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Trinuclear Metal(III) Trifluoroacetates

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Hydrated and anhydrous trinuclear metal(III) trifluoroacetates of Cr and Fe were prepared by reaction of freshly precipitated metal oxides with trifluoroacetic acid, while manganese analogs by "acid exchange". IR data show the presence of bidentate trifluoroacetate groups. The diffuse reflectance spectra suggest octahedral environment around metals. *Mössbauer* spectra show that iron atoms in the compounds are high spin hexacoordinated; two types of iron sites are suggested in hydrated iron compound. Low magnetic moment of chromium and iron compounds indicate antiferromagnetic coupling. Th anhydrous compounds decompose in single step with the evolution of $(CF_3CO)_2O$. $M_3O(O_2CCF_3)_7$ form complexes $[M_3O(O_2CCF_3)_6 \cdot 3\,Py]^+ [O_2CCF_3]^-$ with pyridine.

(Keywords: $M_3O(O_2CCF_3)_7 \cdot H_2O$; $M_3O(O_2CCF_3)_7$; $[M_3O(O_2CCF_3)_6 \cdot 3\,Py][O_2CCF_3]$, M = Cr, Mn, Fe; IR; *Diffuse reflectance; Mössbauer spectra; Magnetic moments)*

Dreikernige Metall(III)-Trifluoracetate

Es wurden hydratisierte und wasserfreie dreikernige Metall(III)-Trifluoracetate von Cr und Fe mittels der Reaktion von frisch gefälltem Metalloxid und Trifluoressigsäure dargestellt; die Mangan-Analogen wurden über „Säure-Austausch“ gewonnen. Die IR-Daten zeigen die Präsenz von zweizähnigen Trifluoracetat-Gruppen an. Die diffuse-reflectance-Spektren sprechen für eine octahedrale Umgebung rund um das Metall. Die *Mössbauer*-Spektren zeigen, daß die Eisenatome in den entsprechenden Verbindungen high-spin hexakoordiniert sind; dabei werden in den hydratisierten Eisenverbindungen zwei Typen von Eisenatomen gezeigt. Ein niederes magnetisches Moment der Chrom- und Eisen-Verbindungen zeigen eine antiferromagnetische Kopplung an. Die wasserfreien Verbindungen zersetzen sich in einem einzigen Schritt unter Entwicklung von $(CF_3CO)_2O$. Mit Pyridin bilden die Verbindungen $M_3O(O_2CCF_3)_7$ die Komplexe $[M_3O(O_2CCF_3)_6 \cdot 3\,Py]^+ [O_2CCF_3]^-$.

Introduction

The systematic investigations of the complexes of iron(III) with carboxylic acids was first carried out by *Weinland*[1]. The crystal structure of $[Fe_3O(O_2CCF_3)_6 \cdot 3\,H_2O]^+$ has demonstrated the presence of an equilateral triangle of iron atoms with an oxygen atom in the center of the triangle[2]. *Swarts*[3] reported the preparation of $Fe_3O(O_2CCF_3)_7$. In order to find out if such compounds contain μ_3-oxo-triiron cluster; $Fe_3O(O_2CCF_3)_7$ and its hydrated analog have been prepared. Similar trifluoroacetato chromium and manganese(III) derivatives, which are not reported in the literature, were also prepared. $M_3O(O_2CCF_3)_7$, M = Cr, Mn, Fe, form complexes with pyridine. The compounds have been characterized from their elemental analysis, IR, diffuse reflectance spectra, magnetic susceptibility measurements and thermal analysis. In case of the iron compound *Mössbauer* spectra were also studied.

Experimental

$Mn_3O(O_2CCH_3)_7 \cdot H_2O$ and $Mn_3O(O_2CCH_3)_7 \cdot CH_3CO_2H$ were prepared as described[4]. Pyridine and the solvents were purified before use. Trifluoroacetic acid (BDH) was distilled in N_2 atmosphere before use (b.p. 71.5°/745 Torr). 6 mmol each of $Mn_3O(O_2CCH_3)_7 \cdot H_2O$ and $Mn_3O(O_2CCH_3)_7 \cdot CH_3CO_2H$ were refluxed with ~ 47 mmol of trifluoroacetic acid respectively for 4 h. A clear solution obtained in each case was evaporated to dryness *in vacuo* to get the desired products: [$Mn_3O(O_2CCF_3)_7 \cdot H_2O$, crystalline white solid; Found: C 16.92; F 39.85; Mn 15.98; Reqd.: C 16.97; F 40.31; Mn 16.65%; yield 95%. $Mn_3O(O_2CCF_3)_7$, crystalline white solid; Found: C 16.92; F 41.08; Mn 16.20; Reqd.: C 17.28; F 41.05; Mn 16.96%; yield 97%]. Freshly precipitated $Fe_2O_3 \cdot xH_2O$ and $Cr_2O_3 \cdot xH_2O$ obtained from 10 g of $FeCl_3 \cdot xH_2O$ or $CrCl_3 \cdot xH_2O$, were refluxed with 25 ml of trifluoroacetic acid for 4 h. The compounds formed were filtered and dried. The anhydrous compounds were obtained by heating the hydrated samples at 70–90° under vacuum. $Fe_3O(O_2CCF_3)_7 \cdot H_2O$, orange solid; Found: C 16.40; F 39.93; Fe 16.12; Reqd.: C 16.92; F 40.20; Fe 16.88; yield 85%. $Fe_3O(O_2CCF_3)_7$, orange solid; Found: C 17.00; F 40.24; Fe 17.30; Reqd.: C 17.23; F 40.94; Fe 17.19. $Cr_3O(O_2CCF_3)_7 \cdot H_2O$, green solid; Found: C 16.92; F 40.06; Cr 16.12; Reqd.: C 17.12; F 40.67; Cr 15.90; yield 87%. $Cr_3O(O_2CCF_3)_7$, green solid; Found: C 17.02; F 41.00; Cr 16.19; Reqd.: C 17.44; F 41.43; Cr 16.20%.

10–12 fold excess pyridine diluted with 20 ml CCl_4 was added to a suspension containing known weight (~ 10 mmol) of the anhydrous trinuclear-trifluoroacetate in 25 ml CCl_4. The contents were stirred at room temperature for 4 h. Solids formed were filtered under dry N_2, washed with carbontetrachloride and finally dried *in vacuo*. $Mn_3O(O_2CCF_3)_7 \cdot 3\,Py$; Found: C 28.53; N 3.2; F 32.84; Mn 13.20; Reqd.: C 28.78; N 3.47; F 33.00; Mn 13.64. $Cr_3O(O_2CCF_3)_7 \cdot 3\,Py$; Found: C 28.56; N 3.33; F 32.93; Cr 12.85; Reqd.: C 29.00; N 3.50; F 33.25; Cr 13.00. $Fe_3O(O_2CCF_3)_7 \cdot 3\,Py$; Found: C 28.43; N 3.28; F 32.54; Fe 13.51; Reqd.: C 28.72; N 3.46; F 32.83; Fe 13.82%]. Cr, Mn and Fe were determined by standard methods, fluorine (Ref.[5]), carbon and nitrogen microanalytically.

The IR spectra of the compounds were recorded (4000–200 cm^{-1}) as mulls (nujol/hexachlorobutadiene) using a Perkin-Elmer 621 spectrophotometer. Diffuse reflectance spectra were recorded on a Unicam SP-735 spectrometer using freshly sublimed MgO as a reflecting surface. Magnetic susceptibility was determined at room temperature on a *Guoy* balance. *Mössbauer* spectral measurements were made at room and liquid nitrogen temperatures. The isomer shift and quadrupole splitting values were recorded with respect to natural iron. Thermal analysis was carried out by means of MOM Budapest Derivatograph (Type: Paulik, Paulik and Erdey) at a heating rate of 5°/min and covering a temperature range of 20–800°. All manipulations were carried out in a dry box filled with nitrogen.

Results and Discussion

$Fe_3O(O_2CCF_3)_7 \cdot H_2O$ was prepared by a similar method adopted by *Swarts*[3]. The hydrated salt on heating under vacuum at 90° for 2 h gives $Fe_3O(O_2CCF_3)_7$. Reaction of freshly precipitated hydrated oxide of chromium(III) with trifluoroacetic acid gave a green coloured compound. Its analytical data correspond to $Cr_3O(O_2CCF_3)_7 \cdot H_2O$, which on heating to 70° *in vacuo* loses weight corresponding to loss of one molecule of water and gives $Cr_3O(O_2CCF_3)_7$. Hydrated and anhydrous trinuclear manganese(III) trifluoroacetates were prepared from the corresponding acetates by "acid exchange". All these compounds are insoluble in common non-polar organic solvents indicating polymeric nature. However, compounds slowly dissolve in trifluoroacetic acid indicating slow breakage of polymeric structure.

The IR spectra of these compounds have been recorded in 4000–200 cm^{-1} region. The salient features of the spectra and their tentative assignments are given in Table 1. The magnitude of $\Delta\nu CO_2$ ($\nu_{as}CO_2 - \nu_s CO_2$)[6,7] or the position of $\nu_{as}CO_2$ alone[8] have been used to assign the modes of coordination of the trifluoroacetate groups. The positions of $\nu_{as}CO_2$ bands and the magnitude of $\Delta\nu CO_2$ in these compounds indicate the bidentate bridging trifluoroacetate groups[9]. Medium to strong intensity bands in the 510–540 cm^{-1} region are assigned to νM_3O as has been suggested by various workers[10,11]. Other bands ascribed to trifluoroacetate group have also been assigned (Table 1).

The low magnetic moment values of iron(III) and chromium(III) compounds [$Fe_3O(O_2CCF_3)_7 \cdot H_2O$, 3.25; $Fe_3O(O_2CCF_3)_7$, 3.18; $Cr_3O(O_2CCF_3)_7 \cdot H_2O$, 2.68; $Cr_3O(O_2CCF_3)_7$, 2.61 BM] are in the same range as observed for their corresponding carboxylates[12–14]. These low values may be ascribed to antiferromagnetic interaction as well as polymeric nature in the solid state. The magnetic moments of manganese(III) compounds $Mn_3O(O_2CCF_3)_7 \cdot H_2O$, 4.90; $Mn_3O(O_2CCF_3)_7$, 4.83 BM are close to high spin octahedral manganese(III) complexes[15].

Table 1. *IR spectra* (cm^{-1}) *for* $M_3O(O_2CCF_3)_7$

M = Fe ($\cdot H_2O$)	M = Fe	M = Cr ($\cdot H_2O$)	M = Cr	M = Mn ($\cdot H_2O$)	M = Mn	Assignments
3300–3100 b	—	3180 mb	—	3180 mb	—	νOH
1650 sb	1625 sb	1650 sb	1650 sb	1660 s	1660 s	$\nu_{as}CO_2$
1470 m	1475 sb	1485 s	1435 sb	1450 s	1450 s	$\nu_s CO_2$
1430 m	1440 sb					
1200 m	1200 m	1200 m	1200 s	1185 sb	1200 m	νCF
1160 m	1155 m	1140 m	1150 m	1125 s	1160 m	νCF
855 s	855 s	850 s	845 s	840 s	850 s	$\nu C—C$
788 s	795 s	790 s	790 s	788 s	795 s	δOCO
715 s	728 s	720 s	725 s	715 s	720 s	δCF
695 m	665 m	652 w	645 m	622 m	630 s	δCF
595 m	600 m	610 m	600 w	610 w	605 w	δOCO
540 m	530 m	520 s	520 s	510 s	510 s	νM_3O
—	—	425 m	420 m	435 m	460 m	δOCO
340 m	340 m	330 m	330 m	—	—	δOCO

Long et al.[11] studied the electronic spectra of trinuclear iron carboxylates and assigned the bands in the region 1000–909 nm and 675–649 nm to $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4A_{2g}$, respectively. The bands [$Fe_3O(O_2CCF_3)_7 \cdot H_2O$: 965, 570; $Fe_3O(O_2CCF_3)_7$: 965, 540 nm] may be assigned to the above transitions. The bands at 350 and 375 nm, respectively, in the two compounds may be assigned to charge transfer bands as in $Fe(O_2CCF_3)_3$[16]. The diffuse reflectance spectra of

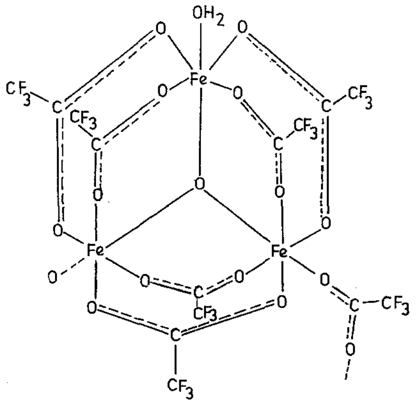

Fig. 1. Probable structure of $Fe_3O(O_2CCF_3)_7 \cdot H_2O$

Table 2. *Diffuse reflectance spectra (nm)*

Assignments	$Cr_3O(O_2CCF_3)_7 \cdot H_2O$	$Cr_3O(O_2CCF_3)_7$
${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$	700	700
${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F)	620	600
${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F)	460	450
${}^4A_{2g} \rightarrow {}^4T_{1g}$ (P)	300	280

$Cr_3O(O_2CCF_3)_7 \cdot H_2O$ and its anhydrous analog have been tabulated in Table 2 with tentative assignments. The bands are in good agreement with those reported for other trinuclear chromium species[16,17].

The diffuse reflectance spectra of trinuclear managanese(III) trifluoroacetates show broad bands with maxima at ca. 470 nm, which may be assigned to ${}^5E_g \rightarrow {}^5T_{2g}$ transitions[18–21] indicating hexa-coordination of manganese.

The isomer shift, δ and the quadrupole splitting ΔE_q [$Fe_3O(O_2CCF_3)_7 \cdot H_2O$: δ, 0.51 (25°); 0.61 (—195°). ΔE_q, 1.56 (25°); 1.98 (—195°). $Fe_3O(O_2CCF_3)_7$: δ, 0.41 (25°); 0.53 (—195°). ΔE_q, 1.39 (25°); 1.73 (—195°) $mm\,s^{-1}$] have the magnitude expected for high spin iron(III) complexes[22], and show as expected a slight increase with decrease in temperature[11]. These values are comparable with those of other trinuclear iron(III) carboxylates[11]. On comparison, it is further revealed that the change in carboxylate group with varying electron withdrawing power has little effect on the s-electron density at the iron nucleus. The larger quadrupole splitting values of trinuclear iron(III) trifluoroacetates as compared to those of other trinuclear iron(III) carboxylates are attributed to the greater electronegativity of the trifluoroacetate groups.

The large line width (ca. 4 $mm\,s^{-1}$) of the quadrupole split lines of these compounds may be the consequence of the iron atoms being non-equivalent[11]. Some type of relaxation caused by line broadening is ruled out because the *Mössbauer* parameters do not exhibit large temperature dependence. The *Mössbauer* spectrum of $Fe_3O(O_2CCF_3)_7 \cdot H_2O$ shows two types of iron sites. The area ratio (2 : 1) of the peaks indicate that out of the three iron atoms, one has a different environment from the other two. This may be explained on the basis of the fact that one water molecule is present in the complex, which is confirmed by thermal analysis, whereas $Fe_3O(O_2CCF_3)_7$ has only one type of iron atoms.

Thermograms of $M_3O(O_2CCF_3)_7$, M = Cr, Mn, Fe, were recorded up to 750°. All three compounds decompose in a similar manner in a single step with the evolution of $(CF_3CO)_2O$. The residue is M_2O_3. Total mass loss in each case is in agreement with the values calculated on the basis of their proposed formulae. The evolution of $(CF_3CO)_2O$ during decomposition of these compounds was confirmed from the IR spectra of the volatiles obtained by heating the compounds separately in an evacuated system. On the basis of the present studies the compounds with same stoichiometry are isostructural being μ_3-oxo-trinuclear clusters, metals being hexacoordinated.

Pyridine Complexes of $M_3O(O_2CCF_3)_7$: These trinuclear metal trifluoroacetates give $[M_3O(O_2CCF_3)_6 \cdot 3\,Py]^+ [O_2CCF_3]^-$, M = Cr, Mn, Fe, on reaction with pyridine. These formulations have been suggested in analogy to some known adducts of trinuclear basic chromium(III) acetate[17]. The IR spectra of these complexes show all the characteristic bands which were observed in the parent trifluoroacetates. The magnetic moments of these complexes [$Cr_3O(O_2CCF_3)_7 \cdot 3\,Py$, 2.65; $Mn_3O(O_2CCF_3)_7 \cdot 3\,Py$, 4.86; $Fe_3O(O_2CCF_3)_7 \cdot 3\,Py$, 3.2 BM] are in the same range as those of the parent compounds indicating that the basic frame work of their structures is not disturbed on complexation. New bands at ca. 1680 cm^{-1} and $\Delta\nu CO_2$ of the order of 240 cm^{-1} show the presence of ionic trifluoroacetate group as well, as warranted by the proposed structure [KO_2CCF_3: $\nu_{as}CO_2$, 1678; ν_sCO_2, 1437; $\Delta\nu CO_2$, 241 cm^{-1}][23], in addition to bridging trifluoroacetate groups. The shift of ν_{8a}, ν_{6a} and ν_{16b} to higher frequencies at ca. 1600, ca. 620 and ca. 430 cm^{-1}, respectively, and an appearance of a medium intensity band at ca. 1250 cm^{-1} in these complexes show that pyridine is coordinated to metal atoms[24].

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