

Trifluoroacetates of Iron(III)

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The trifluoroacetates of the type $MFe(O_2CCF_3)_4$ (where $M = Me_4N, K, Rb, Cs$), $Cs_2Fe(O_2CCF_3)_5$ and $Cs_3Fe(O_2CCF_3)_6$ have been prepared by the reaction of anhydrous $FeCl_3$, MCl/MBr and AgO_2CCF_3 in nitromethane. The compounds have been characterized on the basis of their elemental analyses, molar conductivities, magnetic susceptibilities, and IR, X-ray diffraction and Mössbauer data.

In alkylammonium and cesium tetranitratoferrates(III)¹ the $Fe(NO_3)_4$ moiety contains bidentate nitrate groups². Since trifluoroacetate ion is isoelectronic with nitrate ion, it was considered of interest to prepare and characterise analogous trifluoroacetate derivatives, viz. $MFe(O_2CCF_3)_4$ [where $M = Me_4N(1), K(2), Rb(3), Cs(4)$], $Cs_2Fe(O_2CCF_3)_5(5)$ and $Cs_3Fe(O_2CCF_3)_6(6)$. Preparation and characterisation of transition metal trifluoroacetates have been reported earlier³⁻⁵ from our laboratory.

Materials and Methods

All the experiments were conducted under dry N_2 atmosphere. Tetramethylammonium chloride was recrystallised from water and dried *in vacuo*. Metal halides ($KCl, RbCl, CsCl, CsBr$; all BDH, AR) were used after drying in an oven at $110-20^\circ C$. Anhydrous $FeCl_3$ (ref. 6) and silver trifluoroacetate⁷ were prepared by literature methods. Tetramethylammonium tetrachloroferrate(III) was prepared in almost quantitative yield by refluxing together 10 mmol each of anhydrous $FeCl_3$ and Me_4NCl in acetonitrile (30 ml) (Found: Fe, 20.05; Cl, 51.98, Me_4NFeCl_4 requires Fe, 20.52; Cl, 52.2%).

The solvents were dried and distilled before use. Cesium and ferric trifluoroacetates were prepared by known methods⁸. Trifluoroacetic acid (BDH, AR) was distilled under N_2 atmosphere before use, b.p. $71.5^\circ/745$ torr.

Preparation of tetramethylammonium and potassium tetrakis(trifluoroacetato)ferrates(III)

(a) Me_4NFeCl_4 (14 mmol) was mixed with AgO_2CCF_3 (56 mmol) in nitromethane (50 ml) and stirred for 2 hr. The precipitated silver chloride was

filtered off under N_2 atmosphere and the filtrate evaporated to dryness. The dry mass was stirred with dry ether for 1 hr to get compound (1) as a powdery solid, which was filtered and dried *in vacuo*; yield 96%.

(b) Potassium chloride (7 mmol) and anhydrous $FeCl_3$ (7 mmol) were mixed with trifluoroacetic acid (75 ml) and slowly refluxed under dry N_2 atmosphere for 40 hr. After removing excess trifluoroacetic acid, red coloured sticky mass was stirred with dry ether, filtered and the desired red-coloured compound (2) dried *in vacuo*; yield 95%.

Alternatively, $KFe(O_2CCF_3)_4$ was obtained in quantitative yield by stirring for 1 hr a mixture containing 10 mmol each of KCl and anhydrous $FeCl_3$, 40 mmol of AgO_2CCF_3 and nitromethane (75 ml) for 1 hr. The reaction mixture was filtered to remove $AgCl$ and the filtrate evaporated *in vacuo*. The gel-like mass obtained was stirred with ether, to obtain a powdery solid, which was filtered and dried *in vacuo*. Compounds (3-6) were obtained in an analogous manner. For 5 and 6, in place of $CsCl, CsBr$ was used.

Physical measurements

The IR spectra ($2000-400\text{ cm}^{-1}$) of compounds (1-6) were recorded as nujol/hexachlorobutadiene mulls in $AgCl$ and KBr plates using Perkin-Elmer 621 spectrophotometer. Magnetic susceptibilities were determined on a Guoy balance. Conductances of $10^{-3}M$ solutions of compounds (1-6) were determined using a Philips conductivity bridge type PR 9500. Mössbauer spectra were recorded on a Harwell Mössbauer spectrometer in the acceleration mode employing ORTEC model 620 multichannel analyser. The source used was a $25\text{ mCi } ^{57}\text{Co}$ in Rh matrix. The spectrometer was calibrated against a standard iron foil. X-ray powder diffraction data were obtained on a Phillips diffractometer model PW 1729 using CuK_α radiation and nickel

Table 1—Analytical Data of Various Trifluoroacetates

Compound	Found (Calc.)%		
	Fe	F	C
Me ₄ N Fe(O ₂ CCF ₃) ₄ (1)	9.96 (9.62)	39.09 (39.18)	24.70 (24.75)
K Fe(O ₂ CCF ₃) ₄ (2)	10.08 (10.21)	41.09 (41.68)	17.02 (17.55)
Rb Fe(O ₂ CCF ₃) ₄ (3)	9.75 (9.43)	38.12 (38.42)	15.80 (16.17)
Cs Fe(O ₂ CCF ₃) ₄ (4)	9.05 (8.75)	35.76 (35.58)	14.40 (14.98)
Cs ₂ Fe(O ₂ CCF ₃) ₅ (5)	6.88 (6.31)	31.98 (32.14)	13.20 (13.53)
Cs ₃ Fe(O ₂ CCF ₃) ₆ (6)	5.13 (4.94)	30.10 (30.19)	12.34 (12.71)

*H, 2.10(2.06); and N, 2.50(2.40)

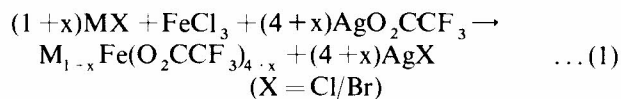
Table 2—X-ray Powder Diffraction Data [*d*-values in Å]

CsFe(O ₂ CCF ₃) ₄	Fe(O ₂ CCF ₃) ₃	CsO ₂ CCF ₃	CsO ₂ CCF ₃
8.6833	14.5265	8.6852	2.0113
5.5579	9.4891	5.6007	1.9926
4.8382	4.2586	4.4123	1.9847
4.4163	3.5673	3.9639	1.9208
4.3584	3.2325	3.9402	1.8686
3.9252	2.4188	3.8519	1.8125
3.8931	2.4094	3.8256	1.8103
3.8427	2.3085	3.7911	1.7952
3.8290	2.2210	3.0518	1.7759
3.8051	2.2140	3.0045	
3.7785	2.0940	2.5640	
3.6954	2.0928	2.5258	
3.6834	1.9682	2.4728	
	1.8082	2.3884	
	1.7236	2.3475	
	1.6654	2.2939	
	1.6326	2.1017	
	1.4900	2.0962	
	1.4771		

filter. The samples were run between 4° to 70° (*d*-values in Å) with 10°/min rotation.

Results and Discussion

All the trifluoroacetates (1-6) were formed in accord with Eq. (1).



Compounds (1-6) are red-coloured hygroscopic solids, insoluble in non-polar organic solvents indicating polymeric structures. However, their slow dissolution in trifluoroacetic acid indicates slow cleavage of the polymeric structures. Table 1 gives the analytical data of compounds (1-6). Molar conductances of 10⁻³M solutions of 1-6 in nitromethane (80-100 ohm⁻¹ cm² mol⁻¹) indicates that these behave as 1:1 electrolytes⁹.

The IR spectra of compounds 1-6 have been examined in the range 2000-400 cm⁻¹. The magnitude of $\Delta\nu\text{COO}^- (\nu_{\text{as}}\text{COO}^- - \nu_{\text{s}}\text{COO}^-)^{10,11}$ or the position of $\nu_{\text{as}}\text{COO}^-$ alone has been used to assign mode¹² of coordination of the trifluoroacetate groups. The difference $\Delta\nu\text{COO}^-$ in 1-6 [$\nu_{\text{asy}}\text{CO}_2(\nu_{\text{sym}}\text{CO}_2)$: 1, 1700 sh, 1660 s (1460 m, 1400 m); 2, 1680, 1655 s (1465 m, 1400 sb); 3, 1685 s, 1655 s (1420 m, 1400 sb); and 4, 1700 sh, 1655 s (1420 m, 1400 sb)] indicates the presence of both uni- and bi-dentate trifluoroacetate groups^{13,14}. The following bands have also been assigned: 1150-1205 (νCF_3), 830-855 ($\nu\text{C}-\text{C}$), 785-790 (δOCO), 530-720 (CF_3 band and $\nu\text{M}-\text{O}$). A strong band at 1620 with a shoulder at 1660 cm⁻¹ and a band at 1410 cm⁻¹ have been assigned to $\nu_{\text{as}}\text{COO}^-$ and $\nu_{\text{s}}\text{COO}^-$ respectively in compound (5). The corresponding bands in compound (6) appear at 1660 and 1460 cm⁻¹; the positions and the intensity of bands and the magnitude of $\Delta\nu\text{COO}^-$ in (5) and (6) indicate bidentate bridging trifluoroacetate groups.

To establish the identity of these trifluoroacetates as definite entities, X-ray powder diffraction data of CsFe(O₂CCF₃)₄, CsO₂CCF₃ and Fe(O₂CCF₃)₃ were obtained. The observed *d*-values (Å) are given in Table 2. The *d*-values of CsFe(O₂CCF₃)₄ (4) are found to be different from those of CsO₂CCF₃ and Fe(O₂CCF₃)₃, ruling out the possibility of the presence of trifluoroacetates as free entities in CsFe(O₂CCF₃)₄. It is reasonable to assume that other M_{1+x}Fe(O₂CCF₃)_{4+x} are also definite entities rather than stoichiometric mixtures.

Room temperature magnetic moments of 1 (2.10), 2 (2.18) and 3 (2.40 B.M.) indicate these to be low spin complexes. The magnetic moments of 4 (3.47) and 5 (3.03 B.M.) point to the presence of some antiferromagnetic coupling¹⁵ in these compounds. The magnetic moment of 6 (5.74 B.M.) is slightly less than the spin only value of 5.92 B.M. for the high spin iron(III) complexes.

The Mössbauer spectra of compounds (1 and 2) were recorded both at room and liquid N₂ temperatures, while the spectrum of 3 was recorded only at room temperature. The spectra of 4 and 5 were of poor quality, whereas a large proportion of Cs in 6 gave a flat spectrum.

The Mössbauer spectra of 1 at room temperature and liquid N₂ temperature are shown in Fig. 1. The least square fitted Mössbauer parameters at room temperature (corresponding values at liquid N₂ temperature are given in parentheses) are: 1, δ , 0.42, 0.43(0.54, 0.55); ΔE_{q} , 0.34, 1.11(0.88, 1.54); 2, δ , 0.43, 0.62(0.59, 0.54); ΔE_{q} , 0.87, 1.28(1.19, 0.87); 3, δ , 0.51, 0.53; ΔE_{q} , 0.69, 1.25 mms⁻¹. The isomeric shift values are with respect to iron and the estimated error in the values of δ and ΔE_{q} are ± 0.02 mms⁻¹. Mössbauer

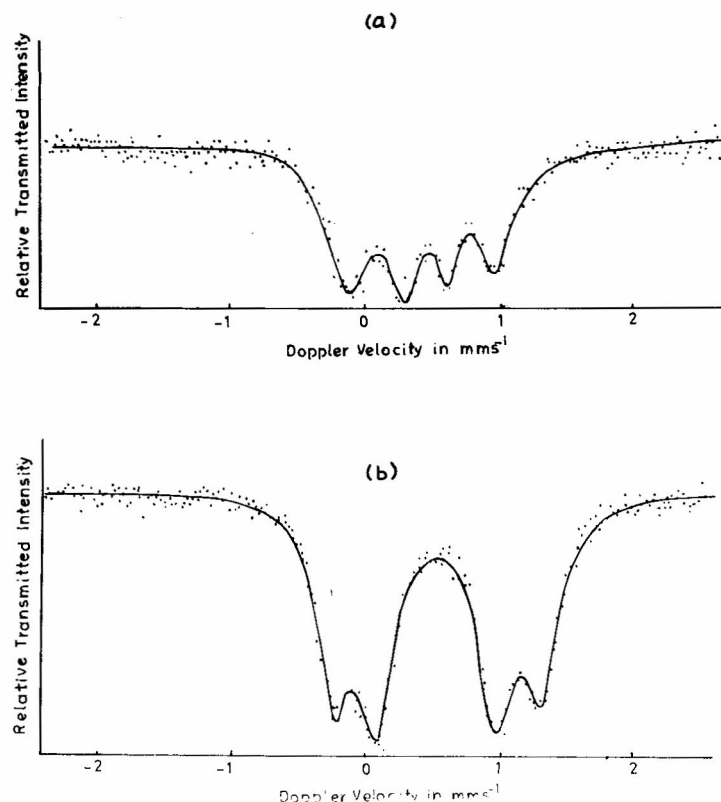
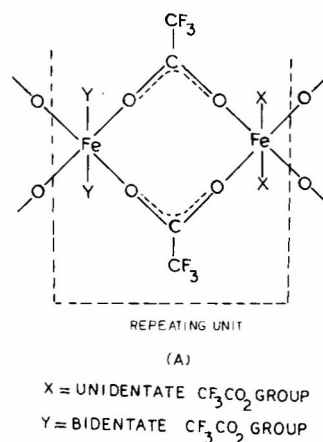


Fig. 1—Mössbauer spectra of $\text{Me}_4\text{NFe}(\text{O}_2\text{CCF}_3)_4$ (compound 1) at room temperature (a) and liquid nitrogen temperature (b)

parameters of compound (1) indicate two iron sites. The close isomer shift values¹⁶ at room and liquid N_2 temperatures indicate that these two sites have almost same s -electron density around iron nucleus. On the other hand, quadrupole splitting has reasonably different values for the two sites and show an increase with decrease in temperature. The significantly large ΔE_q values at liquid N_2 temperature show that both the iron sites are in low spin state, an observation in agreement with the conclusion drawn from its magnetic moment. The different values of quadrupole splitting indicate different surroundings for the two iron sites. A small temperature-dependent anisotropy in the area ratio of individual lines of a doublet indicates the possible presence of Goldanskii-Karyagin effect. The polymer structure (A) has been proposed for $\text{Fe}(\text{O}_2\text{CCF}_3)_4$ on the basis of Mössbauer and IR spectra. The isomer shift and the quadrupole parameters of compounds (2 and 3) are comparable to those of 1 indicating that 1-3 have almost similar structures. The spectrum of 4, though could not be deconvoluted, yet indicated two iron sites as in 1-3. These studies indicate that unlike tetranitratoferrate(III) derivatives, compounds 1-4 are polymeric having hexacoordinated iron(III).



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