

Research Article

Synthesis and Characterization of Metal Tribromoacetates and Their Alkali Metal Derivatives

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Complexes of composition $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$, $[(\text{Me}_4\text{N})_2][\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, $\text{K}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, $\text{Rb}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, $\text{Cs}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, $[(\text{Me}_4\text{N})_2][\text{Co}(\text{O}_2\text{CCBr}_3)_4]$, $[(\text{Me}_4\text{N})_2][\text{Mn}(\text{O}_2\text{CCBr}_3)_4]$, $[(\text{Me}_4\text{N})_2][\text{Cu}(\text{O}_2\text{CCBr}_3)_4]$, and $[(\text{Me}_4\text{N})_2][\text{Ni}(\text{O}_2\text{CCBr}_3)_4]$ have been prepared by metathetical reactions using nitromethane as solvent. All these compounds have been characterized by elemental analysis, molar conductance, infrared, reflectance and thermogravimetric studies.

1. Introduction

In continuation of our previous studies [1–8] of the solvolytic reactions and synthesis of bromoacetates of metals such as Ti(IV), V(III), Cr(III), Al(III), and Mn(II), and their complexes with various bases, in the present investigation, we report the synthesis of iron (III), cobalt(II), nickel(II), copper(II), and manganese(II) tribromoacetates and their alkali metal derivatives. Synthesis, reactivity, and structures of mono- and dihaloacetato complexes of copper(I) and copper(II) have been reported [9]. Recently the synthesis of coordination compounds via dehalogenation of zinc bromoacetate in presence of some amines have also been reported [10]. Anhydrous iron(III) chloride and bromide solvolyse in acetic acid to form $\text{FeX}(\text{O}_2\text{CCH}_3) \cdot n\text{H}_2\text{O}$, where $\text{X} = \text{Cl}^-$, Br^- [11]. Iron(III) chloride forms $\text{Fe}_3\text{Cl}_3(\text{O}_2\text{CCH}_3)_6 \cdot \text{HO}_2\text{CCH}_3$ [12] on heating with acetic acid. These observations could not be repeated. At room temperature iron(III) chloride with acetic acid gives $\text{Fe}_2(\text{OH})_2\text{Cl}_2[\text{O}_2\text{CCH}_3]_2 \cdot 2\text{HO}_2\text{CCH}_3 \cdot \text{H}_2\text{O}$ while it forms $\text{Fe}_2(\text{OH})_2\text{Cl}_2[\text{O}_2\text{CCH}_3]_2 \cdot 2\text{HO}_2\text{CCH}_3$ at 130°C. In spite of perfectly anhydrous reagent and dry condition, water was always introduced in the reaction. This concludes that affinity of Fe^{3+} ion for water is so strong that it can abstract water from anhydrous acetic acid. Anhydrous

iron(III) acetate was prepared metathetically from iron(III) chloride and silver acetate in tetrahydrofuran [13]. Anhydrous iron(III) trifluoroacetate was prepared from iron(III) chloride and silver trifluoroacetate [14] in nitromethane.

The reaction of anhydrous iron(III) chloride with fused tribromoacetic acid in different stoichiometric ratios have been carried out. The resulting compounds were characterized by their elemental analysis, molar conductance, infrared, and thermogravimetric studies. The molar ratios of various reactants has been very carefully controlled and the reaction time also needs to be carefully observed.

2. Experimental

2.1. Preparation of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ and $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$. Anhydrous Iron (III) chloride (3.25 g, 20 mmol) was refluxed with tribromoacetic acid (4.88 g, 40 mmol) in CCl_4 under nitrogen atmosphere for about 8 hours. A yellow coloured solid compound separated out. It was filtered and washed with dichloromethane. The solid was finally dried under vacuum. Elemental analysis corresponds to the composition $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$.

The compound $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ (4.101 g, 3 mmol) was refluxed with fused tribromoacetic acid (0.89 g, 3 mmol) in

TABLE 1: Amount, colours, yields, and analysis of $(\text{Me}_4\text{N})_2\text{MCl}_4$, ($\text{M} = \text{Mn, Co, Ni, Cu}$).

Anhydrous metal chloride	Weight g (mmol)	Wt. of $(\text{Me}_4\text{N})\text{Cl}$ g (mmol)	Product obtained	Colour of product	Yield (%)	Analysis found (calculated)	
						M	Cl
MnCl_2	1.259 (10.00)	2.19 (20.00)	$(\text{Me}_4\text{N})_2\text{MnCl}_4$	Light green	78	15.72 (15.93)	40.90 (41.16)
CoCl_2	1.299 (10.00)	2.19 (20.00)	$(\text{Me}_4\text{N})_2\text{CoCl}_4$	Blue	78	16.74 (16.88)	40.24 (40.69)
NiCl_2	1.307 (10.00)	2.19 (20.00)	$(\text{Me}_4\text{N})_2\text{NiCl}_4$	Greenish	68	16.46 (16.83)	40.43 (40.72)
CuCl_2	1.3455 (10.00)	2.19 (20.00)	$(\text{Me}_4\text{N})_2\text{CuCl}_4$	Dark yellow	81	17.58 (17.96)	40.09 (40.17)

carbon tetrachloride for 6 hours with constant stirring. A light pink solid separated out. It was filtered and washed with dichloromethane and finally dried under vacuum. Elemental analysis gave the composition $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$.

Finally, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ (3.255 g, 2 mmol) was refluxed with excess of tribromoacetic acid (0.594 g, 2 mmol) in carbon tetrachloride till the evolution of HCl gas ceased and whole of the solid dissolved to give an orange coloured solution. The solution was evaporated to dryness and an orange red compound $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ was obtained. This compound was also prepared by direct refluxing of anhydrous iron(III) chloride with excess of tribromoacetic acid by a method analogous to reported in literature [6].

2.2. Preparation of Tetramethylammonium tetrachloroferrate(III), That Is, $[\text{Me}_4\text{N}][\text{FeCl}_4]$. Anhydrous iron(III) chloride (1.62 g, 10 mmol) was mixed with tetramethylammonium chloride in carbon tetrachloride (30 mL). The contents were refluxed for 4 hours. Yellow coloured solid formed was filtered and washed with dichloromethane and then dried under vacuum. (Yield 80%, Found: Fe = 20.25, Cl = 51.80; Calculated for $[\text{Me}_4\text{N}][\text{FeCl}_4]$ Fe = 20.54, Cl = 52.23%).

2.3. Preparation of $[\text{Me}_4\text{N}][\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$. $[\text{Me}_4\text{N}][\text{FeCl}_4]$ (2.72 g, 10 mmol) in nitromethane was taken in round bottom flask equipped with anhydrous calcium chloride guard tube. To this was added silver tribromoacetate (16.16 g, 40 mmol). The resulting solution was evaporated to dryness and solid thus obtained was kept in diethylether and stirred well for 4 hours. Finally the solid mass was filtered and dried under vacuum in an atmosphere of nitrogen. This is a dark red coloured compound, insoluble in common organic solvents but soluble in nitromethane and acetonitrile.

2.4. Preparation of $\text{K}[\text{Fe}(\text{CBr}_3\text{COO})_4]$, $\text{Rb}[\text{Fe}(\text{CBr}_3\text{COO})_4]$, and $\text{Cs}[\text{Fe}(\text{CBr}_3\text{COO})_4]$. Potassium chloride, rubidium chloride, and cesium bromide (0.745 g, 10 mmol; 1.21 g, 10 mmol, and 0.852 g, 4 mmol), anhydrous iron(III) chlorides (1.63 g, 10 mmol; 1.63 g, 10 mmol, and 0.65 g, 4 mmol), and silver tribromoacetates (16.16 g, 40 mmol; 16.16 g, 40 mmol, and 6.46 g, 16 mmol), respectively, were mixed in stoichiometric amounts in nitromethane and stirred for 8 hours. Silver halide formed, respectively, were filtered under positive pressure of dry nitrogen and the corresponding filtrate were evaporated to a very small volume. These were treated with dry diethylether and in each case jelly like mass was formed. The corresponding masses were evaporated to dryness under vacuum under the atmosphere of nitrogen. On analysis, the

products formed were found $\text{K}[\text{Fe}(\text{CBr}_3\text{COO})_4]$ (Yield 80%), $\text{Rb}[\text{Fe}(\text{CBr}_3\text{COO})_4]$ (Yield 82%) and $\text{Cs}[\text{Fe}(\text{CBr}_3\text{COO})_4]$ (Yield 81%).

2.5. Preparation of Bis(Tetramethylammonium)Tetrachloro metallates(II), That Is, $(\text{Me}_4\text{N})_2\text{MCl}_4$ Where $\text{M} = \text{Mn, Co, Ni, Cu}$. In a typical preparation, anhydrous metal chloride and tetramethylammonium chloride in 1 : 2 molar ratio were separately dissolved in absolute ethanol. On mixing the two solutions, a solid was precipitated out which was filtered and dried in vacuum. Amount, colour, yield, and elemental analysis of various products obtained are given in Table 1.

2.6. Preparation of Bis(Tetramethylammonium) Tetratrimoacetato Metallates(II) of Mn, Co, Ni, and Cu. These tribromoacetates were prepared by mixing the Bis(tetramethylammonium) tetrachloro metallates, that is, $[\text{Me}_4\text{N}]_2[\text{MnCl}_4]$ (1.35 g); $[\text{Me}_4\text{N}]_2[\text{CoCl}_4]$ (1.047 g); $[\text{Me}_4\text{N}]_2[\text{NiCl}_4]$ (1.046 g); $[\text{Me}_4\text{N}]_2[\text{CuCl}_4]$ (1.061 g), respectively, with silver tribromoacetate (4.848 g, 12 mmol in each case) in nitromethane in stoichiometric amounts. Silver chloride formed after stirring for 8 hours was filtered under dry nitrogen. Filtrate was evaporated to dryness under nitrogen atmosphere. Product obtained were $[\text{Me}_4\text{N}]_2[\text{Mn}(\text{O}_2\text{CCBr}_3)_4]$ (light Green in colour, yield 84%); $[\text{Me}_4\text{N}]_2[\text{Co}(\text{O}_2\text{CCBr}_3)_4]$ (pinkish violet in colour, yield 85%); $[\text{Me}_4\text{N}]_2[\text{Ni}(\text{O}_2\text{CCBr}_3)_4]$ (green in colour, Yield 80%); $[\text{Me}_4\text{N}]_2[\text{Cu}(\text{O}_2\text{CCBr}_3)_4]$ (bluish green in colour, yield 85%).

3. Results and Discussions

Anhydrous iron(III) chloride (3.25 g, 20 mmol) when refluxed with fused tribromoacetic acid (11.88 g, 40 mmol) under nitrogen atmosphere with stirring for 9-10 hours, a yellow coloured solid compound separated out and it was filtered and washed with anhydrous dichloromethane and finally dried in vacuum. The elemental analysis corresponds to $\text{Fe}_2\text{Cl}_2[\text{O}_2\text{CCBr}_3]_4$. This compound $\text{Fe}_2\text{Cl}_2[\text{O}_2\text{CCBr}_3]_4$ (6.837 g, 5 mmol) was refluxed with tribromoacetic acid (1.1845 g, 5 mmol) in carbon tetrachloride for about 4 hours with stirring. A light pink solid separated out which was filtered and washed with anhydrous dichloromethane and finally dried under vacuum. The elemental analysis corresponds to $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$. This compound $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ (3.255 g, 2 mmol) was refluxed with excess tribromoacetic acid (0.594 g, 2 mmol) in carbon tetrachloride till evolution of HCl gas ceased and whole

TABLE 2: Physical and analytical data, molar conductance, and magnetic moments of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$.

Compound	Colour	Analysis (%) found (calculated)						$\mu_{\text{eff.}}$ (B.M.)	Molar conductance $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$ in CH_3CN
		M	Br	Cl	C	H	N		
$\text{Fe}(\text{O}_2\text{CCBr}_3)_3$	Orange red	5.86 (5.92)	75.78 (76.28)	—	7.42 (7.63)	—	—	3.48	10.28
$\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$	Yellow	7.96 (8.17)	69.89 (70.24)	4.95 (5.19)	6.89 (7.02)	—	—	4.52	46.82
$\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$	Light pink	6.67 (6.86)	72.15 (73.74)	2.15 (2.18)	7.15 (7.37)	—	—	3.54	23.48

TABLE 3: Infrared spectral bands (cm^{-1}) of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$.

$\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$	$\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$	$\text{Fe}(\text{O}_2\text{CCBr}_3)_3$	Assignments
1655 s	1635 s	1680, 1630	COO asym.str.
1480 m	1470 m	1488 s	COO sym.str.
1200 s	1195 s	1205 s	CBr_3 str.
1180 m	1160 sh	1170	CBr_3 str.
860 s	850 w	862	C–C str.
790 s	790 m	800 s	O–C–O deform.
730 s	720 s	742 s	CBr_3 bend.
640 s	—	670 w	—
630 s	610 s	645 w	CBr_3 bend.
520 s	530 m	545 w	CBr_3 bend.
475 m	465 w	455	M–O
385 m	—	480	CCO bend.
325 m	—	—	M–Cl
240 w	—	280 w	CBr_3 rock.

s: strong, m: medium, w: weak.

of the solid dissolved to give an orange coloured solution. This solution was evaporated to dryness. An orange red compound $\text{Fe}(\text{CCBr}_3)_3$ was obtained.

Both these compounds $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ and $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ are hygroscopic solids insoluble in common organic solvents but soluble in nitromethane and acetonitrile to give red coloured solution. It is difficult to assign particular molecular formula to these compound but they are expected to be higher polymer like other iron(III) carboxylates [15]. The dimeric formulation for $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ is favoured in view of its reaction with fused tribromoacetic acid to give $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$. Molar conductance of millimolar solutions of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ and $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ in nitromethane are 46.82 and 23.48 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, respectively, ruled out their possibility of their ionic nature. The compound $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ is found soluble in diethylether and acetonitrile. Molar conductance of its millimolar solution is 10.28 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ruling out its ionic nature (Table 2).

Infrared spectra of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$ and $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ shows strong asymmetric and medium intensity symmetric stretching modes of tribromoacetic group at 1655 cm^{-1} , 1635 cm^{-1} and 1480 cm^{-1} , 1470 cm^{-1} , respectively. $\Delta\nu_{\text{COO}}$ of the order of 175 cm^{-1} and 165 cm^{-1} are comparable to those of many metal tribromoacetate

complexes in which bridging tribromoacetate groups are anticipated.

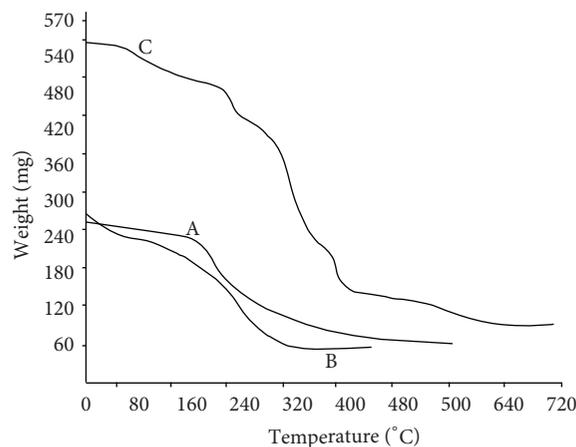
Metal-chlorine stretching frequencies usually reported [16, 17] in the range $225\text{--}375 \text{ cm}^{-1}$. For tetrahedral FeCl_4^- anion, $\nu_{\text{Fe-Cl}}$ was observed at 378 cm^{-1} . This frequency is expected to shift progressively to lower frequency as the coordination number of metal increases from 4 to 6. Although the trend may be confused by the effect of steric interactions, double bondings and differences in a d-subshell population [18]. In $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, the medium intensity band at 325 cm^{-1} is assigned to Fe-Cl stretching mode. In case of $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ this band could not be assigned due to poorly resolved spectrum observed in the lower region.

Similar infrared spectra was observed for $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ what one obtained from the reaction of $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ with fused tribromoacetic acid and also by metathetical reactions of ferric chloride with silver tribromoacetate. The magnitude of $\nu_{\text{asym COO}}$ band in $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ indicate the presence of unidentate and bidentate bridging tribromoacetate groups. Some important assignments are given in Table 3.

The ultraviolet and visible reflectance spectrum of $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ have been reported and assignments have been made on the basis of octahedral environment around the metal atom. The diffused reflectance spectra of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ in

TABLE 4: Diffused reflectance spectra (cm^{-1}) of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$.

$\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$	$\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$	$\text{Fe}(\text{O}_2\text{CCBr}_3)_3$	Assignments
495 Sh	460	519	${}^6A_{1g}$ to ${}^4A_{1g}$ (G)
938	923	942	${}^6A_{1g}$ to ${}^4T_{1g}$ (G)
—	—	347	Charge transfer



Curve A = $\text{Fe}_2\text{Cl}_2(\text{CBr}_3\text{COO})_4$

Curve B = $\text{Fe}_2\text{Cl}(\text{CBr}_3\text{COO})_5$

Curve C = $\text{Fe}(\text{CBr}_3\text{COO})_3$

FIGURE 1: Thermogravimetric curves of $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$.

the range $200\text{--}2000\text{ cm}^{-1}$ are given in Table 4 along with the tentative assignments.

Magnetic susceptibility measurement studies of these compounds have also been made to throw more light on the nature of these compounds. In an octahedral ligand field d^5 configuration can give rise to compounds of either high spin ($S = 5/2$) or low spin ($S = 1/2$) types [19]. High-spin compounds are expected to possess magnetic moment value very close to spin only value of 5.92 B.M. and to be independent of temperature as the ground term is ${}^6A_{1g}$. The low spin compound gives rise to ${}^2T_{2g}$ and the temperature dependence of magnetic moment is a function of spin-orbit coupling parameter, that is, $\lambda = -460\text{ cm}^{-1}$. This value of wavelength leads to a magnetic moment of 2.4 B.M. which falls with temperature to approach 1.73 B.M. at 0 K. Tetrahedral complexes also leads to ${}^6A_{1g}$ ground term and for them the magnetic moments are also anticipated to be near 5.92 B.M. and to be independent of temperature.

These compounds $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ and $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ are paramagnetic having magnetic moment 4.52, 3.54 and 3.48 B.M., respectively, at room temperature. These values are significantly lower from spin only value of 5.9 B.M. which is experimentally observed for iron(III) complexes [19]. These low values suggest that like

many other iron(III) carboxylates, these tribromoacetates show some antiferromagnetic coupling between iron atoms [20].

Thermogravimetric studies have also been carried out on these complexes. T.G. curves for tribromoacetate are produced in the present discussion. DTG and DTA curve have been omitted. DTG minima have been used to locate clearly various inflection points on TG curves so that the weight changes belongs to every step are determined with greater accuracy.

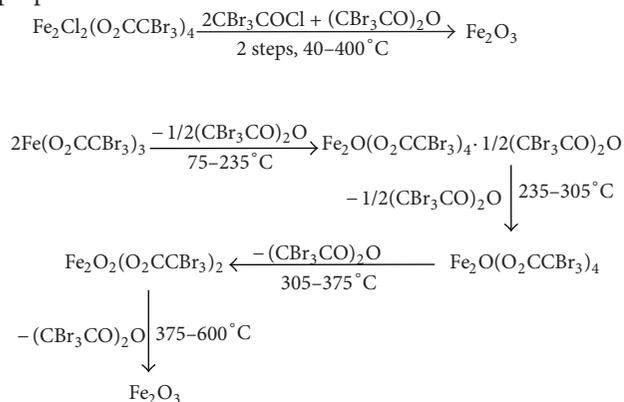
The curve for $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$ (Curve A and B, respectively, in Figure 1) show that thermal decomposition of these complexes consists of two steps as indicated by DTG curve and those two steps overlap and exact temperature at which first step is complete could not be determined. These compounds starts decomposing at 40°C and formation of final residue Fe_2O_3 is complete at 400°C . The total weight loss in each case is in agreement with the value calculated on the basis of their proposed formula. (Weight loss for $\text{Fe}_2\text{Cl}_2(\text{O}_2\text{CCBr}_3)_4$, observed: 87.70%; calc: 88.30%; weight loss for $\text{Fe}_2\text{Cl}(\text{O}_2\text{CCBr}_3)_5$, observed: 89.40%; calc: 90.17%). These two compounds were heated in vacuum at about 150°C and volatiles were trapped and identified as CCBr_3COCl and $(\text{CBr}_3\text{CO})_2\text{O}$. Tribromoacetic anhydride was characterized from infra red spectrum ($\nu_{\text{asym COO}} 1875$,

TABLE 5: Infrared spectral bands (cm^{-1}) of $\text{M}[\text{Fe}(\text{CBr}_3\text{COO})_4]$, where $\text{M} = \text{Me}_4\text{N}^+$, K^+ , Rb^+ and Cs^+ .

$[\text{Me}_4\text{N}][\text{Fe}(\text{CBr}_3\text{COO})_4]$	$\text{K}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	$\text{Rb}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	$\text{Cs}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	Assignments
1650 sh	1700 sh	1680 s	1670 sh	COO asym.str.
1580 s	1655 s	1655 s	1655 s	
1475 sh	1410	1410	1440 sh	COO sym.str.
1400 sh	1400 sh	1400 sh	1420 sh	
1200 b	1205	1200 m	1195 sh	CBr_3 str.
1150 b	1150 m	1150 m	1150 m	CBr_3 str.
885 vw	890 vw	895 vw	—	
830 s	850 s	845 s	850 s	
840 s	—	—	840 s	C–C str.
785 s	785 s	785 s	790 s	
720 s	720 s	720 s	720 s	OCO deform
655 w	655 w	650 w	660 w	CBr_3 bend
595 s	595 s	595 w	595 w	CBr_3 bend
510 s	510 s	520	510 w	CBr_3 bend
470 s	465 sh	470 s	475 s	CBr_3 bend
370 w	370 w	365 w	370 w	M–O
1475 s	—	—	—	Band due to Me_4N
945 s	—	—	—	

sh: shoulder, b: broad, m: medium, v: sharp, w: weak, vw: very weak.

1815 cm^{-1}). Thus overall thermal decomposition may be proposed as:



Tribromoacetic anhydride was obtained in good yield on heating $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ in vacuum above 200°C and trapping the gaseous products.

TG curve C for $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ in Figure 1 shows that decomposition consists of several steps. DTG minima have been projected on TG curve to get inflection point marked by small arrows on curve. The compound starts decomposing at 75°C . The weight loss up to 235°C corresponds to one half molecule of $(\text{CBr}_3\text{CO})_2\text{O}$, if we start with two molecule of $\text{Fe}(\text{O}_2\text{CCBr}_3)_3$ (weight loss, observed: 14.42%, calc: 15.25%). From 235 to 305°C another half molecule of tribromoacetic anhydride is lost. (weight loss observed: 29.80%, calc: 30.50%). Two molecules of tribromoacetic anhydride are lost between $305\text{--}600^\circ\text{C}$ in two steps, one followed immediately by the other. (weight loss observed: 90.15%, calc: 91.525%).

The compound $[\text{Me}_4\text{N}][\text{Fe}(\text{CBr}_3\text{COO})_4]$ has been prepared by metathetical reaction of $[\text{Me}_4\text{N}][\text{FeCl}_4]$ with silver tribromoacetate in 1 : 4 molar ratio using nitromethane as solvent. The resulting solution was evaporated to dryness. Solid obtained was kept in diethylether and stirred for four hours and finally the solid mass was filtered under dry nitrogen atmosphere. The composition of compound was confirmed by elemental analysis. This is a dark red coloured compound insoluble in common organic solvents but soluble in nitromethane and acetonitrile. On the basis of insolubility in organic solvents, the compound is believed to be polymeric in nature. The molar conductance of its millimolar solution in nitromethane shows it to be 1 : 1 electrolyte.

Infrared spectrum of this compound has been studied in the range $2000\text{--}200\text{ cm}^{-1}$ (Table 5). The bands at 1650 and 1580 cm^{-1} have been assigned as $\nu_{\text{asym COO}}$ and bands at 1475 and 1400 cm^{-1} due to $\nu_{\text{sym COO}}$. The splitting of both these carboxylate stretching frequency clearly indicate that unidentate tribromoacetato group is present in addition to bidentate bridging group. The magnitude of the values of $\Delta\nu_{\text{COO}}$ of 175 and 180 cm^{-1} indicate unidentate and bidentate bridging group. The bands at 1470 and 945 cm^{-1} are due to tetramethyl ammonium part of the compound. Other assignment have been made in a manner to analogous to compound reported in literature [21]. The room temperature magnetic moment for $[\text{Me}_4\text{N}][\text{Fe}(\text{CBr}_3\text{COO})_4]$ has been observed as 2.19 B.M. and this shows that it is a low spin iron complex.

Anhydrous iron(III) chloride when refluxed with tribromoacetic acid in presence of anhydrous KCl in the required stoichiometric ratio in nitromethane as solvent for about 20 hours under dry nitrogen atmosphere. A red coloured

TABLE 6: Amount, color, analysis, magnetic moments and molar conductance of $M[\text{Fe}(\text{CBr}_3\text{COO})_4]$, where $M = \text{Me}_4\text{N}^+$, K^+ , Rb^+ and Cs^+ .

Compound	Colour	Analysis (%) found (calculated)						$\mu_{\text{eff.}}$ (B.M.)	Molar conductance $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$ in CH_3CN
		Fe	M	Br	C	H	N		
$[\text{Me}_4\text{N}][\text{Fe}(\text{CBr}_3\text{COO})_4]$	Dark red	4.16 (4.25)	—	71.90 (73.06)	10.55 (10.95)	0.85 (0.91)	1.00 (1.065)	2.19	99.7
$\text{K}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	Red	4.21 (4.37)	3.00 (3.05)	74.40 (75.05)	7.35 (7.51)	—	—	2.47	85.2
$\text{Rb}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	Red	4.10 (4.22)	6.32 (6.52)	71.80 (72.43)	6.99 (7.25)	—	—	2.43	80.4
$\text{Cs}[\text{Fe}(\text{CBr}_3\text{COO})_4]$	Red	3.95 (4.07)	9.35 (9.67)	68.70 (69.90)	6.65 (6.99)	—	—	2.15	84.6

TABLE 7: Physical and analytical data of $[(\text{Me}_4\text{N})_2][\text{M}(\text{CBr}_3\text{COO})_4]$, where $M = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Mn}(\text{II})$, and $\text{Cu}(\text{II})$.

Compound	Colour	Analysis (%) found (calculated)						$\mu_{\text{eff.}}$ (BM)
		M	Br	C	H	N		
$[(\text{Me}_4\text{N})_2][\text{Co}(\text{CBr}_3\text{COO})_4]$	Violet pink	4.15 (4.23)	67.85 (69.02)	13.52 (13.80)	1.68 (1.72)	1.90 (2.01)	4.27	
$[(\text{Me}_4\text{N})_2][\text{Ni}(\text{CBr}_3\text{COO})_4]$	Green	4.15 (4.22)	67.85 (69.03)	13.45 (13.80)	1.70 (1.72)	1.95 (2.01)	3.28	
$[(\text{Me}_4\text{N})_2][\text{Mn}(\text{CBr}_3\text{COO})_4]$	Pink	3.89 (3.96)	67.65 (69.22)	13.59 (13.84)	1.70 (1.73)	1.98 (2.02)	6.15	
$[(\text{Me}_4\text{N})_2][\text{Cu}(\text{CBr}_3\text{COO})_4]$	Bluish green	4.40 (4.55)	66.80 (68.79)	13.48 (13.75)	1.69 (1.72)	1.96 (2.01)	2.00	

solution is obtained. This red coloured solution on evaporation to a small volume, red coloured sticky mass was formed, and this mass was dissolved in diethylether and this was evaporated to dryness in vacuum. The elemental analysis of this compound corresponds to $\text{K}[\text{Fe}(\text{CBr}_3\text{COO})_4]$ as shown in Table 6.

In a typical preparation alkali metal halide, anhydrous iron(III) chloride, and silver tribromo acetate were mixed in stoichiometric ratio in nitromethane and stirred for four hours. Silver halide was filtered under positive pressure of dry nitrogen and filtrate was evaporated to a very small volume and this was treated with diethylether. A jelly like mass was formed. This mass was evaporated to dryness. All these compounds are red in colour, extremely hygroscopic solid which are insoluble in non-polar organic solvents but soluble in acetonitrile and nitromethane. Molar conductance value of their millimolar solutions of $\text{K}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, $\text{Rb}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$, and $\text{Cs}[\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$ indicate them to be 1:1 electrolyte in nitromethane as expected from empirical formula of these complexes. An interesting observation regarding these complexes is that unlike $[\text{Me}_4\text{N}][\text{Fe}(\text{O}_2\text{CCBr}_3)_4]$ these compounds form jelly like solid when these compounds dissolved in diethylether and that may be attributed to their polymeric structure with large interstitial space in polymeric layer and solvent molecule get embedded in those spaces.

Infrared spectra of these compounds have been recorded in range $2000\text{--}200 \text{cm}^{-1}$ (Table 5). The higher frequency band at 1670 , 1680 , and 1700cm^{-1} in cesium, rubidium and potassium complexes, respectively, may be assigned to $\nu_{\text{asym COO}}$ corresponding to unidentate tribromo acetate group whereas band at 1655cm^{-1} in all these compounds indicate the presence of bidentate bridging groups.

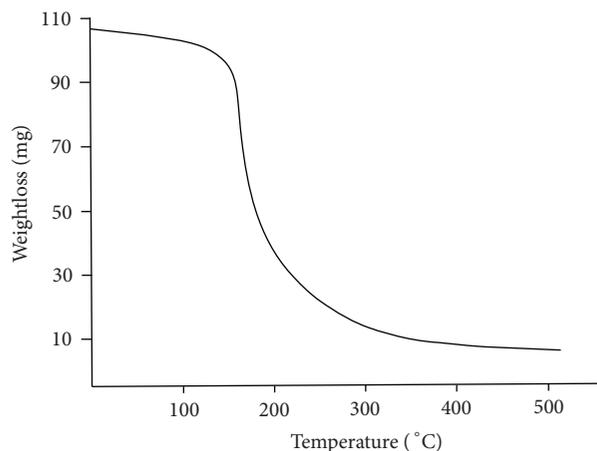
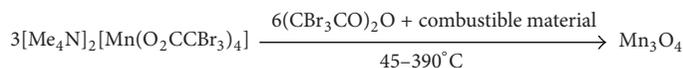
Metathetical reactions of $[\text{Me}_4\text{N}]_2[\text{MCl}_4]$ with silver tribromoacetate in nitromethane yield solution of corresponding tribromoacetate. This solution on evaporation to dryness gives the corresponding tribromoacetate complex as shown in Table 7. These complexes are hygroscopic solid, soluble in polar organic solvents acetonitrile and nitromethane but insoluble in non polar organic solvents. The reaction of $[\text{Me}_4\text{N}]_2[\text{MCl}_4]$ with tribromoacetic acid do not give completely substituted product and the metathetical reaction in absolute ethanol are not promising. The molar conductance value of millimolar solution in acetonitrile, that is, $250 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ are well in the range expected for ionic formulation.

The infrared spectra of the compound have been recorded in the range $2000\text{--}200 \text{cm}^{-1}$ (Table 8). The characteristics feature of the spectra are appearance of $\nu_{\text{asym COO}}$ at 1680cm^{-1} . The band around 1430cm^{-1} has been assigned as $\nu_{\text{sym COO}}$. The $\Delta\nu_{\text{COO}}$ values of 250cm^{-1} compare well with that of 271cm^{-1} reported for analogous compound [22]. Strong band around 1490 and 950cm^{-1} are assigned to tetramethylammonium group.

The electronic spectra in the octahedral field energy level diagram for $\text{Mn}(\text{II})$ (d^5 configuration) is same as tetrahedral field energy level sequence. It follows that same energy level diagram may be used for tetrahedral, octahedral, and cubic field. In octahedral field, this configuration gives spin forbidden as well as parity forbidden transitions and thus extremely pale yellow coloured compound were observed [23]. In tetrahedral environment, the transitions are still spin forbidden but no longer parity forbidden. The compound having light green colour and very weak band at 325 , 415 , 565 , and 695cm^{-1} in diffused reflectance spectra of Manganese complex favour a tetrahedral environment around

TABLE 8: Infrared Spectral Bands (cm^{-1}) of $[(\text{Me}_4\text{N})_2] [\text{M}(\text{CBr}_3\text{COO})_4]$, where $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Mn}(\text{II}),$ and $\text{Cu}(\text{II})$.

$[(\text{Me}_4\text{N})_2]$ $[\text{Mn}(\text{CBr}_3\text{COO})_4]$	$[(\text{Me}_4\text{N})_2]$ $[\text{Co}(\text{CBr}_3\text{COO})_4]$	$[(\text{Me}_4\text{N})_2]$ $[\text{Ni}(\text{CBr}_3\text{COO})_4]$	$[(\text{Me}_4\text{N})_2]$ $[\text{Cu}(\text{CBr}_3\text{COO})_4]$	Assignments
1685 s	1680 s	1680 s	1685 s	COO asym. Str.
1425 m	1420 s	1420 s	1425 m	COO sym. Str.
1190 m	1195 s	1200 s	1205 m	CBr_3 str.
1160 vw	1165 sh	1170 sh	1170 w	CBr_3 str.
1100 w	1105 m	1105	1170 w	CBr_3 str.
1490 s	1485 s	1488 s	1485 s	Band due to
945 s	945 s	950 s	945 s	Me_4N^+ group
835 s	830 m	830 s	835 s	C–C str.
800 s	795 s	800 s	975 s	
725 s	725 s	725 s	730 s	OCO deform.
630 s	—	630 w	630 s	CBr_3 bend
540 vw	535 w	—	545 vw	CBr_3 bend
465 vw	460 m	465 w	470 w	M–O
265 m	270 m	270 m	270 m	CBr_3 Wag.

FIGURE 2: Thermogravimetric curves of $[\text{Me}_4\text{N}]_2 [\text{Mn}(\text{CBr}_3\text{Coo})_4]$.

manganese atom. These bands are similar to other tetrahedral $\text{Mn}(\text{II})$ complexes [24]. The band at 250 cm^{-1} is assigned to charge transfer band.

In the spectra of tetrahedral cobalt(II) derivatives ν_2 [${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$] and ν_3 [${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$] transitions appear as multiple absorption in the near infrared and visible regions, respectively [25]. The assignment in the diffused reflectance spectrum of cobalt(II) have been observed by comparing it with spectra of several other tetrahedral cobalt(II) complexes in which ligands are bonded through oxygen such as $\text{Co}[(\text{C}_6\text{H}_5)_3\text{PO}]_4^{2+}$ ion [26] and $\text{Co}[(\text{Me}_2\text{N})_2\text{PO}]_4^{2+}$ ion [27]. In $[\text{Ph}_4\text{As}]_2[\text{Co}(\text{O}_2\text{CCF}_3)_4]$ [28] ν_2 and ν_3 appears at 1408 and 574 cm^{-1} , respectively. The diffused reflectance spectra of $[\text{Me}_4\text{N}]_2[\text{Co}(\text{O}_2\text{CCBr}_3)_4]$

shows ν_2 at 945 and 1230 cm^{-1} and ν_3 at 570, 645 and 695 cm^{-1} and favour tetrahedral environment around cobalt.

Octahedral and six coordinate nickel(II) complexes exhibit a spectrum involving transitions from ${}^3\text{A}_{2g}$ to ${}^3\text{T}_{2g}$, ${}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{T}_{1g}(\text{P})$ levels. These occur in the range $1420-765$, $905-495$, $525-365 \text{ cm}^{-1}$, respectively [29]. Typical nickel(II) complexes have a multiple visible band near 625 cm^{-1} assigned to ${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$ (ν_3) transitions. Weak bands on low energy side and on high energy side are assigned as spin forbidden transitions components of ${}^1\text{D}$ and ${}^1\text{G}$, respectively. A near infrared band around 1250 cm^{-1} is assigned as ${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$ (ν_2) transition. In certain circumstances the ${}^3\text{T}_1 \rightarrow {}^3\text{T}_2$ (ν_1) band can also be observed.

In diffused reflectance spectra of $[\text{Me}_4\text{N}]_2[\text{Ni}(\text{O}_2\text{CCBr}_3)_4]$, ν_3 and ν_2 appear at 545 and 1135 cm^{-1} with probable assignment of charge transfer band at 430 cm^{-1} [29]. Thus, a tetrahedral environment is favoured around nickel atom.

Tetragonally distorted, six coordinate copper(II) complexes give rise to one absorption band in the visible region near 625 cm^{-1} which is often resolved into three components and exhibit a broad tail into the near infrared region [28]. Regular tetrahedral copper(II) complexes are expected to give a single broad band in the near infrared region and to be blank between $1000\text{--}500\text{ cm}^{-1}$. Thus Cs_2CuCl_4 shows band at 1111 cm^{-1} and Cs_2CuBr_4 at 1250 cm^{-1} , respectively [30, 31]. Neither complex shows any more absorption band below 500 cm^{-1} . A single band at 1690 cm^{-1} ($d_{z^2} \rightarrow d_{xy}$) in the diffused reflectance spectrum of $[\text{Me}_4\text{N}]_2[\text{Cu}(\text{O}_2\text{CCBr}_3)_4]$ favours tetrahedral environment around copper atom.

The high spin manganese(II) compounds are expected to show magnetic moments very close to spin only value of 5.92 B.M. and independent of temperature, irrespective of whether the ligand arrangement is octahedral, tetrahedral, or is of lower symmetry. Magnetic moment of $[\text{Me}_4\text{N}]_2[\text{Mn}(\text{O}_2\text{CCBr}_3)_4]$ is 6.15 B.M. which is very close to spin only value.

The ground term for a tetrahedral cobalt(II) complexes is $^4\text{A}_2$ and the magnetic moment values of four coordinate high spin cobalt(II) complexes fall in the range of 4.19 to 4.90 B.M.. The complex $[\text{Me}_4\text{N}]_2[\text{Co}(\text{O}_2\text{CCBr}_3)_4]$ has magnetic moment value of 4.27 BM, close to 4.5 BM reported for analogous compounds.

$^3\text{T}_1$ is the ground state for tetrahedral nickel(II) complexes and it is anticipated that tetrahedral complex should show magnetic moment between 3.2 BM to 4.0 BM at room temperature [19]. Magnetic moment value of 3.28 BM for $[\text{Me}_4\text{N}]_2[\text{Ni}(\text{O}_2\text{CCBr}_3)_4]$ is well in the expected range.

The $[\text{Me}_4\text{N}]_2[\text{Cu}(\text{O}_2\text{CCBr}_3)_4]$ has magnetic moment value of 2.0 BM at room temperature and is well in the given range. Thus on the basis of infrared, electronic spectra and magnetic moment of $[\text{Me}_4\text{N}]_2[\text{Cu}(\text{O}_2\text{CCBr}_3)_4]$ it may be concluded that unlike tetranitrato metal(II) complexes, these have tetrahedral environment around central metal atom.

All attempts made to prepare the single crystal of these complexes were failed probably due to their insolubility in most of the organic solvents. Therefore, we could not carry out their X-ray studies in order to throw more light on the nature of their structure.

TG-DTG curves of $[\text{Me}_4\text{N}]_2[\text{M}(\text{O}_2\text{CCBr}_3)_4]$ where $\text{M} = \text{Mn}, \text{Cu}, \text{Ni}, \text{Co}$ are similar and show that they decompose in similar manner in two steps. However, these steps overlap (as shown by DTG curves). They begin to lose weight on heating above 45°C . The weight loss is slow at the beginning but becomes rapid around 145°C . The formation of final residue, metal oxide, is complete at about 380°C . Total loss in weight in each case is in agreement with the value calculated on the basis of their proposed formulae. A typical curve for $[\text{Me}_4\text{N}]_2[\text{Mn}(\text{O}_2\text{CCBr}_3)_4]$ is shown in Figure 2. In the first step, there is loss of two molecules of tribromoacetic anhydride followed immediately by the loss of

tetramethyl ammonium part as combustible material (weight loss, observed: 93.10%; Calculated: 94.50%).

The presence of tribromoacetic anhydride was characterized from the infrared spectrum of the trapped volatiles in a separate experiment.

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