Polish J. Chem., **77**, 1121–1129 (2003)

Synthesis, Spectroscopic Characteristics and Conductometric Investigation of New Tetrachloro- and Tetrabromoferrates(1-)

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(Received March 11th, 2003; revised manuscript May 29th, 2003)

Synthetic pathways have been traced for new tetrachloro- and tetrabromoferrates(1-) of empirical formulae [AH][FeX_4], $(AH)_2FeBr_5$, $(AH)_3Fe_2Cl_9$ and $(AH)_4Fe_2Cl_{10}$, where A stands for pyridine, quinoline and their derivatives, and X = Cl, Br. The spectroscopic evidence (IR, far-IR, Raman and UV-Vis) has shown that the FeX_4^- ions preserve their tetrahedral structure and that the nitrogen atom in the rings of pyridine and quinoline is protonated. On the basis of conductometric measurements relative stabilities of the anions were estimated in methanol (MeOH), dimethyl sulfoxide (DMSO) and dichloromethane (CH_2Cl_2), representing both polar (amphiprotic and protic) and non-polar solvents. Dissociation constants of the compounds were calculated based on the expanded Pitt's equation. Results of the conductometric measurements have been supported by electronic spectra.

Key words: tetrachloroferrate(1-), tetrabromoferrates(1-), conductometric measurements

Complex compounds with tetrachloro- and tetrabromoferrate(1-) anions have been extensively studied. Investigations have been focused on their spectroscopic characterization, structural analysis, magnetic properties and, recently, their thermal behaviour [1–16]. In the chemical literature there is, however, a lack of information on interactions between complexes with the $[FeX_4]^-$ anions (where X = Cl, Br) with solvents. Thus, it seemed worthwhile to study the conductance of these salts in non-aqueous solvents.

Our previous article was concerned with tetrachloroferrates(1-) of general formula [AH][$FeCl_4$], where A is pyridine and its derivatives [17]. Now it seems interesting to investigate compounds with a tetrabromoferrate(1-) anion. This contribution deals with the synthesis, spectroscopic properties and conductometric measurements of 24 new tetrachloro- and tetrabromoferrates(1-).

EXPERIMENTAL

Synthesis of the [AH][$FeBr_4$] salts. The synthesis was carried out by a method similar to that previously used for the preparation of the tetrachloroferrate(1-) salts [17]. Thus, to an ethanolic solution of $FeBr_3$, obtained by dissolving 0.01 mol of $FeBr_3$ in 5 mL of ethanol, a stoichiometric quantity of a 40% hydrobromic acid was added. The solution containing tetrabromoferric acid, H[$FeBr_4$] was gently boiled,

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until its colour turned dark-cherry-red. Separately, liquid reagents, pyridine (py), 2-, 3- and 4-methylpyridines (2-Mepy, 3-Mepy and 4-Mepy, resp.), 2-amino-3-methylpyridine (2-NH_2-3-Mepy), 4-ethylpyridine (4-EtPy), 2,4,6-trimethylpyridine (2,4,6-triMepy), 0.01 mol each, were gently heated and added to the H[$FeBr_4$] solution. Solid amines (0.01 mol each) were dissolved in ethanol prior to addition to the solution of tetrabromoferric acid. Under these conditions, brown precipitates fell out which dissolved after prolonged stirring. Finally, the cool solutions were placed in a refrigerator where the compounds precipitated out after a period extending from 5 days to 2 months. The salts were recrystallized from ethanol. During this operation in some solutions black precipitates turned dark-cherry-red or brick-red.

Synthesis of the quinoline [Q] salts, [QH][$FeCl_4$] and [QH][$FeBr_4$]. The procedure was similar to that just described, but stoichiometric quantities of quinoline, anhydrous $FeCl_3$ and 12 M hydrochloric acid were used to synthesize [QH][$FeCl_4$].

Synthesis of [2-Me(QH)][$FeBr_4$], [6-Me(QH)][$FeBr_4$] and [8-Me(QH)][$FeCl_4$]. The procedure was similar to that described above, but to the synthesis of [2-Me[QH]][$FeBr_4$] and [6-Me(QH)][$FeBr_4$] stoichiometric quantities of $FeBr_3$ (0.01 mol) and 40% HBr (0.01 mol) were used, whereas the amine reactants were used in a half of the stoichiometric quantity of H[$FeBr_4$]. Similarly, [8-Me(QH)][$FeCl_4$] was obtained using anhydrous $FeCl_3$ and 12 M HCl.

Synthesis of the $(AH)_3Fe_2Cl_9$ salt, where A is a quinoline derivative. The synthesis was carried out as described above. The only difference was that 6- and 8-methylquinolines (6-MeQ and 8-MeQ, resp.) and 3-methylisoquinoline (3-MeIsoQ) were the reactants and stoichiometric quantities of 12 M HCl were used.

Synthesis of $(AH)_2FeBr_5$. The synthesis was similar to those just described. Stoichiometric quantities of $FeBr_3$, 40% HBr and amines (2-, 6-, 8-MeQ and 3-MeIsoQ) were used.

Synthesis of [2-Me(QH)][$FeCl_4$]. To 5 mL of ethanol, 0.01 mol of anhydrous $FeCl_3$ was added followed by stoichiometric quantity (0.01 mol) of 12 M HCl to afford tetrachloroferric(1-) acid. The amine reactant (0.005 mol) was then added to the solution of the acid and the product was placed in a refrigerator. After a week, a precipitate of $(2\text{-}Me(QH))_4Fe_2Cl_{10}$ fell out. The mother liquor was decanted and again left for crystallization. After 7 days, a compound of expected composition, [2-Me(QH)][$FeCl_4$] was obtained.

All compounds were dried in a desiccator over P_4O_{10}. All compositions were confirmed by analyses. The IR spectra were recorded on a BRUKER IFS 66 spectrophotometer in a KBr pellet over the 4400–650 cm^{-1} range and the far-IR spectra (650–50 cm^{-1} range) were taken in PE. The Raman spectra were recorded on a BRUKER FRA 106 spectrophotometer (λ_{exc} = 1064 nm, Nd:YAG laser, the laser power at the sample was approximately 100 mW), and the UV-Vis spectra on a PERKIN ELMER LAMBDA 18 instrument.

Potentiometric titrations were carried out using standard electrodes, SCE (indicator electrode) and silver electrode (the reference one). Iron was determined by the spectrophotometric method using EDTA and salicylic acid as the indicator. Conductometric measurements were accomplished on a PW 9526 (PHILIPS) conductometer equipped with a PW 7551/60 conductometric cell with a constant k = 0.840 cm^{-1}. The measurements were carried out at 25±0.2°C controlled by an UT-2/77 ultrathermostat.

Dichloromethane and DMSO (Merck) were of spectral purity. Methanol was purified as described elsewhere [18].

RESULTS AND DISCUSSION

The number of chloride ligands coordinated to Fe(III) may vary. Complex anions, containing four, five and six chloride ligands have been reported. Those usually encountered and most stable are $[FeCl_4]^-$ and $[FeCl_6]^{3-}$, less frequently reported are $[FeCl_5]^{2-}$ [20] and an aqua-complex , $[FeCl_5(H_2O)]^{2-}$ [19]. Analogous bromoferrates, of different stability, are also known. The most stable is the $[FeBr_4]^-$ ion, whereas the $[FeBr_5]^{2-}$ and $[FeBr_6]^{3-}$ ions are less stable as compared to their chloride counterparts.

The composition of complexes formed by these anions depends on the cation. Apart from the 1:1 compounds, more complex species can be formed, especially with medium-sized cations. For instance, with Cs^+ iron(III) forms a $Fe_2Cl_9^{3-}$ anion [21]. Again, the $[FeCl_6]^{3-}$ ion is stabilized by bulky cations such as $[Co(NH_3)_6]^{2+}$ and $[Co(pn)_3]^{2+}$ (pn is 1,3-diaminopropane) [22]. However, also smaller cations can stabilize the chloroferrate ion, especially when hydrogen bonding is involved. This phenomenon was reported in [24], where an octahedral methylammonium hexachloroferrate and the cation is much smaller than the anion, but is stabilized by hydrogen bonding. Analogous hexabromoferrate is not stabilized by the small cation. In this case the ferric ion is incorporated as $[FeBr_4]^-$ in $(H_3CNH_3)_2[FeBr_4]Br$, as demonstrated by X-ray diffraction pattern [9]. It is worth noting that the $[FeCl_4]^-$ion can be stabilized by bulky cations, such as $AsCl^{2+}$ [23] and PCl_4^+ [34]. In our study, the protonated amines play a role of bulky cations.

One of the techniques used for identifications of our compounds was the IR spectroscopy. The spectra of selected complexes are presented in Fig. 1. Bands due to stretching and twisting vibrations, M-X, (F_2) and X-M-X, (F_2) emerge respectively over the ranges 365–387 cm^{-1} and 137–133 cm^{-1} for the $[FeCl_4]^-$ ion and 296–294 cm^{-1} and 97–95 cm^{-1} for the $[FeBr_4]^-$ ion.

The IR spectra are supplemented by the Raman spectra. (Fig. 2). The stretching (M-X), (A_1), twisting (X-M-X), (E), stretching (M-X), (F_2) and twisting (X-M-X), (F_2) vibrations active in the Raman spectra of the $[FeCl_4]^-$ ion emerge over the regions 332–330, 113–105, 383–376 and 139–135 cm^{-1}, respectively, whereas the (A_1), (F_2) and (F_2) bands in the spectrum of the $[FeBr_4]^-$ ion emerge at 202–200, 293–286 and 97–87 cm^{-1}, respectively.

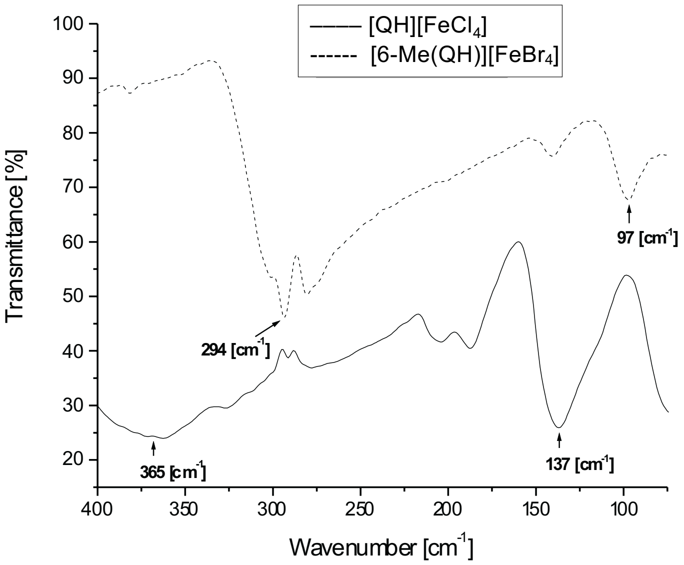

Figure 1. The far-IR spectrum of $[QH][FeCl_4]$ (—) and $[6\text{-}Me(QH)][FeBr_4]$ (---).

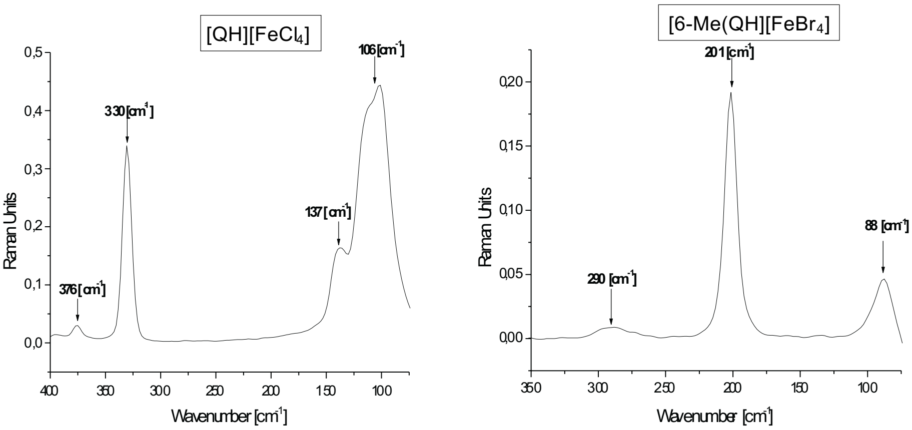

Figure 2. The Raman spectra of [QH][$FeCl_4$] and [6-Me(QH)][$FeBr_4$].

Both the IR and Raman spectra show that in spite of differences in composition of the complexes, their main building block is the $[FeX_4]^-$ ion [25,26]. The IR spectroscopy turned out to be helpful for the determination of protonation sites of the amines (Fig. 3).

For elucidation of the structure of the compounds, crucial were the stretching vibrations (=NH) and ($=\overset{+}{N}H$). In the spectra of primary and secondary amines they usually appear over the ranges 3500–3200 and 2700–2500 cm^{-1}, respectively. With our compounds, these bands, together with crystallographic data, are indicative of attachment of the proton to nitrogen atoms of the pyridine and quinoline rings.

An indirect proof for the presence of the tetrahedral tetrachloro- and tetrabromoferrate(1-) ions in the compounds are electronic spectra of the salts, taken in acetone solution. Positions of the absorption bands are consistent with the literature data for the tetrahedral $[FeCl_4]^-$ and $[FeBr_4]^-$ ions [2,27]. A comparison of the absorbances of equimolar solutions of [QH][$FeCl_4$] and $(8\text{-Me(QH)})_3Fe_2Cl_9$ (Fig. 4) shows that the absorbance of the latter is twice as high as that of [QH][$FeCl_4$]. It can thus

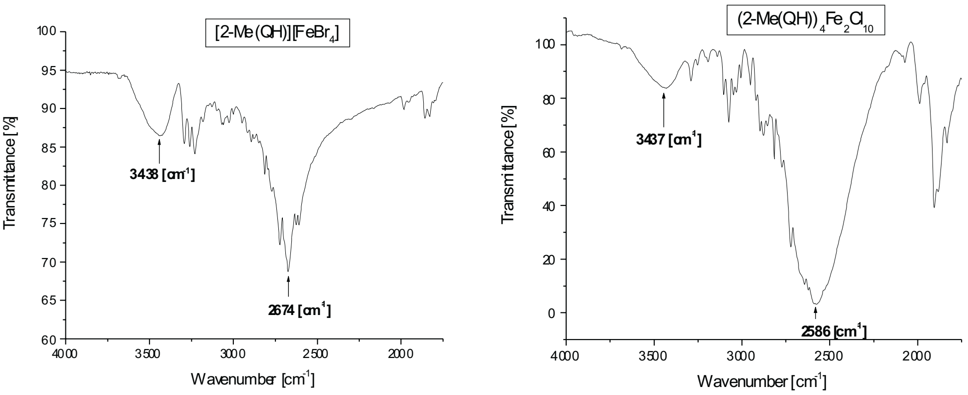

Figure 3. The IR spectra of $(2\text{-Me(QH)})_4Fe_2Cl_{10}$ and [2-Me(QH)][$FeBr_4$].

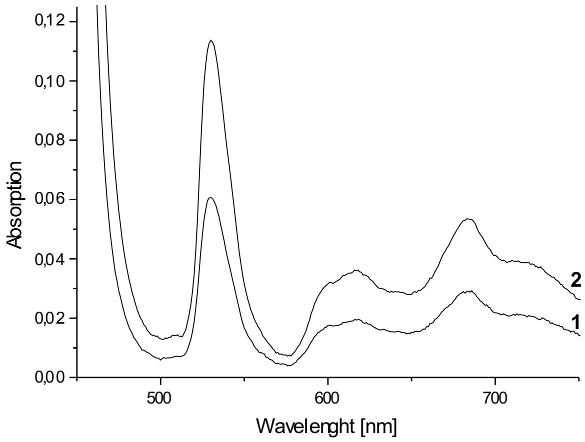

Figure 4. UV-Vis spectra of equimolar solutions of [QH][$FeCl_4$] (1) and (8-Me(QH))$_3Fe_2Cl_9$ (2).

be concluded, that there are two monomeric anions $[FeCl_4]^-$ in the molecule of (8-Me(QH))$_3Fe_2Cl_9$. Similar results were obtained from comparison of absorbances of the following pairs of compounds: [2-Me(QH)][$FeCl_4$] and (2-Me(QH))$_4Fe_2Cl_{10}$; [6-Me(QH)][$FeCl_4$] and (6-Me(QH))$_3Fe_2Cl_9$; [8-Me(QH)][$FeCl_4$] and (8-Me(QH))$_3Fe_2Cl_9$.

It is worth noting that in the family of quinolines, there is a distinct influence of position of the methyl group on the stoichiometry of the complex salts. Thus, unsubstituted quinoline cations form binary (1:1) crystalline salts with the $[FeCl_4]^-$ and $[FeBr_4]^-$ anions at equimolar ratios of reactants. With 6-methyl or 8-methyl substituted quinolines, or 3-methyl substituted isoquinoline, the crystalline compounds with $[FeCl_4]^-$ have the composition $(AH)_3Fe_2Cl_9$. Again, 2-methyl quinolines afford compounds $(AH)_4Fe_2Cl_{10}$ with the $[FeCl_4]^-$ cation.

The situation is different in the family of the bromide compounds. Equimolar quantities of reactants afford precipitates of composition $(AH)_2FeBr_5$, which are the most stable among those formed by methylquinolines with the bromide reactants. Of interest is also the equilibrium set up between the solid complex and solution:

$$(2\text{-Me(QH)})_4Fe_2Cl_{10} = 4[2\text{-Me(QH)}]^+ + 2FeCl_4^- + 2Cl^-$$

After removing of the solid, a new compound, [2-Me(QH)][$FeCl_4$] can be obtained.

Another aim of this work was to investigate the behaviour of the binary complexes in non-aqueous solvents. Of particular interest was comparison of stabilities of the tetrachloro- and tetrabromoferrates(1-) in organic solvents: methanol (MeOH), dimethyl sulfoxide (DMSO) and dichloromethane (CH_2Cl_2). They belong to the class of polar (amphiprotic and aprotic) solvents as well as polar ones. Some of the complexes were insoluble in these solvents, thus, precluding carrying out conductometric measurements. For this reason, only 11 compounds were studied in MeOH, 3 in DMSO and 12 in CH_2Cl_2. Exemplary results of these investigations for [2-Me(QH)][$FeCl_4$] are presented in Fig. 5. As seen, there is a distinct differentiating influence of solvents on the degree of dissociation of the compound.

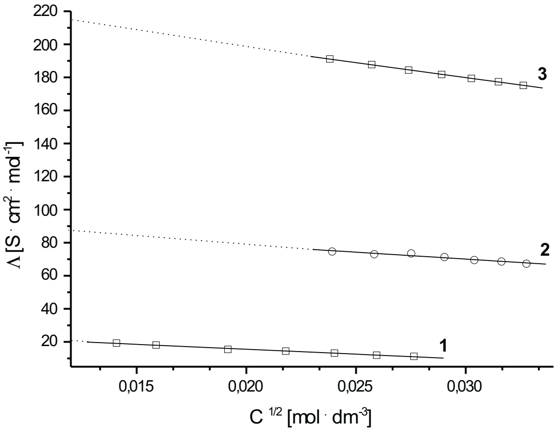

Figure 5. Dependence of molar conductivity on the square root of concentration for [2-Me(QH)][FeCl$_4$] in dichloromethane (1), dimethyl sulfoxide (2) and methanol (3).

Similar relationships were obtained for the remaining complexes. On the basis of these results, molar conductivities were determined at infinite dilution as well as correlation coefficients, r, by means of linear regression for all the systems studied (Table 1). A comparison of the molar conductivities at infinite dilution of the complexes in methanol and dimethyl sulfoxide shows them to be distinctly higher than those of the 1:1 electrolytes in the solvents [28–30]. Molar conductivities at infinite dilution in methanol usually oscillate around 100 [S · cm^2 · mol^{-1}], while those of our compounds are 2–2.5-fold as high. Also in DMSO, instead of the expected values oscillating around 40 [S · cm^2 · mol^{-1}], the conductivities are twice as high.

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

Compound	DMSO		CH$_2$Cl$_2$		CH$_3$OH	
	Λ_o	r	Λ_o	r	Λ_o	r
[PyH][FeBr$_4$]	105.77	0.996	20.86	0.998	321.82	0.993
[2-PicH][FeBr$_4$]	–	–	–	–	323.1	0.995
[3-PicH][FeBr$_4$]	–	–	16.49	0.986	328.73	0.999
[4-PicH][FeBr$_4$]	–	–	18.77	0.989	318.99	0.998
[2-NH$_2$-PyH][FeBr$_4$]	–	–	17.27	0.988	358.62	0.994
[4-EtPyH][FeBr$_4$]	–	–	17.18	0.982	–	–
[2,4,6-ColH][FeBr$_4$]	–	–	23.35	0.992	–	–
[ChH][FeCl$_4$]	–	–	10.08	0.997	263.76	0.993
[ChH][FeBr$_4$]	–	–	35.08	0.998	374.14	0.989
[2-CH$_3$-ChH][FeCl$_4$]	85.11	0.967	20.74	0.996	213.11	0.999
[2-CH$_3$-ChH][FeBr$_4$]	–	–	24.07	0.999	292.1	0.999
[8-CH$_3$-ChH][FeCl$_4$]	69.26	0.999	23.9	0.999	180.7	0.996
[8-CH$_3$-ChH][FeBr$_4$]	–	–	19.94	0.993	224.1	0.998

This indicates that there is a higher number of ions in these systems than would be expected from a simple dissociation of the complexes into a cation and an anion. In the inert solvent, dichloromethane, the conductivities at infinite dilution attain values similar to those characteristic of binary electrolytes. It can thus be concluded that the complexes are unstable in polar solvents (methanol and DMSO). It is also possible that the tetrachloro- and tetrabromoferrates(1-) undergo dissociation to certain extent releasing the Cl^- and Br^- ions, which elevate the conductivity.

Decomposition of the $[FeCl_4]^-$ and $[FeBr_4]^-$ ions in DMSO and MeOH is confirmed by the UV-Vis spectra. In dichloromethane, characteristic absorption bands appear at 610, 628, 697, 718, 760, 786 and 840 nm for the $[FeBr_4]^-$ ion and at 533, 607, 620, 685 and 722 nm for $[FeCl_4]^-$ [2,3], (Figures 6a and 6b). In DMSO and MeOH these bands are missing.

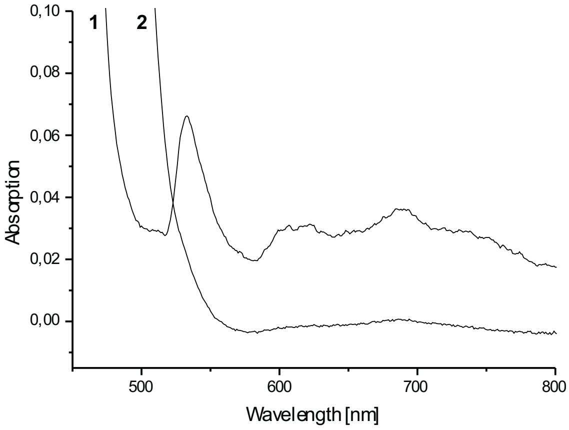

Figure 6a. UV-Vis spectra of [8-Me(QH)][$FeCl_4$] in CH_2Cl_2 (1) and DMSO (2).

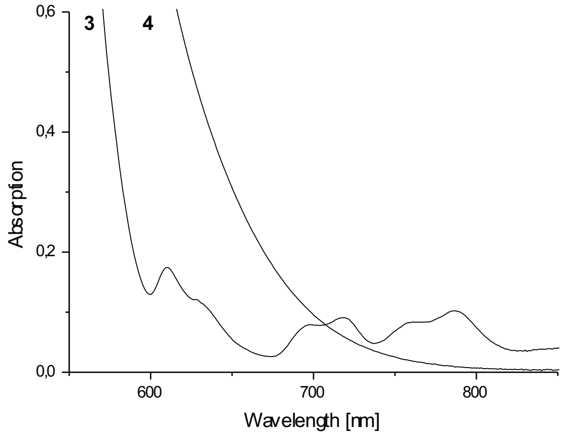

Figure 6b. UV-Vis spectra of [2-NH_2(pyH)][$FeBr_4$] in CH_2Cl_2 (3) and MeOH (4).

It can thus be concluded that the relatively stable tetrachloro- and tetrabromoferrates(1-) undergo degradation in DMSO and MeOH. As a result the dissociation constants, $K_d = [AH^+][FeX_4^-]/[AH][FeX_4]$ could only be determined in CH_2Cl_2. To do this, a computer program based on Pitt's method [31–33] was employed. The results are collected below (standard deviations in parentheses).

Compound	K_d
$[PyH][FeBr_4]$	$3.8 \cdot 10^{-4}$ $(1.59 \cdot 10^{-4})$
$[3\text{-}Me(pyH)][FeBr_4]$	$3.0 \cdot 10^{-4}$ $(1.43 \cdot 10^{-4})$
$[4\text{-}Me(pyH)][FeBr_4]$	$5.01 \cdot 10^{-4}$ $(0.7 \cdot 10^{-4})$
$[2\text{-}NH_2(pyH)][FeBr_4]$	$5.7 \cdot 10^{-4}$ $(1.3 \cdot 10^{-4})$
$[2,4,6\text{-}triMe(pyH)][FeBr_4]$	$1.2 \cdot 10^{-4}$ $(0.9 \cdot 10^{-4})$
$[QH][FeCl_4]$	$4.08 \cdot 10^{-4}$ $(1.2 \cdot 10^{-4})$
$[QH][FeBr_4]$	$3.92 \cdot 10^{-4}$ $(0.6 \cdot 10^{-4})$
$[2\text{-}Me(QH)][FeCl_4]$	$3.88 \cdot 10^{-5}$ $(1.64 \cdot 10^{-4})$

The K_d values indicate that the complexes are electrolytes of medium strength and the organic cations of the tetrachloro- and tetrabromoferrate(1-) ions, arising from the dissociation, are weakly solvated by dichloromethane.

Acknowledgments

This research was supported by the Polish State Committee for Scientific Research under grant DS/8230-4-0088-3.

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