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Synthesis and crystal structure of trinuclear carboxylate complexes $M_3(\mu_3\text{-}O)(CF_3COO)_6L_3$

Tatyana Yu. Glazunova,* Alexander I. Boltalin and Sergey I. Troyanov

Departament of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.
Fax: +7 095 939 0998; e-mail: glazunova@inorg.chem.msu.ru

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Oxocarboxylate complexes of 3*d* metals containing a trinuclear neutral or cationic $[M_3(\mu_3\text{-}O)(CF_3COO)_6L_3]^{0,+}$ unit (M = Cr, Fe; L = MeCOOH, H_2O, CF_3COO^-, THF) were obtained by electrolytic dissolution of a metal in CF_3COOH or by a reaction of a metal (or its compound) with CF_3COOH; the crystal structures of three complexes were studied by single X-ray crystallography.

Trinuclear complexes $[M_3O(OOCR)_6L_3]^+$ have interesting physical and chemical properties because of the presence of an oxide-centered triangular trinuclear unit.[1,2] Antiferromagnetic coupling between metal ions and electron delocalization in cases when the metal ions form mixed-valence compounds was actively studied. The bonding of peripheral ligands L is also of interest.[3,4] This work was devoted to the synthesis and crystal structure of 3*d* metal trinuclear oxotrifluoroacetate complexes.

Trifluoroacetate complex $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3](NO_3)(H_2O)$ **1** was prepared by the reaction of $Cr(NO_3)_3\cdot 9H_2O$ with 99% trifluoroacetic acid. A deep green solution was gradually concentrated until the formation of crystals. The structure of the compound was determined by X-ray single crystal analysis (Table 1).

According to chemical analysis, IR spectroscopy and X-ray powder diffraction data, the reactions of $Fe(NO_3)_3\cdot 9H_2O$, $CrCl_3\cdot 9H_2O$ and $FeCl_3\cdot 9H_2O$ with trifluoroacetic acid result in the formation of similar trinuclear oxotrifluoroacetate complexes consisting of $[M_3(\mu_3\text{-}O)(CF_3COO)_6(L)_3]^+$ and Cl^- or NO_3^- ions. The use of metal nitrate mixtures led to the precipitation of heterometallic complexes: $FeCrCo(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3$ in the case of $Fe(NO_3)_3\cdot 9H_2O$, $Cr(NO_3)_3\cdot 9H_2O$ and $Co(NO_3)_2\cdot 6H_2O$;

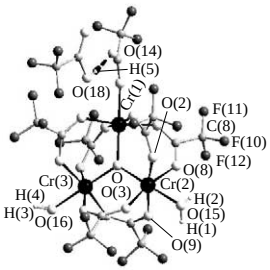

Figure 1 Structure of $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_2(CF_3COO)](CF_3COOH)$.

the Fe:Cr:Co ratio equal to 1:1:1 was found by X-ray fluorescence spectroscopy (XFS). The XFS analysis of mixed-metal complex was performed using well-formed single crystals.

Trichromium(III,III,III) trifluoroacetate complex $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_2(CF_3COO)](CF_3COOH)$ **2** was prepared by refluxing metallic chromium cuttings with a mixture of 99% trifluoroacetic acid and H_2O_2 (2:1) for 40 h. Note that this interaction does not occur in the absence of hydrogen peroxide. A blue solution was kept in a dessicator with sulfuric acid until the liquid phase disappeared and well-formed crystals arose. Crystallographic data for **2** are listed in Table 1.

Chromium(III) complex $Cr_3(\mu_3\text{-}O)(CF_3COO)_6(MeCOOH)_2(CF_3COO)$ **3** and chromium(III,III,II) complex $Cr_3(\mu_3\text{-}O)(CF_3COO)_6(MeCOOH)_2(THF)$ (THF = tetrahydrofuran) **4** were prepared by the anodic dissolution of chromium metal in 1:1 mixtures of trifluoroacetic acid and acetonitrile or THF, respectively.[5]

The crystallization of $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3](H_2O)_{3.5}$, which was prepared according to a published procedure,[6] from acetone resulted in the formation of a deeply red crystalline product $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3][MeC(O)Me]_6$ **5**. Crystallographic data are given in Table 1.

A common feature of trinuclear oxocarboxylate complexes is the presence of a nearly (for **1**) equilateral oxygen-centered triangle with six bridging carboxylic groups and three terminal L ligands.

The average M–μ_3-O distances in the complexes are 0.05– 0.06 (in trivalent complexes **1**, **2** and **3**) and 0.12–0.15 Å (in mixed-valence complexes **4** and **5**), which are shorter than the M–O distances to bridging trifluoroacetic groups. The latter significantly depend on the nature and oxidation state of transition metals. The M–O_L distances (to a terminal ligand) strongly depend on the nature of L (neutral or anionic).

Table 1 Crystal data for $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3](NO_3)(H_2O)$ **1**, $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_2(CF_3COO)](CF_3COOH)$ **2** and $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3][MeC(O)Me]_6$ **5**.

Parameter	**1**	**2**	**5**
Formula weight	1083.24	1113.20	1263.48
Crystal system	Hexagonal	Monoclinic	Triclinic
Space group	$P6_3/m$	$P2_1/c$	$P\bar{1}$
a/Å	9.893(1)	12.195(3)	10.698(1)
b/Å	9.893(1)	15.117(2)	11.968(2)
c/Å	19.366(4)	20.399(4)	20.040(4)
α/°			85.18(2)
β/°		106.51(3)	78.24(1)
γ/°	120.00		67.35(1)
V/Å^3	1641.4(4)	3606(1)	3826.9(8)
Z	2	4	4
d_{calc}/g cm^{-3}	2.008	2.051	1.578
μ(MoKα)/cm^{-1}	10.77	10.26	10.01
Crystal size/mm	0.25×0.10×0.08	0.30×0.25×0.16	0.35×0.21×0.11
T/K	293(2)	150	298
θ_{max}/°	29.95	23	28.0
Collected/unique reflections	1637/897	7564/4244	28356/12563
Diffrn reflns number/reflns number observed	1069/128	22717/7564	10656/387
wR_2	0.0641	0.1069	0.1133
R_1	0.0355	0.0558	0.0647

Table 2 Important distances in $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3](NO_3)(H_2O)$ **1**, $[Cr_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_2(CF_3COO)](CF_3COOH)$ **2**, $Cr_3(\mu_3\text{-}O)(CF_3COO)_6(MeCOOH)_2(CF_3COO)$ **3**, $Cr_3(\mu_3\text{-}O)(CF_3COO)_6(MeCOOH)_2(THF)$ **4** and $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3][MeC(O)Me]_6$ **5**.

Distance	**1**	**2**	**3**	**4**	**5**
M(1)–M(2)	3.311	3.354	3.344	3.352	3.333
M(2)–M(3)		3.350	3.387	3.333	3.339
M(1)–M(3)		3.312	3.368	3.322	3.339
M(1)–μ_3O	1.912(2)	1.942(2)	1.900(3)	1.952(2)	1.912(3)
M(1)–O(1)	1.968(2)	1.980(2)	2.001(3)	2.072(2)	2.039(3)
M(1)–O(4)		1.983(2)	1.995(2)	2.102(2)	2.094(3)
M(1)–O(5)	1.964(2)	1.991(2)	1.991(3)	2.09(2)	2.022(3)
M(1)–O(7)		1.982(2)	2.002(3)	2.086(2)	2.043(3)
M(1)–O_L	2.015(2)	1.992(2)	2.030(3)	2.115(2)	2.055(3)
M(2)–μ_3O		1.918(2)	1.948(3)	1.878(2)	1.897(3)
M(2)–O(2)		2.051(2)	2.002(3)	2.045(2)	2.047(3)
M(2)–O(3)		1.967(2)	2.002(3)	2.063(2)	2.061(3)
M(2)–O(8)		1.970(2)	1.971(4)	2.049(2)	2.030(3)
M(2)–O(9)		1.965(2)	1.980(3)	2.073(2)	2.049(3)
M(2)–O_L		1.985(2)	1.985(3)	2.070(2)	2.017(3)
M(3)–μ_3O		1.923(2)	1.982(2)	1.947(2)	1.971(3)
M(3)–O(6)		1.982(2)	2.017(3)	2.078(2)	2.067(3)
M(3)–O(10)		1.976(2)	1.989(3)	2.092(2)	2.050(3)
M(3)–O(11)		2.007(2)	1.962(2)	2.093(2)	2.040(3)
M(3)–O(12)		1.979(2)	1.982(3)	2.072(2)	2.068(3)
M(3)–O_L		1.966(2)	2.005(3)	2.089(2)	2.118(3)

In trichromium(III,III,III) complex **1**, the cation is located on the twofold axis; consequently, the Cr_3O triangle is planar. The NO_3 group and the H_2O molecule are situated outside of the trinuclear unit on the threefold axis. All metal atoms are equivalent, and distances between chromium and oxygen atoms are similar (Table 2).

The trinuclear unit in compound **2** (Figure 1) is neutral with the terminal ligands of two H_2O molecules and one CF_3COO^- anion (in contrast to the structure of **1**). The CF_3COOH molecule is situated outside the metal complex forming a hydrogen bond to the trifluoroacetic anion. A comparison of **1** and **2** shows that the replacement of a 'hard' ligand (NO_3^- in **1**) by a softer stabilising ligand (CF_3COO^- in **2**) results in a change of the complex type (cationic in **1** and neutral in **2**).

The crystal structures of complexes **3** and **4** were described earlier.[5] The only difference in the molecular structures of **3** and **4** is the presence of an anionic (CF_3COO^-) or neutral (THF) ligand in one of the terminal positions. Therefore, the complex type changed from III,III,III (**3**) to III,III,II (**4**). However, the position of Cr^{II} in the latter cannot be localised.

Apparently, the oxidation states (III,III,II) in the heterovalent complex $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_3][MeC(O)Me]_6$ **5** are delocalised. This can be deduced from the proximity of Fe–O distances to bridging CF_3COO groups. The shorter distances μ_3-O–Fe and O_{water}–Fe(2) cannot be traced clearly (Figure 2).

The theoretical calculation of the geometry of the $[M_3(\mu_3\text{-}O)(CF_3COO)_6O_3]$ fragment for M = Fe, Co, Cr and Mn demonstrated the energetic stability. Thus, the isolation of an M_3O unit containing compounds from solutions of a metal(III) nitrate or chloride in a carboxylic acid can be easily performed (**1** is a typical example). For the most active metal (such as iron), the same type of complexes can be prepared by a direct reaction of the metal with trifluoroacetic acid; however, chemical (H_2O_2)

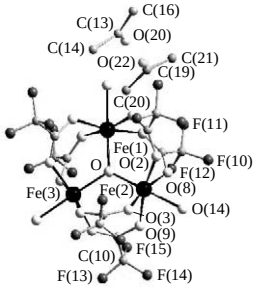

Figure 2 Structure of $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(H_2O)_2][MeC(O)Me]_6$.

or electrochemical oxidation is necessary in the case of a less active metal (Cr).

As a rule, the trinuclear fragment $M_3(\mu_3\text{-}O)(CF_3COO)_6$ retains its structure after crystallization from another solvent (as for compound **5**).

The formation of homovalent (III,III,III) or heterovalent (III,III,II) complexes may occur differently. The reaction carried out under similar conditions ($M + CF_3COOH + H_2O_2$) can produce homovalent ($Cr^{III,III,III}$) or heterovalent ($Fe^{III,III,II}$) complexes depending on the nature of the metal. The localization of metal atoms in different oxidation states is impossible using X-ray data. The temperature dependence of magnetic susceptibility shows a weak antiferromagnetic interaction. The magnetic moment μ_{eff} corresponds to an intermediate number of unpaired electrons for each metal atom. Thus, the magnetic susceptibilities of chromium complex **4** show that the delocalization of Cr^{II} takes place up to 2 K.

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