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THE PREPARATION AND SOME PROPERTIES OF FERRICINIUM TRICHLOROFERRATE(II) AND FERRICINIUM TRIBROMOFERRATE(II)

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SUMMARY

The preparation and characterization of ferricinium trichloroferrate(II) and ferricinium tribromoferrate(II) are reported. The first salt crystallizes in the form of square, thin, platelets of $d = 1.654$ g/cm^3. Its unit cell was determined to be orthorhombic with $a = 14.49$ Å, $b = 14.52$ Å, $c = 13.38$ Å and $Z = 8$. The second salt crystallizes in the form of thin parallelopiped platelets of $d = 1.964$ g/cm^3. Its unit cell was determined to be also orthorhombic with $a = 9.92$ Å, $b = 13.96$ Å, $c = 11.79$ Å and $Z = 4$.

INTRODUCTION

Ferricinium salts containing iron in the anion have been reported[1-10]. In all the reports but one[11] the iron is in the ferric state. Spilners[11] reported the formation, in benzene, of a ferricinium salt having a hydrated $Fe_2Cl_6^-$ as its anion. This anion, containing both ferric and ferrous ions, is unstable and upon recrystallization decomposes to yield $FeCl_2$ and tetrachloroferrate(III). Nesmeyanov *et al.*[2] reported the direct preparation of ferricinium tetrachloroferrate(III) from 2/1 ratio of $FeCl_3$ to ferrocene, in ether, according to the following:

$$C_{10}H_{10}Fe + 2\,FeCl_3 \rightarrow (C_{10}H_{10}Fe)^+FeCl_4^- + FeCl_2$$

Ferricinium tetrabromoferrate(III) was prepared[1,3] by the use of excess bromine in such solvents as CCl_4, heptane, hexane, etc.

The reactions leading to the ferricinium tetrahaloferrate(III) were all run in the presence of excess oxidizing agent and in a non-solvent for the reaction products.

We wish to report the preparation and some properties of novel ferricinium salts, prepared in the presence of excess ferrocene in a mutual solvent for the reactants and products, in which the anion contains iron only in the ferrous state. These salts are ferricinium trichloroferrate(II) and ferricinium tribromoferrate(II).

RESULTS AND DISCUSSION

It was found that in a solvent for ferrocene, ferricinium ion and ferric chloride, with an excess of ferrocene present, the oxidation of ferrocene to ferricinium proceeds with the concurrent complete reduction of the ferric chloride to the trichloroferrate(II) anion, as follows:

$$C_{10}H_{10}Fe\ (\text{excess}) + FeCl_3 \rightarrow (C_{10}H_{10}Fe)^+FeCl_3^-$$

Contrary to the observations of Nesmeyanov *et al.*[2] no $FeCl_2$ precipitate was observed in our procedure. Using benzene and ether solutions for his reaction media, Spilners[11] obtained ferricinium and biferricinium salts probably with anions consisting of mixed Fe^{II} and Fe^{III}. Ferricinium salts are not soluble in the above media. In our case, working in a solvent mixture where all reagents are soluble, the reaction proceeded to completion.

One would expect $FeBr_3$ to react with ferrocene in much the same way as $FeCl_3$ does. The reaction of ferrocene with elemental bromine to produce, initially, $(C_{10}H_{10}Fe)^+Br^-$ must be different, as ferricinium ion is not stable towards bromide ion, which attacks to liberate Fe^{III} and then form $FeBr_4^-$. This was described by Riemschneider and Helm[1] and Nesmeyanov[3]. In our case, with an excess of reducing agent, ferrocene, and in a mutual solvent, we obtained a 5% yield of ferricinium tribromoferrate(II).

Chemical analyses as described in the experimental section show conclusively that the synthesized components were ferricinium trihaloferrates(II).

Large anions such as the tetrahaloferrate(III)[3], tetrachlorogallate[12], triiodide[13], are known to stabilize the ferricinium cation. On the other hand, bulky singly charged cations such as the rubidium or the cesium cations form stable trichloroferrate(II) salts[14-16]. In our case we have a combination of bulky anion and cation, each stabilizing the other, forming together relatively stable salts. In dry air, the compounds showed no deterioration after storage for over a year.

This report demonstrates the importance of reaction conditions in determining the end products. When other investigators worked with excess of oxidizing agent or in solvents where the product was insoluble (*e.g.* CCl_4, benzene or ether) the end product was the tetrahaloferrate(III) or mixed salts. In the present report, all reactions were run using an excess of reducing agent, ferrocene, in a mutual solvent where the starting materials and products could interact. Thus, ferricinium salts of trihaloferrate(II) could be isolated easily and even quantitatively, in one case, though the tetrahaloferrate(III) salts are probably more stable.

EXPERIMENTAL

Materials

Prior to use the ferrocene was recrystallized from hot absolute ethanol. The anhydrous ferric chloride was Fisher reagent grade. The elemental bromine was Matheson, Coleman and Bell, reagent grade. Both reagents were used as received. All solvents were of reagent or spectrograde grades and were used as received, except methyl ethyl ketone which was distilled.

Preparation of ferricinium trichloroferrate(II)

To a solution of 0.040 mole (7.44 g) of ferrocene in 200 ml methyl ethyl ketone and 100 ml absolute ethanol under nitrogen was added over a period of a few minutes a solution of 0.030 mole (4.86 g) of anhydrous $FeCl_3$ in 250 ml ethyl ether, yielding a deep green solution. The solution was placed in a rotary vacuum evaporator, at 40 mm in a water bath at 70° to remove solvent. When the solution volume was reduced to about 50 ml, the pressure was allowed to climb to 1 atmosphere, the heat source was removed, and the flask cooled to room temperature. After 18 h, a large amount of dark crystals had formed and were filtered off. The solvent now was orange-brown in color. The crystals were washed twice each with ether, acetone, MEK, ethanol and CCl_4, dried under 25 mm at room temperature: weight 9.90 g (0.028 mole, 95% yield). (Found: C, 33.50; H, 2.75; Cl, 30.06; Fe, 33.19. $C_{10}H_{10}Cl_3Fe_2$ calcd.: C, 34.48; H, 2.88; Cl, 30.55; Fe, 32.09%.) Volhard method titration resulted in 29% by weight chloride. Ceric ammonium sulfate titration gave 16.2% Fe^{II}. Potassium ferro- and ferricyanide tests showed that the ionic iron was virtually all in Fe^{II} state with only faint traces of Fe^{III}. The compound did not melt or decompose below 300°.

Ferricinium trichloroferrate(II) crystallized out from MEK/ethanol solution as rather large square platelets, dark violet in color. When observed with a transmitted light, the crystals show beet-red color.

Preparation of ferricinium tribromoferrate(II)

To 0.10 mole (18.60 g) of ferrocene dissolved in 200 ml of MEK was added 0.04 mole (3.20 g) of elemental bromine as a solution in 20 ml CCl_4. Most of the MEK, containing practically all of the CCl_4, was then evaporated under reduced pressure at room temperature. The resultant solution was concentrated such that addition of 20 ml toluene caused the precipitation of a minor amount of solids. This precipitate was filtered off and the filtrate was left for 24 h under a nitrogen flow to evaporate very slowly. A small amount of ferricinium tribromoferrate(II) precipitated and was collected by filtration. Washing and drying was the same as for ferricinium trichloroferrate(II): weight 0.32 g (0.00067 mole, 5% yield). (Found: C, 24.59; H, 2.11; Br, 49.50; Fe, 23.41. $C_{10}H_{10}Br_3Fe_2$ calcd.: C, 24.95; H, 2.08; Br, 49.72; Fe, 23.25%.) Volhard method titration yielded 49.8% bromide, and ceric ammonium sulfate titration gave 11.6% Fe^{II}. Here again potassium ferro- and ferricyanide tests showed the presence of only traces of Fe^{III} with practically all the ionic iron in the Fe^{II} state. Similar tests showed that the material dissolved in the filtrate comprised of a mixture of ferrocene and ferricinium tetrabromoferrate(III). The ferricinium tribromoferrate(II) decomposed at 238° without passing through a melting point.

Ferricinium tribromoferrate(II) crystallized from MEK as small, dark-red crystals of parallelopiped shape, with angles of 80° and 100°. When observed with transmitted light, the crystals have a brown-red brick color.

Characterization

Infrared spectra were obtained on 1% by weight of material in CsI, pelletized under vacuum. Perkin–Elmer model 421 and Beckman IR5 CsBr model spectrometers were used.

The spectra of the two compounds were very similar to those obtained by Pavlik and Klikorka[5] and Pavlik and Plechacek[17] for ferricinium tetrachloroferrate(III) and tetrabromoferrate(III).

Weissenberg and oscillating cylindrical cameras were used to obtain X-ray patterns of single crystals of ferricinium trichloroferrate(II), using a copper target and a nickel foil filter. Powder patterns for both compounds were obtained from well ground crystals in a 57.3 mm radius Debye–Scherrer camera with chromium target and a vanadium foil covering half the film as a filter. The powder patterns of both substances contained each over 25 reflections that were indexable in orthorhombic unit cell with the following parameters: Ferricinium trichloroferrate(II): $a = 14.49$ Å, $b = 14.52$ Å, $c = 13.38$ Å; $V = 2815$ Å^3 and $Z_{calc} = 7.96$ ($Z = 8$). Ferricinium tribromoferrate(II): $a = 9.92$ Å, $b = 13.96$ Å, $c = 11.69$ Å; $V = 1632$ Å^3 and $Z_{calc} = 4.01$ ($Z = 4$).

For the trichloroferrate(II) compound, the indexing was guided by the oscillation and Weissenberg photographs. Extensive twinning prevented further structure determination work.

The densities of the compounds were measured by flotation in CCl_4/CH_2I_2 and yielded $d = 1.634$ g/cm^3 for the ferricinium trichloroferrate(II) and $d = 1.964$ g/cm^3 for the ferricinium tribromoferrate(II).

A Reichert–Zetopan optical microscope was used for optical observations. With both compounds it was noted that the crystal color depended on its thickness. In transmitted light thin layers were greenish, deepening through orange-yellow into deep red in thick layers. This behavior is similar to the dichroism encountered with ferricinium solutions in polar solvents. In both cases polarized light extinguished along the angle bisectors.

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