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Synthesis and Crystal Structure of Tetrabutylammoniumtetrachloroferrate(III)

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Tetrabutylammoniumtetrachloroferrate(III) compound, $[n\text{-}Bu_4N]^+[FeCl_4]^-$ has been prepared and characterized by elemental analysis and X-ray studies. It crystallizes in the orthorhombic system, space group Pnna, with Mr = 220.05 ($C_8H_{18}N_{0.5}Cl_2Fe_{0.5}$), a = 18.510(4) Å, b = 11.553(2) Å, c = 11.442(2) Å, V = 2446.8(8) Å^3, Z = 8, D_c = 1.195 g/cm^3, F(000) = 932, μ = 1.051 mm^{-1}, the final R = 0.0825, wR = 0.0860 and S = 1.101. The total reflections were 4727 and the independent ones were 2196 (R_{int} = 0.0697), of which 827 were observed with $I > 2\sigma(I)$. The crystal structure consists of one independent $[FeCl_4]^-$ anion and one independent $[n\text{-}Bu_4N]^+$ cation. In the $[FeCl_4]^-$ anion, the central Fe atom adopts distorted tetrahedral geometry with the four Cl atoms, and the Fe-Cl distances are 2.122(14) and 2.1807(17) Å, respectively. In the $[n\text{-}Bu_4N]^+$ cation, the N atom adopts a slightly distorted tetrahedral geometry. In the solid state, the hydrogen bondings link $[FeCl_4]^-$ anion and $[n\text{-}Bu_4N]^+$ cation which stabilize the structure.

Key Words: Tetrabutylammoniumtetrachloroferrate(III), Crystal structure.

INTRODUCTION

Considerable interest has been shown over recent years in the transition metal halide complexes and among them, the tetrahalometalates with various organic counteractions have been the subject of theoretical[1], structural[2-4], magnetostructural[5] and spectroscopic[6] studies. The hydrogen bonding[7] and noncovalent π-interaction between aromatic rings of organic cation[8] in this type of molecules control molecular recognitions and self-assembly processes and exercise important effects on the solid-state structure and the properties of many compounds relevant to biological and material sciences[9]. Numerous salts of the well-known yellow $[FeCl_4]^-$ anion have been obtained from the interaction of various cations with Fe(III) in hydrochloric acid solution[10-12]. In this work, the crystal structure of the tetrabutylammoniumtetrachloroferrate(III) complex is reported.

EXPERIMENTAL

All chemicals were obtained from a commercial source and used without further purification. Solutions of $FeCl_3$ (0.16 g, 1 mmol) in concentrated HCl and tetrabutylammonium chloride (0.32 g, 1 mmol) in ethanol (50 mL) were mixed and stirred at approximately 50ºC for 2 h. The yellow solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a light yellow square crystalline solid appeared two days later and was separated by filtration. The C, H and N contents were determined by elemental analysis (Anal. Calcd. (%) for $C_{16}H_{36}NCl_4Fe$: C, 36.95; H, 6.98; N, 2.69. Found (%): C, 36.92; H, 6.85; N, 2.59.).

X-ray structure determination: A light yellow crystal $C_{16}H_{36}NCl_4Fe$ with dimensions of 0.30 × 0.20 × 0.24 mm was measured at 20°C using MoK_α radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan with θ limits $2.09 < \theta < 27.51°$ for the title compound. The structures of $C_{16}H_{36}NCl_4Fe$ was solved by direct methods and refined by least squares on F_{obs}^2 by using the SHELXTL[13] software package. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final least-square cycle of refinement included 111 parameters gave R = 0.0825, $R_w = 0.0860$; the weighing scheme, $w = 1/[\sigma^2(F_o^2) + (0.0328P)]^2$, where $P = (F_o^2 + 2Fc^2)/3$. The maximum peak in the final difference Fourier map is 0.172 e·Å^{-3} and the minimum peak is -0.166 e·Å^{-3}. The molecular graphics were plotted using SHELXTL.

RESULTS AND DISCUSSION

Atomic parameters and equivalent isotropic thermal parameters of non-hydrogen atoms for the [*n*-Bu_4N][$FeCl_4$] are given in Table-1. A displacement ellipsoid plot with the numbering scheme is shown in Fig.1. Fig.2 shows a perspective view of the crystal packing in the unit cell. Selected bond distances and angles are listed in Table-2. The crystal structure of this compound consists of discrete $[FeCl_4]^-$ anion and [*n*-$Bu_4N]^+$ cation held together by the C-H···Cl hydrogen bonding. In the $[FeCl_4]^-$ anion, The Fe-Cl distances [2.1807(17) Å] involved in the hydrogen bonding are slightly longer than the other one Fe-Cl distances [2.122(14) Å] and in good agreement with the corresponding $[FeCl_4]^-$ complexes, such as 2.1832(2) Å in $(C_{10}H_{15}N_2)[FeCl_4]$[10]; 2.1812(5) Å in $[FeCl_2(CH_3CN)_4]$-$[FeCl_4]$[12]. But slightly shorter than those of $(C_{13}H_{14}N_5S_2)_2[FeCl_4]BF_4$ [2.1930(5) Å][11]. The slight elongation of these bond distances is presumably due to a reduction of electron density on the chloride ions. The Cl(1A) atom is found to be disordered, the occupancies of the disordered atoms were initially refined and later fixed. The populations of the Cl(1A) and Cl(1B) components are all 50%. The Cl-Fe-Cl bond angles vary within the range 93.6(6)-116.3(2)º. So the $[FeCl_4]^-$ anion can be described as a distorted tetrahedral geometry around the Fe atom. In the $[n\text{-}Bu_4N]^+$ cation, the N atom adopts a slightly distorted tetrahedral geometry with the C-N-C bond angles ranging from 108.6(3) to 112.1(6)°. The C-N and C-C bond lengths fall within the normal range[14]. There are three hydrogen bond from the $[n\text{-}Bu_4N]^+$ cation to the chlorine, the donor and acceptor distances are C(4)···Cl(1D) 2.8435 Å, C(8)···Cl(2) 2.9108 Å and C(7)···Cl(2) 3.0642 Å, respectively. In the solid state, these hydrogen bondings link $[FeCl_4]^-$ anions and $[n\text{-}Bu_4N]^+$ cations which stabilize the structure.

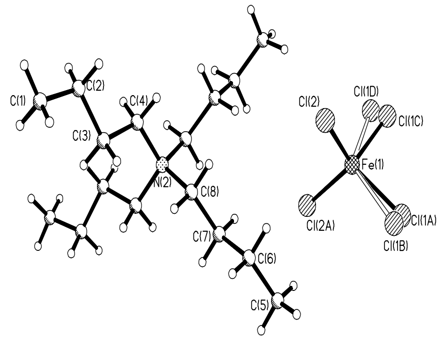

Fig. 1. Molecular structure for $C_{16}H_{36}NCl_4Fe$ with the atomic numbering scheme

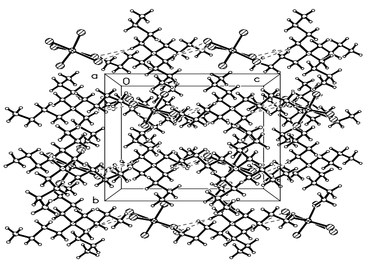

Fig. 2. View of the crystal packing down the a axis for $C_{16}H_{36}NCl_4Fe$

TABLE-1

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Fe(1)	4082(1)	2500	2500	89(1)
Cl(1A)	4867(7)	2064(8)	1223(12)	134(4)
Cl(1B)	4637(7)	1613(8)	960(10)	115(3)
Cl(2)	3412(1)	1083(1)	3143(2)	111(1)
N(2)	636(3)	2500	2500	55(2)
C(1)	-1413(4)	-335(7)	3112(7)	182(4)
C(2)	-814(4)	294(6)	3578(6)	125(3)
C(3)	-405(3)	1005(5)	2658(6)	92(2)
C(4)	178(3)	1708(4)	3258(5)	72(2)
C(5)	2572(4)	1956(5)	-650(6)	127(3)
C(6)	2053(4)	1491(5)	210(6)	117(3)
C(7)	1614(3)	2340(5)	889(5)	77(2)
C(8)	1103(3)	1748(4)	1707(5)	68(2)

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist
Fe(1)-Cl(1A)	2.122(14)	Fe(1)-Cl(2)	2.1807(17)
Fe(1)-Cl(1B)	2.282(13)	N(2)-C(4)	1.520(6)
N(2)-C(8)	1.525(6)		
Angle	**(°)**	**Angle**	**(°)**
Cl(1A)#1-Fe(1)-Cl(1A)	93.6(6)	Cl(1A)#1-Fe(1)-Cl(2)	109.6(4)
Cl(1A)-Fe(1)-Cl(2)	116.3(2)	Cl(2)-Fe(1)-Cl(2)#1	110.74(11)
Cl(1A)#1-Fe(1)-Cl(2A)	116.3(2)	Cl(1A)-Fe(1)-Cl(2)#1	109.6(4)
Cl(1A)-Fe(1)-Cl(1B)	18.8(4)	Cl(1A)#1-Fe(1)-Cl(1B)	109.3(2)
Cl(2)-Fe(1)-Cl(1B)	100.3(2)	Cl(2)#1-Fe(1)-Cl(1B)	109.4(3)
Cl(1B)#1-Fe(1)-Cl(1B)	126.5(6)	C(4)-N(2)-C(8)	108.3(3)
C(8)#1-N(2)-C(8)	111.0(5)	C(4)-N(2)-C(4)#1	112.1(6)

Symmetry transformations used to generate equivalent atoms: #1: x, $-y+1/2$, $-z+1/2$

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