

## Structure of the Pyridine–Ferric Chloride (4:1) Complex, $\text{Fe}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3 \cdot \text{C}_5\text{H}_5\text{N}$ , at 190 K

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**Abstract.**  $M_r = 478.6$ , orthorhombic,  $C22_1$ ,  $a = 8.861(2)$ ,  $b = 16.712(5)$ ,  $c = 14.280(4)$  Å,  $V = 2112.0(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.505$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.14$  mm<sup>-1</sup>,  $F(000) = 980$ . Final  $R = 0.059$  for 1205 counter reflections. The  $\text{Fe}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3$  complex has  $C2$  symmetry. The pyridine molecules in the mixed chains of  $\text{Fe}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3 \cdot \text{C}_5\text{H}_5\text{N}$  form stacks parallel to the  $c$  axis. The distances between the atoms of two consecutive pyridine molecules are of the order of the van der Waals distance.

**Introduction.** Recently, there has been extensive interest in the electrical and magnetic properties of one-dimensional systems (Shchegolev, 1972; Ackerman, Cole & Holt, 1974). Most of the anomalies appearing in low and highly conductive systems or magnetic systems are related to low-dimensionality effects arising from the existence of linear chains (André, Bieber & Gautier, 1976; Goldberg & Shmueli, 1973). As a part of the study of the electrical and magnetic properties of one-dimensional systems, a low-dimensional system of this complex has been prepared (Pietrzak, Januszczyk & Obuszko, 1979; Januszczyk, Pietrzak & Stecki, 1981). We reported the existence of an extraordinary maximum in d.c. conductivity of a single crystal of the pyridine–ferric chloride complex at 237 K.

The crystal and molecular structure of the title compound determined by an X-ray analysis is reported in this paper.

**Experimental.** Anhydrous  $\text{FeCl}_3$  added to pyridine, solution stirred at 300 K then kept for a few days in a thermostat at 284 K; red–brown plate-like crystals

obtained; elementary analysis indicated a stoichiometric ratio of pyridine–ferric chloride of 4:1 (Januszczyk, 1982).

The crystal was unstable at room temperature and was therefore sealed in a glass capillary with pyridine vapour or was covered with a thin layer of paraffin oil with pyridine 6%. In the preliminary X-ray study made on the crystal in the capillary tube in the presence of pyridine, the crystal decomposition was delayed so that the parameters of the monoclinic system could be approximately determined as  $a = 4.745(7)$ ,  $b = 14.395(9)$ ,  $c = 7.861(14)$  Å,  $\beta = 93.93^\circ$ . However, the latter results cannot be treated as decisive. At 237 K the phase transition was found to occur (Januszczyk *et al.*, 1981). Since the low-temperature modification was more stable the measurement of reflection intensities was performed at 190 K.

Single crystal,  $0.3 \times 0.5 \times 0.6$  mm. Four-circle Syntex  $P2_1$  diffractometer equipped with a low-temperature device LT-1, Mo  $K\alpha$  radiation monochromatized by a flat graphite crystal, temperature measured where crystal was mounted. 222, 240 and equivalents used for measuring lattice parameters. No absorption correction applied. Control reflection measured every hour,  $\pm 6\%$  variation in intensity. Total of 1324 independent reflections ( $0 \leq h \leq 11$ ,  $0 \leq k \leq 21$ ,  $0 \leq l \leq 18$ ) collected in range  $0 < 2\theta < 55^\circ$ , 1205 for which  $I > 1.96\sigma(I)$  used in further calculations. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). Positions of H atoms calculated from the geometry and included in refinement with constrained C–H distances [1.08(1) Å]. Function minimized  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma^2(F_o) + 0.000238F_o^2]^{-1}$ . Structure refined anisotropically (H isotropic) to  $R = 0.059$ ,  $R_w = 0.065$  (*SHELX*, Sheldrick, 1976),  $S = 7.65$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). For geometrical calculations programs *GEOME* and *PLANE* (Jaskólski, 1981) and *PLUTO* (Clegg, 1979) applied.

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**Discussion.** The final positional parameters are listed in Table 1.\* Contrary to preliminary suppositions X-ray analysis proved, that ligands in the complex studied consist of only three pyridine molecules as the self-symmetry of the complex of  $\text{Fe}(\text{py})_3\text{Cl}_3$  is  $C_2$ . Thus, the compound under investigation differs from ferric chloride hydrate  $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\cdot\text{Cl}\cdot 2\text{H}_2\text{O}$  (Lind, 1967), or from hexapyridine magnesium bromide  $[\text{Mg}(\text{py})_4\text{Br}_2]\cdot 2\text{py}$  (Halut-Desportes, 1977). In both cases the complexes have four ligands having  $2m$  and  $222$  symmetry, respectively.

\* Lists of structure factors, anisotropic thermal parameters and coordinates of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38567 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-H atoms with their e.s.d.'s in parentheses

	$x$	$y$	$z$	$B_{\text{eq}}$
Fe	0	1630 (1)	2500	1.84 (4)
Cl(1)	2626 (2)	1678 (1)	2546 (2)	2.51 (5)
Cl(2)	0	250 (1)	2500	2.78 (8)
N(1)	0	2990 (4)	2500	2.0 (2)
C(11)	1210 (8)	3403 (4)	2241 (5)	3.0 (3)
C(12)	1271 (10)	4234 (5)	2238 (6)	3.7 (4)
C(13)	0	4656 (6)	2500	3.6 (4)
N(2)	102 (8)	1697 (3)	985 (3)	2.1 (2)
C(21)	-724 (9)	2223 (4)	485 (5)	2.3 (2)
C(22)	-683 (10)	2245 (5)	-491 (5)	3.2 (3)
C(23)	211 (12)	1727 (4)	-959 (4)	3.4 (3)
C(24)	1085 (11)	1184 (5)	-464 (5)	3.3 (3)
C(25)	999 (10)	1191 (5)	517 (6)	3.0 (3)
N(3)	4161 (11)	0	0	6.1 (7)
C(31)	4979 (18)	583 (4)	387 (8)	5.4 (5)
C(32)	6490 (15)	616 (8)	394 (7)	6.6 (6)
C(33)	7271 (16)	0	0	6.4 (9)

$$B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

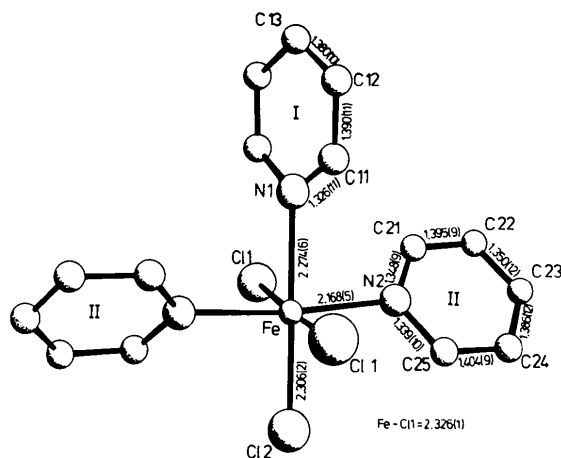


Fig. 1. Bond distances ( $\text{\AA}$ ) in the  $\text{Fe}(\text{py})_3\text{Cl}_3$  molecule with the numbering of atoms.

Table 2. Bond lengths for pyridine (III) ( $\text{\AA}$ ) and all bond angles ( $^\circ$ ) with their e.s.d.'s in parentheses

N(3)—C(31)	1.332 (12)	C(32)—C(33)	1.362 (15)
C(31)—C(32)	1.340 (19)		
C(31)—N(3)—C(31)	114.3 (8)	C(21)—N(2)—C(25)	118.6 (6)
N(3)—C(31)—C(32)	125.1 (11)	N(2)—C(21)—C(22)	122.2 (6)
C(31)—C(32)—C(33)	118.2 (11)	C(21)—C(22)—C(23)	119.5 (7)
C(32)—C(33)—C(32)	119.0 (10)	C(22)—C(23)—C(24)	119.6 (7)
C(11)—N(1)—C(11)	117.3 (6)	C(13)—C(24)—C(25)	118.3 (7)
N(1)—C(11)—C(12)	123.5 (7)	C(24)—C(25)—N(2)	122.4 (7)
C(11)—C(12)—C(13)	118.6 (7)	N(1)—Fe—N(2)	87.0 (1)
C(12)—C(13)—C(12)	118.5 (6)	N(1)—Fe—Cl(1)	88.0 (<1)
		N(2)—Fe—Cl(1)	89.1 (2)

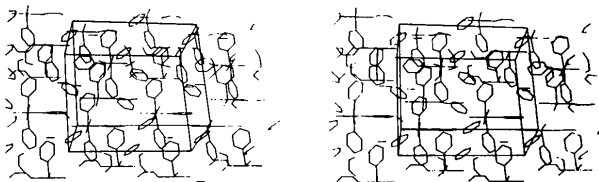


Fig. 2. Stereoscopic view of the unit cell ( $b$  axis horizontal,  $c$  axis vertical, origin at lower, front, left-hand corner).

The bond distances within the ferric complex are presented in Fig. 1. The geometry of pyridine (III) as well as the valency angles are listed in Table 2.

The  $\text{Fe}^{3+}$  cation is coordinated octahedrally by three Cl atoms and three N atoms of pyridine molecules (I) and (II), as shown in Fig. 1. The  $\text{Fe}(\text{py})_3\text{Cl}_3$  complex lies on a twofold axis passing through the atoms C(13), N(1), Fe and Cl(2). The bond distances and angles in the pyridine rings are close to the values commonly found in other pyridine derivatives. Slightly greater e.s.d.'s in the case of pyridine (III) are caused by increased vibrations of C(31) and C(32) (see Table 1). However, significant differences are observed in the bond distances between the  $\text{Fe}^{3+}$  cation and the ligands. The Fe—N(1) and Fe—N(2) bonds differ from each other by more than 12 times the average e.s.d. Such a great discrepancy is caused by strong intermolecular coupling between pyridines (I) and (III) along the  $c$  axis.

The four pyridine molecules each interacting with two neighbouring ones (one below and one above) together form a stack, which can be easily seen in Fig. 2. The shortest distances are found between C(31)···C(13), C(32)···C(12) and C(33)···C(12): 3.392 (11), 3.508 (14) and 3.554 (9)  $\text{\AA}$ , respectively. The elongation of the Fe—N(1) bond is probably due to electrostatic interactions in the stacks of pyridine molecules, resulting from the mutual positions of rings (I) and (III). The fact that the Fe—Cl(2) bond is simultaneously shortened may be the cause of a slight deviation of the angle N(1)—Fe—N(2) from  $90^\circ$  (Table 2). The angle between the normals to the planar rings (II) and (III) is  $75.0 (6)^\circ$ . Inside the complex, rings (I) and (II) are inclined with respect to the plane of N(1)FeN(2)Cl(2) atoms at an angle  $68.9 (4)^\circ$  and  $41.4 (4)^\circ$  respectively.

Taking into consideration the intermolecular distances only weak van der Waals interactions are expected to be found between pyridines (II) and (III) (Fig. 2). The shortest of these distances are 3.431 (12) [C(24)···N(3)] and 3.669 (18) Å [C(25)···C(31)]. The molecular packing is shown in the stereoscopic view of the unit cell (Fig. 2).

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## The Structure of Indenyluranium Trichloride–Bis(tetrahydrofuran), [U(C<sub>9</sub>H<sub>7</sub>)]Cl<sub>3</sub>·2C<sub>4</sub>H<sub>8</sub>O

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**Abstract.**  $M_r = 603.8$ , monoclinic,  $P2_1/c$ ,  $a = 9.137$  (3),  $b = 15.970$  (3),  $c = 14.318$  (5) Å,  $\beta = 108.17$  (3)°,  $V = 1985$  (2) Å<sup>3</sup>,  $D_x = 2.020$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $T = 295$  (1) K,  $\mu = 82.453$  cm<sup>-1</sup>,  $F(000) = 1136$ . The crystal structure was solved by direct methods. Full-matrix least-squares refinement with all atoms, except H atoms, treated anisotropically gave an  $R$  value of 0.043. The coordination geometry about the uranium ion is pseudo-octahedral with one  $\eta^5$ -C<sub>9</sub>H<sub>7</sub> ligand and one coordinated H<sub>4</sub>f (THF) molecule occupying *trans* axial positions, and the other H<sub>4</sub>f molecule and three Cl atoms occupying equatorial positions.

**Introduction.** The number of questions regarding the mode of bonding in organoactinide compounds has increased during the last ten years since actinide

elements possess several unique features not found among transition elements. Actinides exhibit very sizable ionic radii that give rise to variable formal coordination numbers and unusual coordination geometries depending upon the ligand systems. The presence of *5f* valence orbitals, whose involvement in the bonding may be important, is another characteristic of actinides that distinguishes them from the lanthanides and the *d*-block elements.

The largest proportion of organouranium complexes whose molecular structures have been described in the literature are complexes of the cyclopentadienide ligand (Atwood, Hains, Tsutsui & Gebala, 1973; Bombieri, De Paoli, Delpra & Bagnall, 1978; Burns, 1974; Eigenbrot & Raymond, 1981; Ernst, Kennelly, Day, Day & Marks, 1979; Fischer, Klahne & Kopf, 1978; Leong, Hodgson & Raymond, 1973; Perego, Cesari, Farina & Lugli, 1975, 1976; Wong, Yen & Lee, 1965). Only one structural determination has been reported for organouranium complexes of the indenide ligand (Burns & Laubereau, 1971).

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