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Investigation of Pyridinium Tetrachloroferrates(1-)

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Physico-chemical studies of salts with complex anions, *e.g.* $[M_2X_9]^{3-}$, where X is Cl, Br and I, are an area of active research interest. In particular, structural, spectroscopic and magnetic investigations have been focused on compounds with paramagnetic M^{3+} ions [1–11]. Chloroferrates(1-) with N-containing organic bases constituting their cations, namely $(pyH)_3Fe_2Cl_9$, $(pyH)_5Fe_2O_{11}$ and $(QH)_4Fe_2Cl_{10}$ (where Q stands for quinoline) were first reported in [12]. On the basis of elemental analyses the complexes were deemed to be binuclear species with six chloride ions attached to the ferric ion, thus, constituting an octahedral geometry. To the ennea-, deca- and hendecachlorides respective μ-tri-, μ-di- and μ-mono-chloride bridges have tentatively been assigned. These structures have additionally been supported by magnetic susceptibility measurements [13]. However, subsequent accurate magnetic measurements, carried out at lower temperatures together with results obtained by other techniques, did not confirm the existence of the dimeric species with octahedral central ions. On the other hand, there are many dimeric anions, $[M_2X_9]^{3-}$ of chromium, molybdenum and tungsten with structural entities $[X_3M(\mu\text{-}X)MX_3]^{3-}$ [1,2,8,10,11] with the octahedral structure of the central ion. Ginsberg and Robin [1] have demonstrated, however, that compounds with the $[Fe_2Cl_9]^{3-}$ anion are not dimeric, but have a double-salt structure, *i.e.* that of bis[pyridinium tetrachloroferrate(1-)]-pyridinium chloride, $2[pyH][FeCl_4]\cdot[pyH]Cl$.

Similar compounds with 4-chloro- and 4-bromopyridinium cations have also been reported [14,15]. The lattice structure implies that one molecular formula contains two $[FeCl_4]^-$ tetrahedral ions and one chloride ion strongly bonded to three pyridinium cations [16].

These contribution is concerned with the synthesis and conductometric investigation of ten new tetrachloroferrates(1-) of the empirical formula $[AH][FeCl_4]$, where A denotes the pyridine (py), 2-, 3- and 4-methylpyridine (2-Mepy, 3-Mepy, 4-Mepy resp.), 2,4,6-trimethylpyridine (2,4,6-triMepy), 4-ethylpyridine (4-Etpy), 2-aminopyridine (2-NH_2py), 4-aminopyridine (4-NH_2py), 2-amino-3-methylpyridine (2-NH_2-3-Mepy) and 2-amino-4-methylpyridine (2-NH_2-4-Mepy). To the best of our knowledge, coordination compounds containing substituted pyridines as cations have not been reported so far.

$[pyH][FeCl_4]$ was synthesized as follows: to a solution of ferric chloride hexahydrate (13.225 g = 0.05 mol) in 50 mL of ethanol, 4 mL of conc. hydrochloric acid and 4 mL (0.05 mol) of freshly distilled pyridine were added. The solution was then concentrated to a half of initial volume and left for 24 hrs. The precipitate was filtered off and recrystallized twice from ethanol slightly acidified with dilute hydrochloric acid. The product was dried and kept over P_4O_{10} in a desiccator. The remaining complexes were obtained in a similar way.

All analyses confirmed $[AH][FeCl_4]$ compositions. The IR spectra were taken on a Bruker IFS 66 spectrophotometer either in KBr pellets (over the 4400–3700 cm^{-1} range) or in Nujol mulls (the 500–300 cm^{-1} range). For the measurements of Raman spectra the Bruker FRA 106 instrument was applied. Absorption spectra (UV, VIS) were recorded on a Perkin Elmer Lambda 18 spectrophotometer.

The tetrachloroferrate(1-) ion in the complexes was identified on the basis of its infrared spectra. There are characteristic absorption bands over the range 400–100 cm^{-1} [18,19]. Those due to skeletal and stretching Fe-Cl vibrations emerge in the range 390–383 cm^{-1} and 333–328 cm^{-1} respectively. Another proof in favour of the $[FeCl_4]^-$ ion as a structural entity was provided by Raman spectroscopy, where the most characteristic strong peak usually appears at 330 cm^{-1} [19]. It also appears in the spectra of our compounds, *e.g.* in those of $[2\text{-}NH_2\text{-}3\text{-}Me(pyH)][FeCl_4]$ and $[4\text{-}NH_2\text{-}(pyH)][FeCl_4]$ it emerged at 332.9 and 332.7 cm^{-1} respectively.

Conductometric titrations were performed using a PW 9526 (Philips) conductometer with a PW 7551/60 conductivity cell with a cell constant k = 0.840 cm^{-1}. All measurements were run at $25 \pm 0.2^\circ C$ maintained by a UT-2/77 thermostat. Methanol and dimethyl sulphoxide were purified as described previously [20,21]. Their conductivities were respectively 2×10^{-7} and 3×10^{-8} S cm^{-1}. A spectrograde methylene chloride (Mallinckrodt) was used as received.

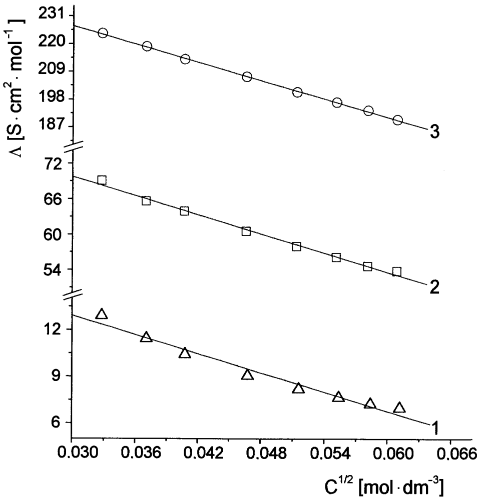

Figure 1. Molar conductivity *vs.* square root of concentration of $[2\text{-}NH_2\text{-}3\text{-}Me(pyH)][FeCl_4]$ in dichloromethane (1) dimethyl sulfoxide (2), and methanol (3).

The purpose of the conductometric experiments was to study the behaviour of the complexes in non-aqueous media. In particular, it was interesting to estimate stability of the tetrachloroferrate(1-) ion in organic solvents, methanol, dimethyl sulfoxide (DMSO) and dichloromethane, *i.e.* the representatives of both polar (amphiprotic and aprotic) and non-polar solvents. Some of the complexes were insoluble in some solvents, thus making conductometric measurements impossible. For this reason, nine in ten complexes were studied in DMSO, and only seven in methanol and dichloromethane. Representative results of the investigations for the arbitrary selected complex [2-NH$_2$-3-Me(pyH)][FeCl$_4$] are shown in Fig. 1. The linear relationship of Λ *vs.* $\sqrt{c}$ reveals distinct dissociation of the compound in the solvents. Similar relationship was obtained for the remaining complexes. Based on these data the molar conductivities at infinite dilution, Λ_o, as well as correlation coefficients, r, were determined by the linear regression method for all systems (Table 1).

Table 1. Molar conductivities at infinite dilution, Λ_o, in Scm^2 mol^{-1} and correlation coefficient, r, for the systems studied.

Compound	DMSO		CH$_2$Cl$_2$		CH$_3$OH	
	Λ_o	r	Λ_o	r	Λ_o	r
[(pyH][FeCl$_4$]	88.93	0.999	–	–	188.27	0.995
[2-Me(pyH)][FeCl$_4$]	81.41	0.998	20.74	0.982	225.41	0.995
[3-Me(pyH)][FeCl$_4$]	85.09	0.999	19.72	0.987	229.68	0.997
[4-Me(pyH)][FeCl$_4$]	91.39	0.998	19.56	0.983	189.12	0.994
[4-Et(pyH)][FeCl$_4$]	85.07	0.999	17.13	0.988	–	–
[2,4,6-triMe(pyH)][FeCl$_4$]	82.72	0.999	–	–	229.55	0.999
[2-NH2-3-Me(pyH)][FeCl$_4$]	85.87	0.989	19.05	0.969	262.83	0.999
[2-NH2-4-Me(pyH)][FeCl$_4$]	85.57	0.999	17.54	0.988	–	–
[2-NH2(pyH)][FeCl$_4$]	85.69	0.999	15.37	0.987	217.97	0.997

As seen in Table 1, the molar conductivities at infinite dilution of the complexes in methanol and dimethyl sulfoxide are markedly higher than those reported in [22–24] for 1-1 electrolytes in these solvents. In methanol, the molar conductivities at infinite dilution usually oscillate around 100 S cm^2 mol^{-1}, whereas those of our compounds are 2–2.5-fold as high. Similarly, in dimethyl sulfoxide, instead of the expected value of *ca* 40 S m^2 mol^{-1}, the conductivities are twice as high. This is indicative of a higher number of ions in the system considered than that owing to dissociation into a complex anion and a cation. In the case of the inert solvent, dichloromethane, the molar conductivities at infinite dilution are compatible with the binary behaviour of the compounds. Consequently, the complexes should be labile in polar solvents, methanol and dimethyl sulfoxide. It is also likely that the tetrachloroferrate(1-) ion undergoes dissociation to certain extent, thus, producing excessive chloride ions. These, in turn, enter into new equilibria enhancing the solvent conductivity. The breakup of the tetrachloroferrate(1-) ion is further supported by the spectra taken over the visible region. In dichloromethane, absorption bands appear at 18730 cm^{-1} and around 16530, 16200, 14500 and 13900 cm^{-1}. These bands are characteristic of the tetrachloroferrate(1-) ion [25,26]. They all are missing in the spectra taken in dimethyl sulfoxide and methanol. It can, thus, be assumed that the relatively stable $[FeCl_4]^-$ ion undergoes degradation in the two solvents. As a consequence, dissociation constants, $K_d = [AH^+]\cdot[FeCl_4^-] / [AH][FeCl_4]$ could be determined in dichloromethane only. To do this, a computer program based on the Pitts's method has been used [27]. The following constants have been obtained: (values in parentheses are standard deviations).

Compound	K_d
$[2\text{-Me(pyH)}][FeCl_4]$	6×10^{-3} (1.7×10^{-4})
$[3\text{-Me(pyH)}][FeCl_4]$,	2×10^{-3} (0.6×10^{-4})
$[4\text{-Me(pyH)}][FeCl_4]$	5×10^{-3} (1.4×10^{-4})
$[4\text{-Et(pyH)}][FeCl_4]$	1×10^{-3} (0.3×10^{-4})
$[2\text{-}NH_2\text{-3-Me(pyH)}][FeCl_4]$	4×10^{-3} (1.1×10^{-4})
$[2\text{-}NH_2\text{-4-Me(pyH)}][FeCl_4]$	3×10^{-3} (0.8×10^{-4})
$[2\text{-}NH_2\text{(pyH)}][FeCl_4]$	0.5×10^{-3} (0.1×10^{-4})

As the data show, the complexes are electrolytes of intermediate strength in the inert solvent.

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REFERENCES

1. Ginsberg A.P. and Robin M.B., *Inorg. Chem*., **2**, 817 (1963).
2. Stranger R., Grey I.E., Madsen I.C. and Smith P.W., *J. Solid State Chem*., **69**, 162 (1987).
3. Kovsarnechan M.T., Roriere J. and Mascherpa-Coral M., *J. Inorg. Nucl. Chem*., **40**, 2009 (1978).
4. Johnstone I.W., Briat B. and Lockwood D., *J. Solid State Commun*., **35B**, 689 (1980).
5. Drillon M. and Georges R., *Phys. Rev. B*, **26**, 3882 (1982).
6. Leuenberger B., Stebler A., Güdel H.U., Furrer A., Feil R. and Kjems J.K., *Phys. Rev. B*, **30**, 6300 (1984).
7. Leuenberger B., Güdel H.U., Kjems J.K. and Petitgrand D., *Inorg. Chem*., **24**, 1035 (1985).
8. Dean N.J. and Maxwell K.J., *Chem. Phys*., **106**, 233 (1986).
9. Leuenberger B. and Güdel H.U., *Inorg. Chem*., **25**, 181 (1986).
10. Stranger R., Smith P.W. and Grey I.E., *Inorg. Chem*., **28**, 1271 (1989).

11. Kummer S. and Babel D., *Solid State Chem.*, **63**, 446 (1989).
12. Weiland R.F. and Kissling A., *Z. Anorg. Allg. Chem.*, **120**, 209 (1922)
13. Earnshow A. and Lewis J., *J. Chem. Soc.*, 396 (1961)
14. Zora J.A., Seddon K.R., Hitchcock P.B., Lowe C.B., Shum D.P. and Carlin R.L., *Inorg. Chem.*, **29**, 3302 (1990).
15. Lowe C.B., Carlin R.L., Schultz A.J. and Loong C.K., *Inorg. Chem.*, **29**, 3309 (1990).
16. Shaviv R., Lowe C.B., Zora J.A., Aakeröy, Hitchcock P.B., Seddon K.R. and Carlin R.I., *Inorg. Chim. Acta*, **198**, 613 (1992).
17. Welcher F.I., The Analytical Uses of Ethylenediamine Tetraacetic Acid (in Polish), WNT, Warszawa, 1963.
18. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, J Wiley & Sons. Inc. NY 1986.
19. Colthup N.B., Daly L.H. and Wiberley S.E., Introduction to Infrared and Raman Spectroscopy, Academic Press, NY, 1975.
20. Wawrzyniak G. and Jasiński T., *Polish J. Chem.*, **59**, 1181 (1989).
21. Wawrzyniak G., *Polish J. Chem.*, **65**, 1667 (1991).
22. Krotochvil B. and Yeager H.L., Topics in Current Chemistry, vol. 27, Springer, Berlin (1972).
23. Dobos D., Electrochemical Data. Budapest, 1975.
24. Conway B.E. and Bockris J.O.M. Eds., *Modern Aspects of Electrochemistry*, Butterworths, London 1979.
25. Gill N.S., *J. Chem. Soc.*, 3512 (1961).
26. Hathaway B.J. and Holah D.G., *J. Chem. Soc.*, 2408 (1964).
27. Pitts E., Tabor B.E. and Baley J., *Trans. Farad. Soc.*, **66**, 693 (1970).