range $25° \le 2\theta \le 45°$ gave a rhombohedral unit cell, and in each case this was transformed to an R-centered trigonal unit cell ($-h + k + l = 3n$) with the dimensions given in Table I.

Compound 1. The intensities were measured for reflections in the range $0 < 2\theta \le 50°$. Systematic absences other than that noted earlier could not be found; structure solution and refinement were therefore undertaken in space group $R32$. Of the 1300 unique data only those 902 for which $I > 3\sigma(I)$ were used. The Patterson function was consistent with space group $R32$ and gave positional coordinates for the chromium atom. Alternate cycles and difference Fourier maps allowed location of all atoms, including those of one molecule of diethyl ether. The CF_2H groups were disordered, and each fluorine atom was refined at three positions each with a fractional occupation of 0.333. This model is somewhat arbitrary but seems to account for the electron density fairly well. The six fractional fluorine atoms, F(1), F(1A), F(1B), F(2), F(2A), and F(2B), were refined isotropically. Carbon atom C(2) was affected by the disorder and/or libration of the fluorine atoms so that under attempted anisotropic refinement, it went non-positive-definite. Therefore, it too was refined isotropically. All other atoms, including those of the diethyl ether molecule, were treated anisotropically. The thermal parameters are available as supplementary material, along with the observed and calculated structure factors. The positional parameters are listed in Table II.

Compound 2. The intensities of 5805 reflections in the range $0 < 2\theta \le 50°$ were measured. The relation $hkl = hk\bar{l}$ indicated $\bar{3}m$ Laue symmetry, and the systematic absence of $h\bar{h}0l$ when $l = 2n$ ($h0\bar{h}l$ with $l = 2n$) uniquely suggested the space group $R\bar{3}c$. Those 2768 reflections having $I > 3\sigma(I)$ were used to solve and refine the structure. With $Z = 12$ the asymmetric unit must consist of one-third of the trinuclear molecule and one-third of a toluene molecule. The coordinates of the chromium atom were determined from a three-dimensional Patterson function and the remaining atoms located in a succession of difference maps and least-squares refinements. The molecule has crystallographic symmetry 3 (C_3). Some difficulties were encountered with one CF_2H group, and refinement was concluded with a model in which one fluorine was refined as two half-atoms, F(2) and F(2A), located at rotational positions of +120° and −120° from F(1). F(1), F(2), F(2A), and C(2) were refined isotropically while all other atoms, including those of the toluene molecule, were refined anisotropically. The toluene molecule resides on a position of 3 symmetry, and the methyl carbon atom was treated as three $1/3$ atoms. The structure factors and thermal parameters are available

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

atom	x	y	z
Cr	0.12592 (6)	0.10615 (6)	0.05421 (2)
O	0.0000 (0)	0.0000 (0)	0.05435 (13)
O(1)	0.1742 (3)	0.0518 (3)	0.07745 (10)
O(2)	0.1012 (3)	0.1718 (4)	0.08025 (8)
O(3)	0.1694 (3)	0.0553 (3)	0.02931 (8)
O(4)	0.1011 (3)	0.1845 (3)	0.03237 (8)
N(1)	0.2684 (4)	0.2220 (4)	0.0539 (1)
N(2)	0.6201 (6)	0.5084 (5)	0.0557 (2)
C(1)	0.1381 (5)	−0.0266 (5)	0.0861 (1)
C(3)	0.1505 (4)	−0.0265 (4)	0.0252 (1)
C(4)	0.2175 (5)	−0.0331 (4)	0.0086 (1)
C(5)	0.2848 (5)	0.3109 (5)	0.0556 (1)
C(6)	0.3747 (5)	0.3877 (5)	0.0556 (1)
C(7)	0.4488 (5)	0.3703 (5)	0.0543 (1)
C(8)	0.4339 (5)	0.2792 (5)	0.0526 (2)
C(9)	0.3409 (4)	0.2056 (5)	0.0524 (1)
C(10)	0.5459 (6)	0.4486 (6)	0.0549 (2)
C(11)	0.6061 (14)	0.3593 (13)	0.1657 (2)
C(13)	0.4810 (50)	0.2050 (26)	0.1675 (5)
C(12)	0.3639 (21)	0.6144 (22)	−0.0013 (3)
F(3)	0.1236 (3)	0.3190 (3)	0.00644 (9)
F(4)	0.3024 (3)	0.0087 (3)	0.01838 (10)
F(1)[b]	0.0839 (6)	0.3096 (7)	0.1047 (2)
F(2)[b]	0.2142 (6)	0.0437 (6)	0.1186 (2)
F(2A)[b]	0.0915 (7)	0.2191 (7)	0.1199 (2)
C(2)[b]	0.1936 (8)	−0.0260 (8)	0.1058 (2)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Refined isotropically.
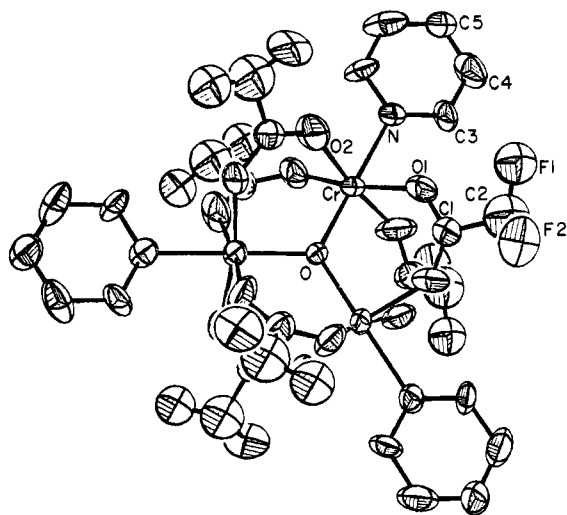
Figure 2. The $Cr_3O(O_2CCF_2H)_6(C_5H_5N)_3$ molecule in compound 1. Thermal ellipsoids enclose 40% of the electron density for each atom, here and in Figure 3.

as supplementary material. The positional parameters are listed in Table III.

Results and Discussion

The molecular structures of compounds **1** and **2** are very similar. However, they crystallize with two different crystallographically imposed symmetries, and it is convenient to discuss each one individually before emphasizing their similarities.

Compound **1** crystallizes in space group $R32$ with three molecules per unit cell. The central oxygen atom, and thus the molecule as a whole, resides on a special position of symmetry 32 (D_3). The molecule is depicted in Figure 2, and the crystallographically independent atoms are labeled. Table IV lists all of the crystallographically distinct bond distances and angles.

Compound **2** crystallizes in space group $R\bar{3}c$ with the trinuclear molecules residing on the 12-fold special position,

Table IV. Bond Distances and Bond Angles for Compound 1

atoms	dist, Å	atoms	dist, Å
Cr–Cr′	3.356 (2)	C(2)–F(1)	1.25 (2)
Cr–O	1.938 (1)	C(2)–F(2)	1.21 (1)
Cr–N	2.158 (7)	N–C(3)	1.326 (7)
Cr–O(1)	2.013 (4)	C(3)–C(4)	1.40 (1)
Cr–O(2)	2.054 (5)	C(4)–C(5)	1.38 (1)
O(1)–C(1)	1.279 (5)	O(11)–C(11)	1.23 (3)
O(2)–C(1)	1.192 (5)	C(11)–C(12)	1.67 (5)
C(1)–C(2)	1.57 (1)		

atoms	angle, deg	atoms	angle, deg
C(1)–C(2)–F(1)	112 (1)	O(1)–Cr–O(1′)	169.6 (3)
–F(2)	119 (1)	O(1)–Cr–O(2)	90.4 (2)
F(1)–C(2)–F(2)	109 (2)	O(2)–Cr–O(2′)	171.8 (3)
C(11)–O(11)–C(11′)	114 (8)	Cr–N–C(3)	119.5 (5)
O(11)–C(11)–C(12)	71 (3)	N–C(3)–C(4)	120.7 (8)
Cr–Cr–Cr	60.00 (0)	C(3)–C(4)–C(5)	119.6 (8)
Cr–Cr–O	30.00 (0)	C(4)–C(5)–C(4′)	118 (1)
Cr–Cr–N	150.00 (0)	C(3)–N–C(3′)	121.1 (9)
O–Cr–N	180.00 (0)	Cr–O(1)–C(1)	130.4 (4)
Cr–O–Cr	120.00 (0)	Cr–O(2)–C(1)	133.8 (5)
O–Cr–O(1)	95.2 (1)	O(1)–C(1)–O(2)	127.9 (7)
O–Cr–O(2)	94.1 (1)	O(1)–C(1)–C(2)	115.7 (4)
N–Cr–O(1)	84.8 (1)	O(2)–C(1)–C(2)	116.4 (4)
N–Cr–O(2)	85.9 (1)		

Table V. Bond Distances and Bond Angles for Compound 2

atoms	dist, Å	atoms	dist, Å
Cr–Cr′	3.336 (1)	C(3)–C(4)	1.529 (8)
Cr–O	1.926 (1)	C(4)–F(3)	1.346 (6)
Cr–N(1)	2.155 (5)	C(4)–F(4)	1.344 (7)
Cr–O(1)	2.023 (4)	N(1)–C(5)	1.352 (7)
Cr–O(2)	2.055 (4)	N(1)–C(9)	1.347 (7)
Cr–O(3)	2.013 (4)	C(5)–C(6)	1.380 (8)
Cr–O(4)	2.019 (4)	C(6)–C(7)	1.385 (9)
O(1)–C(1)	1.233 (7)	C(7)–C(8)	1.393 (9)
O(2)–C(1)	1.223 (7)	C(7)–C(10)	1.46 (1)
C(1)–C(2)	1.49 (1)	C(8)–C(9)	1.397 (8)
C(2)–F(1)	1.31 (1)	C(10)–N(2)	1.120 (9)
C(2)–F(2)	1.27 (1)	C(11)–C(12)	1.23 (3)
O(3)–C(3)	1.243 (6)	C(12)–C(13)	1.52 (4)
O(4)–C(3)	1.246 (6)		

atoms	angles, deg	atoms	angles, deg
Cr–Cr–Cr	60.00 (0)	N(1)–C(9)–C(8)	121.2 (6)
Cr–Cr–O	30.00 (0)	C(6)–C(7)–C(10)	120.1 (7)
Cr–Cr–N(1)	151.8 (1)	C(8)–C(7)–C(10)	118.3 (7)
Cr–O–Cr	120.00 (0)	C(7)–C(10)–N(2)	179 (1)
O–Cr–N(1)	178.2 (1)	C(5)–N(1)–C(9)	120.2 (5)
O–Cr–O(1)	94.5 (2)	Cr–O(1)–C(1)	131.7 (4)
O–Cr–O(2)	93.8 (2)	Cr–O(2)–C(1)	128.6 (4)
O–Cr–O(3)	94.1 (2)	O(1)–C(1)–O(2)	129.9 (6)
O–Cr–O(4)	96.4 (2)	O(1)–C(1)–C(2)	110.7 (7)
N(1)–Cr–O(1)	84.5 (2)	O(2)–C(1)–C(2)	119.3 (7)
N(1)–Cr–O(2)	87.6 (2)	C(1)–C(2)–F(1)	115 (1)
N(1)–Cr–O(3)	84.5 (2)	C(1)–C(2)–F(2)	112 (1)
N(1)–Cr–O(4)	84.7 (2)	Cr–O(3)–C(3)	130.4 (4)
O(1)–Cr–O(2)	85.9 (2)	Cr–O(4)–C(3)	131.7 (4)
O(1)–Cr–O(3)	91.9 (2)	O(3)–C(3)–O(4)	127.8 (6)
O(1)–Cr–O(4)	168.7 (2)	O(3)–C(3)–C(4)	114.1 (5)
O(2)–Cr–O(3)	171.9 (2)	O(4)–C(3)–C(4)	118.1 (5)
O(2)–Cr–O(4)	90.4 (2)	C(3)–C(4)–F(3)	109.6 (5)
O(3)–Cr–O(4)	90.3 (2)	C(3)–C(4)–F(4)	106.2 (5)
Cr–N(1)–C(5)	119.7 (4)	F(1)–C(2)–F(2)	131 (1)
Cr–N(1)–C(9)	120.1 (4)	F(3)–C(4)–F(4)	104.4 (5)
N(1)–C(5)–C(6)	122.2 (6)	C(11)–C(12)–C(11′)	125 (3)
C(5)–C(6)–C(7)	117.4 (6)	C(12)–C(11)–C(12′)	114 (3)
C(7)–C(8)–C(9)	117.5 (6)	C(11)–C(12)–C(13)	117 (5)

which has 3 (C_3) symmetry. The molecule is shown in Figure 3, where the crystallographically independent atoms are labeled. The bond distances and angles are listed in Table V. Although only C_3 symmetry is rigorously present, the molecular structure approximates closely to D_{3h} symmetry; its upper and lower halves are not significantly different. In a
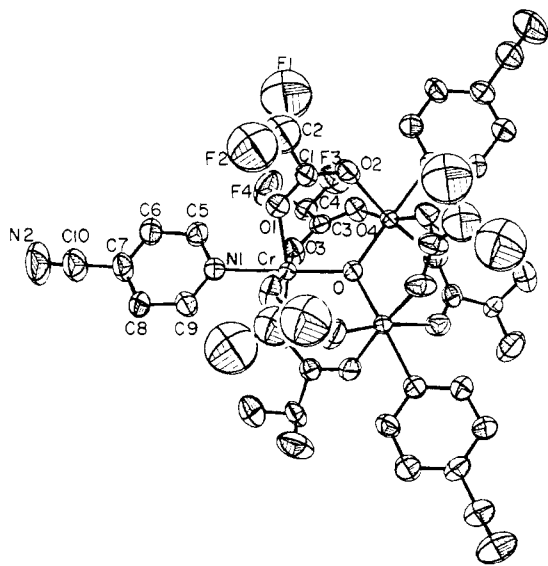
Figure 3. The $Cr_3O(O_2CCF_2H)_6(p\text{-}CNC_5H_4N)_3$ molecule in compound **2**.

Table VI. Average Values of Bond Distances (Å) in Structures 1 and 2 and in the Aquo Cation

	compd 1	compd 2	cation
Cr–Cr	3.356 (2)	3.336 (1)	3.274 [7] [a]
Cr–(μ_3-O)	1.938 (1)	1.926 (1)	1.89 [2]
Cr–O(carbox)	2.03 (4)	2.03 (2)	1.98 [3]
Cr–N	2.158 (7)	2.155 (5)	
Cr–O(H$_2$O)			2.05 [1]

[a] These distances, not given in ref 3, have been calculated by us as Cr(1)–Cr(2) = 3.272 (4) Å, Cr(2)–Cr(3) = 3.282 (4) Å, and Cr(3)–Cr(1) = 3.269 (4) Å; from these the above mean value is obtained.

comparison of it with the molecule in **1**, averaging will be done with assumption of the equivalences that would exist under D_{3h} symmetry.

The two structures are extremely similar, as shown in Table VI. The only significantly different bond distance is the Cr–(μ_3-O) distance (the Cr⋯Cr distances being predictably dependent thereon). The Cr–(μ_3-O) distance is greater by 0.012 (1) Å in the pyridine compound, which is consistent with the fact that pyridine is a stronger donor (stronger base) than 4-cyanopyridine. Even this difference, though it is statistically significant, is minor.

In both of the compounds studied here, the structural results are consistent with the idea that valences are not trapped. The apparent 3-fold symmetry of the molecules appears to be genuine; there is not the slightest suggestion that it is an illusion caused by disordering or large thermal motion of intrinsically unsymmetrical molecules. This evidently means that at least one electron is delocalized over the three chromium atoms, since the change from a III, III, III set of valences, as found in the $[Cr_3O(O_2CCH_3)_6(H_2O)_3]^+$ ion, to the II, III, III set does not result in a structural differentiation of one metal atom from the others.

The result we have obtained here may be compared with the results on the two II, III, III manganese compounds, where in one case[5] the structure is symmetrical while in the other[7] there is distinct trapping of valences. In the symmetrical manganese compound,[5] as in our chromium compounds, the symmetrical molecules are found on crystallographic sites with 3-fold symmetry, whereas in the distorted manganese compound[7] the entire molecule is the asymmetric unit, and there

are no crystallographically imposed symmetry elements. This empirical reciprocity between crystal symmetry and molecular symmetry raises, but certainly does not answer, the question of whether there are cause and effect relationships—and if so in which direction—between crystal symmetry and preferred molecular symmetry.

An interesting comparison can be made with the cation $[Cr_3O(O_2CCH_3)_6(H_2O)_3]^+$, whose structure was determined[3] in an orthorhombic crystal where no rigorous symmetry is imposed. Average values of its principal dimensions are given in Table VI. There are three compositional differences between compounds **1** and **2** and the cation: (1) the change from CH_3CO_2 groups to CHF_2CO_2 groups; (2) the change from pyridine or cyanopyridine as equatorial ligands to H_2O; (3) the change in formal metal atom oxidation numbers from II, III, III to III, III, III. While each one of these might lead to some structural change, we are inclined to expect little if any effect from the first and therefore devote the discussion to the probable consequences of the second and third.

The H_2O molecule is a donor weaker than pyridine, but the oxygen atom lies about 0.10 Å closer to the metal atom. It is thus difficult to predict what effect the replacement of pyridine molecules by H_2O molecules should have on the Cr–(μ_3-O) bond. The lower basicity of H_2O should be conducive to stronger Cr–(μ_3-O) bonds, and there does appear to be some shortening. However, there is considerable scatter in the three crystallographically independent Cr–(μ_3-O) distances, 1.87–1.91 Å, and it is difficult to be sure how meaningful the apparent shortening really is. A more reliable indication of a contraction in the size of the central Cr_3O unit is provided by the Cr⋯Cr distances, which we have calculated from the reported cell dimensions and positional parameters (see Table VI). These differ from one another by amounts that are only barely or not at all significant in a statistical sense and have an average value, 3.274 [4] Å, that is 0.082 (7) Å shorter than that in compound **1** and 0.062 (7) Å shorter than that in compound **2**. It seems quite possible that the contraction in the scale of the Cr_3O unit in the cation as compared to that in the neutral molecules could be due entirely to the replacement of pyridine or 4-cyanopyridine by H_2O in the equatorial positions.

The change from a III, III, III to a II, III, III set of formal oxidation numbers for the metal atoms might also be expected to increase the Cr–(μ_3-O) bond lengths simply because the average oxidation number is decreased from +3 to $+2^2/_3$ and the metal ion size should increase with a reduction in charge. On the other hand the degree of π bonding between the μ_3-O atom and the metal atoms should be reduced—thus lengthening the bonds—when the metal charge is lowered. All in all, it is impossible to predict the influence of the change in mean valence state of the metal atom on the scale of the Cr_3O unit.

Our tentative conclusion is that in going from the III, III, III cationic species to the II, III, III neutral molecules the additional electron is delocalized and that the small increase in the scale of the Cr_3O unit may be due principally to the replacement of pyridine or 4-cyanopyridine by H_2O in the equatorial positions.

Supplementary Material Available: Tables of structure factors and thermal parameters for both compounds (18 pages). Ordering information is given on any current masthead page.