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Preliminary communication

THE SYNTHESIS AND ELECTROCHEMISTRY OF BIS(TETRAMETHYLTHIOPHENE)IRON(II) HEXAFLUOROPHOSPHATE

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Summary

$FeCl_2$ and tetramethylthiophene react in the presence of $AlCl_3$ to afford the diamagnetic bis(tetramethylthiophene)iron(II) cation which was isolated and characterized as its hexafluorophosphate salt and studied by differential pulse polarography and cyclic voltammetry.

There are few reported examples of transition metal complexes containing π-bonded heterocyclic ligands. To our knowledge there are included in this group only two types of cationic complexes; the *N*-methylpyrrole- and thiophene-manganese tricarbonyl cations [1] and the species resulting from the oxidation of azaferrocene [2]. We would now like to report the synthesis of the first complex having a 2+ charge and also having two heterocyclic molecules coordinated to a transition metal atom.

We have found that anhydrous iron(II) chloride and tetramethylthiophene react in the presence of anhydrous aluminum chloride in refluxing cyclohexane to give a red oil which, after hydrolysis and treatment with aqueous ammonium hexafluorophosphate yields red crystals of bis(tetramethylthiophene)iron(II) hexafluorophosphate, (yield 55%, dec. 100°. Found: C, 31.25; H, 4.00; Fe, 8.59; S, 10.18. $C_{16}H_{24}F_{12}FeP_2S_2$ calcd.: C, 30.69; H, 3.86; Fe, 8.92; S, 10.24%). The NMR spectrum in acetone-d_6 shows two sharp singlets of equal intensity at τ 7.34 and 7.50 for the methyl groups of the complexed thiophene rings. Uncomplexed tetramethylthiophene in the same solvent gave two singlets at τ 7.76 and 8.05. The molar conductance of a 5.2×10^{-3} *M* acetonitrile solution of this compound was 98.78 mho cm^2 compared to a molar conductance of 115.5 mho cm^2 obtained for bis(hexamethylbenzene)iron(II) hexafluorophosphate in the same solvent at the same concentration. Characteristic infrared absorption bands (KBr pellet) were 3030 w, 3000 w, 2958 w, 2880 w, 1490 s, 1457 s, 1401 s, 1310 (br), 1250 m, 1160 m, 1105 m, 1092 m, 1037 s, 850 vs(br) and 560 s.

The structure shown in Fig. 1 is suggested for this compound based on the similarity of its physical and spectral properties to other bis-arene-iron(II) salts

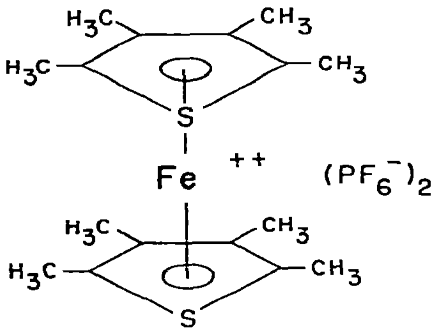

Fig. 1. Proposed structure of bis(tetramethylthiophene)iron(II) hexafluorophosphate.

and by analogy with known thiophene complexes of chromium and manganese. The title compound decomposes slowly in air and rapidly in solution to give tetramethylthiophene and a purple solid which has not been identified. The thermal decomposition of the salt gives only tetramethylthiophene and iron salts. Attempts to prepare iron complexes of thiophenes having fewer than four methyl substituents did not succeed apparently due to the reduced stability of their respective complex haloaluminate salts to the hydrolysis conditions. This behavior is in accord with the generally observed phenomenon of decreasing stability of arene complexes with decreasing methyl substitution [3, 4]. The reaction of anhydrous $RuCl_3$ with tetramethylthiophene and aluminum powder in the presence of $AlCl_3$ failed to give the ruthenium analogue of the title compound.

Some comparative electrochemical studies were performed on the title compound and several other bis-arene-iron(II) salts in 50% aqueous acetone using potassium chloride as supporting electrolyte. The results are shown in Table 1.

TABLE 1

HALFWAVE REDUCTION POTENTIALS FOR $(A)_2Fe(PF_6)_2$ SALTS (vs. SCE)

A	First reduction wave	Second reduction wave
Tetramethylthiophene	−0.27 V	−1.17 V
Mesitylene	−0.28 V	−1.16 V
Hexamethylbenzene	−0.48 V	−1.46 V

Cyclic voltammetry showed that the one electron process associated with the first reduction wave is reversible in all three cases while the second one electron reduction is non-reversible. The electrochemical behavior observed for the bis(tetramethylthiophene)iron(II) cation indicates that it may be possible to isolate a bis(tetramethylthiophene)iron(0) species similar to bis(hexamethylbenzene)iron(0) [5] isolated by Fischer and Röhrscheid. It is also interesting to note that the reduction potentials for the bis(tetramethylthiophene)iron(II) cation and the dimesityleneiron(II) cation are nearly identical. The possibility that these species may behave similar chemically is now being investigated. In this regard we have observed that the title compound will react with sodium borohydride in tetrahydrofuran to give a brown complex which appears to be a hydride adduct. This compound is very unstable, however, and has not been completely characterized.

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