КРАТКИЕ СООБЩЕНИЯ

UDC

THE DOUBLE SALT TRIS(DIISOPROPYLAMMONIUM)TETRACHLORIDOFERRATE(III) DICHLORIDE: SYNTHESIS, CRYSTAL STRUCTURE, AND VIBRATIONAL SPECTRA

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Tris(diisopropylammonium)tetrachloridoferrate(III) dichloride crystallizes in the monoclinic $P2_1/c$ space group ($a = 7.6685(2)$, $b = 17.6079(3)$, $c = 23.3217(4)$ Å, $\beta = 91.396(2)°$, $V = 3148.1(1)$ Å^3, $Z = 4$, $T = 113$ K) with three diisopropylammonium cations (*dip*), one tetrachloridoferrate(III) anion, and two chloride anions in the asymmetric unit. The *dip* cations and the chloride anions form hydrogen bonded one-dimensional polymers along [010]. The tetrachloridoferrate(III) anion, habituated in between these chains, is not involved in any hydrogen bonding. The structural characterization is supported by infrared and Raman spectroscopic data.

K e y w o r d s: hydrogen bonding; diisopropylammonium; tetrachloridoferrate(III); graph-set; hybrid material.

Alkylammonium salts containing the paramagnetic [FeCl$_4$]$^-$ anion are of general interest because they are used as new Friedel-Crafts catalysts. Furthermore, there is growing interest in these compounds because some of them are used as magnetic ionic liquids [1]. Our longstanding interest on alkylammonium salts is focused on their hydrogen bond characteristics that are determined by the hydrogen bond acceptor properties and the topology of the anions. A broad variety of structural types have been characterized for the diisopropylammonium (*dip*) salts: a quasi-molecular unit in $dip_2[SiF_6]$ [2], dimeric cyclic motifs, e.g. in $dip[Ph_3CO_2]$ [3], as well as one-dimensional chain type structures for, e.g., in *dip* halides [4], and two- and three dimensional networks found for $dip_2[SO_4]$ [5] and $dip_2[IrCl_6]$ [6] respectively. The strengths of the hydrogen bonds and the geometry as well as the net charges of the counter anions are important factors that influence the principal structural type of the respective *dip* salt. In the *dip* salt system, strong hydrogen bonds are usually associated with smaller and low-dimensional units, medium strong hydrogen bonds lead to one-dimensional motifs or dimeric ion pairs, and weak hydrogen bonds enforce a higher degree of connectivity [7]. We now report on the structure of the double salt tris(diisopropylammonium)tetrachloridoferrate(III) dichloride.

Experimental. Iron(III)chloride hexahydrate (98 %, Sigma-Aldrich), hydrochloric acid (37 %, Sigma-Aldrich), diisopropylamine (Alfa Aesar) were used as received. IR spectra were recorded on a Digilab FTS-3500 FT-IR spectrometer with a resolution of 4 cm^{-1}. A single crystal was fixed on the ZnSe plate of the single reflection ATR (attenuated total reflectance)-accessory unit (MIRacle, PIKE-Technologies, Madison). The Raman spectrum was recorded using the FT-Raman accessory (Digilab, Krefeld, Germany), which is attached to the IR-spectrometer (FTS-3500); sample container: glass tube (diameter: 1.2 mm, filling height ~1.5 mm). The FT-Raman accessory contains a YAG-laser and a germanium detector. The resolution was 4 cm^{-1} and the power was 379 mW.

Synthesis. 0.27 g of iron(III)chloride hexahydrate were dissolved in 2 ml of hydrochloric acid (37 %) to give a light yellow solution. Diisopropylamine (0.5 ml) was added to this acid solution.

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T a b l e   1

Crystal data and refinement details for $\{[iPr_2NH_2]_3Cl_2\}[FeCl_4]$ *at* 113 K

Empirical formula	$\{[iPr_2NH_2]_3Cl_2\}[FeCl_4]$
Formula weight	575.14
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a, b, c, Å; β, deg.	7.6685(2), 17.6079(3), 23.3217(4); 91.396(2)
Volume, Å^3	3148.1(1)
Z (formula unit)	4
$\mu(MoK_\alpha)$, mm^{-1}	1.0
Crystal dimension, mm	0.30×0.25×0.20
D_{calc}, g/cm^3	1.21
2θ range for data collection, deg.	8.4—60.0
No. reflections collected	84540
No. reflections unique	9144 (R_{int} = 0.033)
No. reflections observed ((F^2) > 2σ((F^2))	7234
No. parameters refined	289
Final R Indices ((F^2) > 2σ((F^2))	$R1$ = 0.0246, $wR(F^2)$ = 0.0451*
Final R indices (all data)	$R1$ = 0.0369, $wR(F^2)$ = 0.0464*
Goodness of fit on F^2	1.08
$\Delta\rho_{max}/\Delta\rho_{min}$ (e/Å^3)	0.39/–0.35

* $w = 1/\sigma^2(F_0^2) + (0.01P)^2 + P]$ where $P = (F_0^2 + 2F_c^2)/3$.

After three days small yellow crystals were grown in the solution. These crystals were collected and then dissolved in warm hydrochloric acid (37 %). Upon cooling light yellow crystals were harvested from the mother liquor.

Spectroscopy. IR (ATR) [cm^{-1}]: ν = 2978 (vs), 2913 (m, sh), 2835(s), 2759 (s), 2724 (s), 2478 (m), 2422 (w), 2093 (w), 1593 (m), 1465 (m), 1395(s), 1381 (m, sh), 1301 (w),1185 (w), 1146, 1102 (m), 974 (w), 949(w), 805 (w);

Raman [cm^{-1}]: ν = 2990 (vs), 2935 (s, broad), 2746 (w), 1477 (w, sh), 1457 (w), 1419 (w), 1340 (vw), 1301 (vw), 1183 (vw), 1187 (vw), 950 (w), 911 (w), 803 (m), 467 (m), 385 (w, [FeCl$_4$]$^-$, ν_3), 332 (vs, [FeCl$_4$]$^-$, ν_1), 133 (m, [FeCl$_4$]$^-$, ν_4), 112 (s, [FeCl$_4$]$^-$, ν_2).

Crystal structure determination. A crystal (0.30×0.25×0.20 mm^3) was fixed at a glass fibre and mounted on an Oxford Xcalibur diffractometer equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Experimental details are given in Table 1. The structure was solved by direct methods and the model was refined using full-matrix least-squares techniques [8]. Hydrogen atoms belonging to CH and the methyl group were included in the latest stages of refinement using a riding model. The positional parameters of the hydrogen atoms of the ammonium groups were refined freely. The displacement parameters were set to $U_{iso}(H)$ = 1.5 $U_{eq}(C)$ for methyl groups and $U_{iso}(H)$ = = 1.2 $U_{eq}(C)$ for CH groups. The isotropic displacement parameters of the hydrogen atoms belonging to NH$_2$ groups were refined freely.

Supplementary material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-772191. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

T a b l e 2

Selected bond lengths and angles (Å, deg.)

Fe1—Cl3	2.1998(3)	N1—C1	1.5114(13)	N1—C4	1.5070(14)
Fe1—Cl5	2.1982(4)	N2—Cl7	1.5061(15)	N2—C10	1.5092(15)
Fe1—Cl4	2.2041(3)	N3—C13	1.5087(14)	N3—C16	1.5093(14)
Fe1—Cl6	2.1869(4)				

All C—C bond lengths are found in the range: 1.508(2)—1.522(2)

Cl3—Fe1—Cl4	109.07(1)	C1—N1—C4	118.51(9)	Cl4—Fe1—Cl5	109.63(1)
Cl3—Fe1—Cl6	110.13(1)	C13—N3—C16	117.89(9)	Cl5—Fe1—Cl6	112.20(2)
Cl4—Fe1—Cl6	106.96(1)	Cl3—Fe1—Cl5	108.81(1)	C7—N2—C10	117.78(9)

T a b l e 3

Hydrogen Bonding Parameters (Å, deg.)

D—H⋯A	D—H	H⋯A	D⋯A	∠D—H⋯A
N1—H11⋯Cl1′	0.889(14)	2.272(14)	3.1577(9)	174.4(12)
N1—H12⋅Cl2	0.859(14)	2.345(14)	3.1953(10)	170.2(12)
N2—H21⋅Cl2	0.868(14)	2.336(14)	3.1920(10)	168.9(12)
N2—H22⋅Cl1	0.890(14)	2.289(14)	3.1748(11)	172.8(12)
N3—H31⋅Cl2	0.891(13)	2.359(13)	3.2446(10)	172.9(11)
N3—H32⋅Cl1	0.891(14)	2.280(14)	3.1587(19)	168.9(12)

′ –x+1, y–1/2, –z+1/2.

Results and Discussion. The reaction of iron(III) chloride with diisopropylamine in concentrated hydrochloric acid yielded light-yellow crystals of tris(diisopropylammonium)tetrachloridoferrate(III) dichloride. The structure of the title compound consists of three crystallographically independent *dip* cations, one tetrachloridoferrate(III) anion, and two chloride anions, all lying on general positions. Bond lengths and angles in the *dip* cations and the tetrachloridoferrate(III) anion are in the expected range (Table 2). The IR spectrum of the title compound shows the typical bands of the *dip* cation, as found, for example, for the respective halides [7]. In addition, in the Raman spectrum, four bands that are characteristic of an almost tetrahedral tetrachloridoferrate(III) anion [8] are found at 385 cm^{-1}, 332 cm^{-1}, 133 cm^{-1}, and 112 cm^{-1}. These values are in excellent agreement with those given in the literature [10, 11]. The IR spectrum of the dried bulk material is identical to the spectrum collected on a single crystal using the ATR accessory.

Each *dip* cation acts as a double hydrogen bond donor to the neighboring chloride anions forming chains along [010]. The bonding parameters derived are in the expected range (Table 3) for the electrostatically supported hydrogen bonding interactions of alkylammonium chlorides [4].

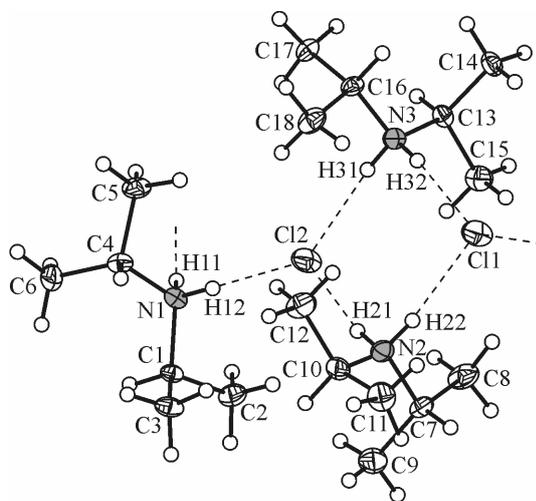The asymmetric structural motif in these chains can be described as a hydrogen bonded cyclic dimer

Fig. 1. Crystallographically independent $(dip_3Cl_2)^+$ unit of the hydrogen bonded chain along [010]

Fig. 2. View along [100] on the structure of the title compound. Weak coordinating tetrachloridoferrate(III) anions fill the gaps between the wavy hydrogen bonded $\frac{1}{\infty}[(dip_3Cl_2)^+]$ chains
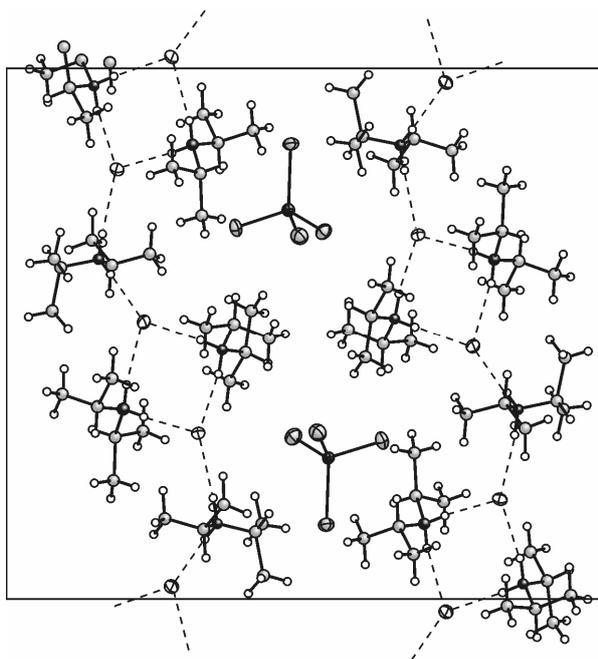
composed of two *dip* cations (N1, N2) and two chloride anions (Cl1, Cl2) and an additional *dip* cation that bridges to the next crystallographically dependent cyclic dimer (Fig. 1). The graph-set symbol for the above mentioned dimer is $R_4^2(8)$ [12]. The tetrachloridoferrate(III) anion fills the gaps between the hydrogen bonded chains without forming any classical hydrogen bonds [13] (Fig. 2). The shortest distances between the chlorine atoms of the tetrachloridoferrate(III) anion and any hydrogen atom are those to the hydrogen atoms belonging to CH and methyl groups of the neighboring *dip* cations (d(C—H···Cl) > 2.80 Å). For related structures it has been shown that the tetrachloridoferrate(III) anion do not inevitably form hydrogen bonds even when hydrogen bond donating groups are present [14].

The title compound is an organic-inorganic hybrid material that consists of cationic organic one-dimensional polymers and habituated tetrachloridoferrate(III) anions which are not involved in the hydrogen bonding at all.

Conclusions. So far, one-dimensional polymeric as well as cyclic dimeric structures containing *dip* cations and various counter anions have been described. The structure of the title compound tris(diisopropylammonium)tetrachloridoferrate(III) dichloride is the first example that combines both of these structural motifs. The polymeric units consist of cyclic dimers $\frac{1}{\infty}[(dip_3Cl_2)^+]$. The tetrachloridoferrate(III) anions are located in between the hydrogen bonded chains not involved in any classical hydrogen bonding.

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