Polyanion Compounds of Iron(III) Acetate

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Compounds of compositions, $\text{Fe(NO}_3\text{)(OH)(CH}_3\text{CO}_2\text{),CH}_3\text{CO}_2\text{H}$, $\text{Fe(NCS)(OH)(CH}_3\text{CO}_2\text{),}$

$\text{(CH}_3\text{)}_2\text{CO}, \text{Fe(BF}_4\text{)(OH)(CH}_3\text{CO}_2\text{)}$, and $\text{Fe(ClO}_4\text{)(OH)(CH}_3\text{CO}_2\text{)}$ have been prepared and characterized on the basis of infrared, thermal analysis, molar conductance and magnetic susceptibility measurements.

Iron(III) chloride is reported to react with acetic acid to form chlorobis(acetato)iron(III), $\text{FeCl(CH}_3\text{CO}_2\text{)}_2$ compounds, with the elimination of HCl. Reinvestigations of this reaction reveals that no hydrogen chloride is evolved and instead acetyl chloride is formed. Furthermore, instead of the chlorobis(acetato) moiety, a new formulation containing chlorohydroxoacetatoiron(III) reveals that no hydrogen chloride is evolved and instead acetyl chloride is formed. Furthermore, instead of the chlorobis(acetato) moiety, a new formulation containing chlorohydroxoacetatoiron(III) reveals that no hydrogen chloride is evolved and instead acetyl chloride is formed.

The nature of chlorohydroxoacetatoiron(III) unit, $\text{FeCl(OH)(CH}_3\text{CO}_2\text{).CH}_3\text{CO}_2\text{H.0.5H}_2\text{O}$ (I), has been proposed on the basis of its reactions with different basess. In order to understand more fully the nature of chlorohydroxoacetatoiron(III) unit, chloro group in (I) has been substituted by polyatomic ligands, nitrate, thiocyanate, tetrafluoroborate and perchlorate. Compounds thus obtained are reported here.

Materials and Methods

Chemical analyses and physical measurements were made as already described. Sulphur content in thiocyanato compound was estimated as sulphate. $\text{Fe(NO}_3\text{)(OH)(CH}_3\text{CO}_2\text{),CH}_3\text{CO}_2\text{H}$ (II) — The compound, $\text{FeCl(OH)(CH}_3\text{CO}_2\text{),CH}_3\text{CO}_2\text{H.0.5H}_2\text{O}$, (I) (10 mmoles) was dissolved in methylene chloride (60 ml) and an equivalent amount of $\text{AgNO}_3$ (10 mmoles) dissolved in the minimum amount of acetonitrile was added to it dropwise. The contents were stirred for 2 hr and the precipitated AgCl was filtered out. The filtrate was concentrated in vacuo to get a brick-red residue. It was crystallized from a mixture of methylene chloride and petroleum ether. The crystals, on keeping for some days or on drying in vacuo, crumble down to give fine powder. $\text{Fe(ClO}_4\text{)(OH)(CH}_3\text{CO}_2\text{)}$ (V) — Silver tetrafluoroborate (10 mmoles) solution in the minimum amount of acetonitrile was added to a solution of (I), (10 mmoles) in ether (60 ml). The mixture was stirred for 6 hr and AgCl removed by filtration. The filtrate was treated with $\text{H}_2\text{P}_{10}$Fe to precipitate out the iron compound. It was filtered and the residue washed with ether and dried in vacuo. The compound melts with decomposition at 101°C. The solubility trends are the same as found in the corresponding nitrate compound. $\mu_{\text{eff}}$ value at room temperature is 4.37 BM.

$\text{Fe(H}_2\text{BF}_4\text{)(OH)(CH}_3\text{CO}_2\text{)}$ (VI) — Silver perchlorate (10 mmoles) dissolved in minimum amount of acetonitrile was added dropwise to a solution of (I) (10 mmoles) in ether (60 ml). The rest of the procedure is the same as in fluoroborate complex. The $\mu_{\text{eff}}$ value is 3.54 BM.

Results and Discussion

Anthranilic and salicylic acids ($XH$) react with $\text{FeCl(OH)(CH}_3\text{CO}_2\text{).CH}_3\text{CO}_2\text{H.0.5H}_2\text{O}$, (I), to form...
substitution products of the type FeClX₂.H₂O and as a result both hydroxo and acetato groups in (I) get replaced. The chloro group in (I), however, remains intact. In order to understand more fully the nature of chlorohydroxoacetatoiron(III) unit, chloro group in (I) has been substituted by poly-anionic ligands having tendency to form ionic compounds. If coordinated, these polyanions can act as monodentate, bidentate or bridging ligands. IR spectra of all the compounds (Table I) show a broad band in the region 3300-3500 cm⁻¹ which may be assigned to the hydroxo group. In addition, the compounds show ν₃ COO and ν₁ COO bands due to the coordinated acetate group in the regions 1575-1580 and 1440-1450 cm⁻¹ respectively.

Silver nitrate reacts with (I) to give Fe(NO₃)(OH)(CH₃CO₂).CH₃CO₂.H (II). Compound (II), on keeping at 150°/10⁻³ torr for 6 hr, loses acetic acid to give Fe(NO₃)(OH)(CH₂CO₂). (III). The nitrate compound (II) shows bands due to monodentate nitrate group and Fe-O mode (Table I). In addition, a band at 1675 cm⁻¹ due to coordinated acetic acid is also observed. The IR spectrum of (III) shows almost no change in the position of bands due to acetato and hydroxo groups but the ν₃ bands of (nitrate group) (II) at 1440 and 1280 cm⁻¹ disappear. These are replaced by new bands at 1530 and 1250 cm⁻¹ with a Δν₃ value of 280 cm⁻¹ which indicates that (III) has probably a bidentate or bridging nitrate group.

Molecular weight of (II) in nitrobenzene is double that of the formula weight but this cannot be considered very reliable as (II) has a low solubility. A precipitate starts separating out on increasing the concentration of (II) in nitrobenzene. Compound (II) and subsequent ones are quite soluble in acetonitrile, DMF, DMSO and THF but due to their tendency to form complexes, the molecular weights cannot be determined. Molecular weight of (II) in DMSO is 1/4 of formula weight. The low values of its molar conductance (1·9 and 9·1 cm² ohm⁻¹ mole⁻¹) in nitrobenzene and nitromethane, respectively, show that compound (II) behaves as a non-electrolyte in solution.

Compound (II), on heating in air, loses a molecule of acetic acid between 50° and 190° in an exothermic fashion. The residue then loses all the organic matter and oxides of nitrogen together in one exothermic step extending up to 400° to leave behind 1/2 Fe₂O₃ (Fig. 1, curve a).

The thiocyanato complex, Fe(NCS)(OH)(CH₃CO₂). (CH₃)₂CO, (IV), shows IR band at 1660 cm⁻¹, typical of coordinated acetone. The positions of bands due to thiocyanato group (Table I) indicate that it is bonded through its terminal nitrogen atom. The νC≡N appears as a strong band at 2040 cm⁻¹ with a strong shoulder at 195 cm⁻¹ arising due to crystal effects in solid state. A band at 320 cm⁻¹ in the spectrum of IV is tentatively assigned to ν(Fe—N) because no such band is present in other compounds discussed here.

Compound (IV), on heating in vacuo (at 160°/10⁻³ torr) loses acetone. The IR bands due to

<table>
<thead>
<tr>
<th>Compound</th>
<th>νFe-O*</th>
<th>ν and δ Fe-O</th>
<th>Polyanion modes</th>
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<tr>
<td>Fe(NO₃)(OH)(CH₃CO₂).CH₃CO₂.H</td>
<td>530wb</td>
<td>380sh, 360s, 350s, 305w, 285w, 235w, 230m</td>
<td>ν₁ 1032m, 802w, 1440s, 1280s, 766m, 722m</td>
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<tr>
<td>Fe(NCS)(OH)(CH₃CO₂). (CH₃)₂CO</td>
<td>525wb</td>
<td>370-350sh, 305w, 290w, 275w, 235w, 230m</td>
<td>ν₁ 2040sh, 470m, 840w</td>
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<tr>
<td>Fe(BF₄)(OH)(CH₂CO₂)</td>
<td>525wb</td>
<td>375-360sh, 300w, 280m, 250w, 220m, 210m</td>
<td>ν₁ 765m, 352sh, 1115sh, 1095s, 1040s</td>
</tr>
<tr>
<td>Fe(ClO₄)(OH)(CH₂CO₂)</td>
<td>515wb</td>
<td>365s, 350sh, 300w, 280w, 250w, 220m</td>
<td>ν₁ 925m, 460w, 1150s, 1100s, 1045s</td>
</tr>
</tbody>
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*In hydroxy bridged ring.

Fig. 1 — TG curves for iron(III) compounds with polyanion ligands (a, nitrate; b, thiocyanate; c, tetrafluoroborate)
acetone are missing in the residue but other bands show little change. Heating in air proceeds similarly with the loss of acetone up to 190° (Fig. 1, curve b). The last endothermic step between 350° and 620° corresponds to the loss of 1/2 H₂O to leave behind 1/2 Fe₂O₃ (Fig. 1, curve b).

The molar conductance of (IV) in nitrobenzene (7·6 cm² ohm⁻¹ mole⁻¹) and nitromethane (16·7 cm² ohm⁻¹ mole⁻¹) show that it undergoes a slight dissociation in these solvents.

The IR spectrum of tetrafluoroborate complex, Fe(BF₄)(OH)(CH₃CO₂), (V), shows that the polyanion is coordinated to the metal atom (Table 1) and the shape of ν₃ is intermediate in type between those of free and a covalent fluoroborate. In addition to bridging acetate and hydroxo groups, it appears that the fluoroborate group bridges to give polymeric structures in the solid state. The lower solubility of (V) supports its polymeric nature. The semicoordination in (V) is further evidenced by the molar conductance value of 14·1 cm² ohm⁻¹ mole⁻¹ in nitromethane. Molecular weight of (V) in DMSO is 1/2 of its formula weight.

The compound (V) on heating at 160°/10⁻³ torr leaves behind a black residue devoid of fluoroborate group. The volatile liquid in the trap gives IR bands of ionic tetrafluoroborate. Decomposition in air proceeds almost similarly, first an endothermic step occurs from 60° to 180° corresponding to a weight loss equivalent to HBF₄ (Fig. 1, curve c). Next, an exothermic step occurs which is attributed to the loss of organic matter to give 1/2 Fe₂O₃ at 360°.

The perchlorate, Fe(ClO₄)(OH)(CH₃CO₂), (VI), shows IR bands of coordinated perchlorate group²⁸ (Table 1). The structure seems to be similar to that of compound (V). Its molar conductance value is 19·1 cm² ohm⁻¹ mole⁻¹ in nitromethane. The compound decomposes violently at about 220°.

The room temperature magnetic moment values are much lower than those normally observed (5·92 BM) for high-spin iron(III) compounds. This suggests that the present compounds, like many other carboxylates, are antiferromagnetic.

References