ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 10, pp. 780–783. © Pleiades Publishing, Ltd., 2009.

Molecular and Crystal Structures of $[FeCl(HMPA)_3(H_2O)_2]^{2+}(FeCl_4)_2^- \cdot 3HMPA$[1]

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Received January 11, 2009

Abstract—IR and single-crystal X-ray diffraction study are carried out for compound, $C_{36}H_{112}Cl_9Fe_3N_{18}O_8P_6$ (I). It crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 14.2992(3)$, $b = 21.4351(4)$, $c = 25.5407(5)$ Å, $V = 7828.3(3)$ Å^3, $\rho_{calcd} = 1.553$ g/cm^3, $Z = 4$. The FeCl fragment is coordinated with chlorine atom of two water molecules and three HMPA molecules to form a cation, with a distorted octahedral coordinate geometry. In the crystal I, the cation is linked with HMPA by the O–H···O hydrogen bond. The chiral crystal is formed through self-assembly even from achiral molecules.

DOI: 10.1134/S1070328409100121

INTRUDUTION

The intentional design and synthesis of specific structural aggregates in the solid state continue to attract considerable attention from researchers in the field of crystal engineering. This interest is due to the fact that a successful incorporation of desirable structural units into a crystal may result in the development of novel materials with improved electrical, optical, or catalytic properties [1]. Despite such complications, great progress has been made in this area over the past few years. Hydrogen bonding interactions are most frequently used to assemble organic molecules and they play an important role in stabilizing supramolecular aggregates. The ligand hexamethylphosphoramide (**HMPA**), plays an important role in many transition metal-mediated organic reactions [2]. Although there are numerous crystal structures available for various transition-metal-HMPA complexes, relatively little is known about the iron structures of these complexes [3–6]. Here we report the facile synthesis, as well as the X-ray crystal structure of compound $[FeCl(HMPA)_3(H_2O)_2]^{2+}(FeCl_4)_2^- \cdot 3HMPA$ (**I**).

The design of chiral crystalline complexes from different achiral molecules [7] is an active field. It has been reported previously that a HMPA adduct crystallizes in the chiral space group $P2_12_12_1$. In this study, the chiral crystal of the title compound was synthesized from chiral compounds.

[1] The article is published in the original.

EXPERIMENTAL

All reagents were reagent grade and commercially available and used as received unless otherwise noted. All manipulations were performed under atmosphere, using the standard Schlenk techniques. HMPA (0.06 mol, 10.74 g) and $FeCl_3 \cdot 6H_2O$ (0.025 mol, 6.76 g) were mixed and dissolved in 70 ml of ethanol by heating to 365 K, when a clear solution was formed. Crystals of compound **I** were formed by gradual evaporation of excess ethanol over a period of one week at 297 K. The title compound is fully characterized by IR. The IR spectra were recorded using a Jasco FTIR-4100 series. IR spectrum (KBr; ν, cm^{-1}): 2832, 2815, 1480, 1305, 1190, 1103, 994, 769, 478. A transparent colorless prismatic single crystal with $0.45 \times 0.44 \times 0.42$ mm was carried out at 273(2) K on a Bruker APEX area-detector diffractometer (MoK_α radiation). The structure was solved by a direct method and subsequently refined in anisotropic approximations using the SHELX-97 program [8]. All hydrogen atom positions were calculated on the basis of stereochemical considerations and refined using the riding model. All calculations were performed with the WinGX program package [9]. All figures and the analysis of intermolecular interactions were made with the SHELXTL program [10]. The crystal data of the compound I: $[FeCl(HMPA)_3(H_2O)_2]^{2+}(FeCl_4)_2^- \cdot 3HMPA$; orthorhombic $P2_12_12_1$, $a = 14.2992(3)$, $b = 21.4351(4)$, $c = 25.5407(5)$ Å, $V = 7828.3(3)$ Å^3, $\rho_{calcd} = 1.553$ g/cm^3, $Z = 4$. The scanning range was $3.0° < \theta < 27.48°$. A total of 14878 independent reflections were collected including 14027 ones with $I \geq 2\sigma(I)$. The final values of agreement factors were $R = 0.0521$ and $Rw = 0.1415$ for

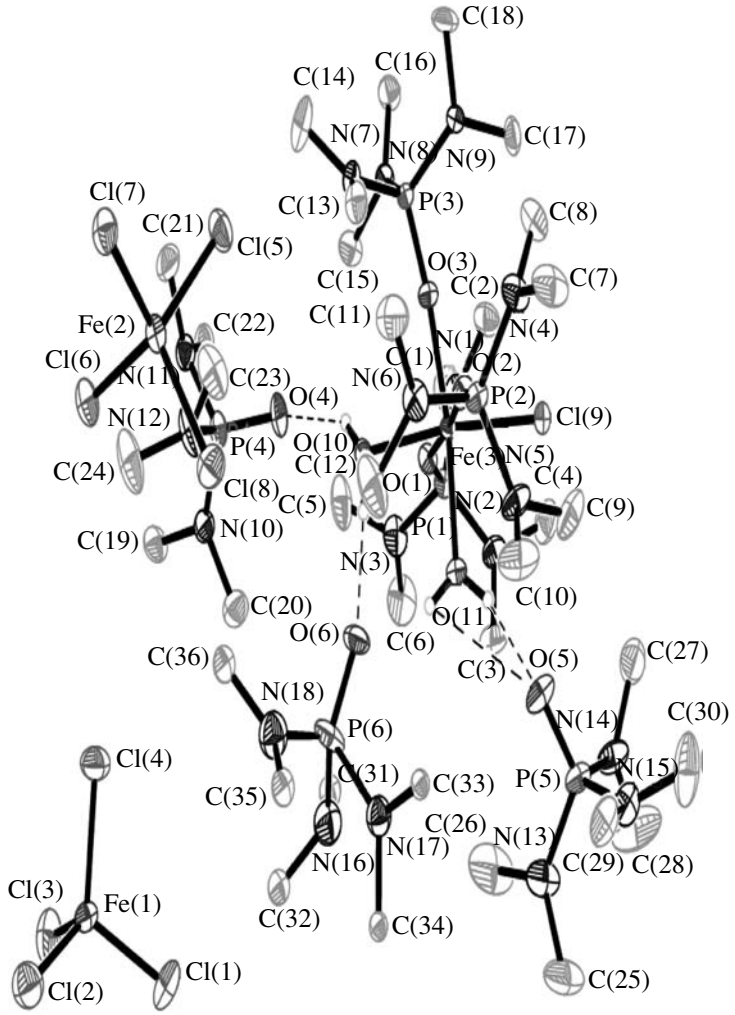

Fig. 1. Molecular structure and atom-labelling scheme for $[FeCl(HMPA)_3(H_2O)_2]^{2+}(FeCl_4)_2^- \cdot 3HMPA$ with thermal ellipsoids at the 30% probability level, showing hydrogen bonds; for the sake of clarity, the minor disordered part of HMPA and all H atoms not involved in hydrogen bond were omitted.

14027 reflections with $F > \sigma(F_2)$. GOOF on F^2 was 1.032. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Center (no. 715121; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSION

As shown in Fig. 1, the asymmetric unit of compound **I** consists of six crystallographically independent molecular assemblies, one $[FeCl(HMPA)_3(H_2O)_2]^{2+}$ cations, two $[FeCl_4]^-$ anion, and three HMPA molecules. The HMPA molecules are linked with H_2O of the cation by strong O(11)–H(*w*3)···O(5), O(11)–H(*w*4)···O(6), O(10)–H(*w*1)···O(4), and O(10)–H(w2)…O(6) hydrogen bonds. The iron atom is six-coordinated by five oxygen atoms from the three HMPA ligand, two H_2O, and a chlorine atom, forming a distorted octahedral geometry. In compound **I**, the Fe–O(HMPA) bond lengths are 1.959(3), 1.978(3), and 2.001(3) Å, giving an average value of 1.979(3) Å, which is slightly shorter than the normal value 2.054(5) Å [11], also the Fe–O(H_2O) bond lengths are 2.042(3) and 2.086(3) Å, the averaged bond length (2.064(3) A) is comparable with that observed in [12] and [13]. The Fe–Cl bond length in the cation integrant is 2.303(10) Å, which is little longer than those (2.1578(17), 2.176(2), 2.1954(13) Å) in the tetrachloroferrate(III) anion. We think that the addition of HMPA has dramatic effects on the iron(III) atom. This may result from a increase in the electron density on the iron atom and the enhanced stability of the Fe(III) species [14]. So, the Fe–Cl bond length becomes longer. The angle of 82.71(12)° is 89.43(13)° which is different from the angle of O(3)Fe(3)O(2) (89.43(13)°) and O(3)Fe(3)O(1) (88.55(12)°). As shown in Fig. 2, the water molecule acts as well as a hydrogen-bond donor for HPMA. In

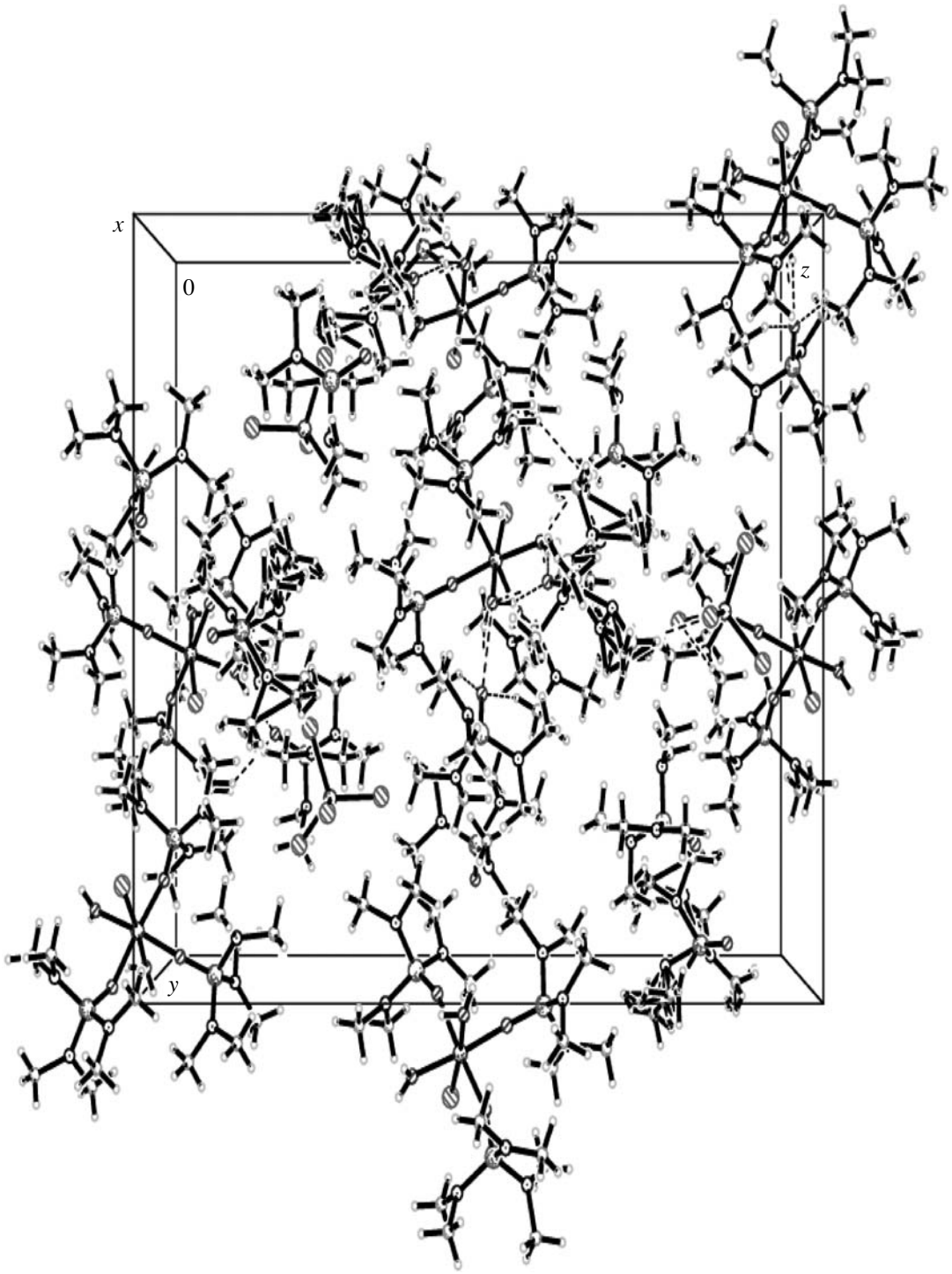

Fig. 2. Crystal packing of the title compound viewed down the *x* axis.

the structure, one of the HMPA molecule is disordered, which is very interesting.

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