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CRYSTAL AND MOLECULAR STRUCTURES OF (η^6-XANTHENE)(η^5-CYCLOPENTADIENYL)IRON(II) HEXAFLUOROPHOSPHATE AND (η^6-2-METHYLTHIANTHRENE)(η^5-CYCLOPENTADIENYL)IRON(II) HEXAFLUOROPHOSPHATE

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Summary

The crystal structures of the hexafluorophosphate salts of (η^6-xanthene)(η^5-cyclopentadienyl)iron (I) and (η^6-methylthianthrene)(η^5-cyclopentadienyl)iron (II) have been determined. The xanthene complex crystallizes in the triclinic system, space group $P\bar{1}$, a 8.585(2), b 10.224(2), c 10.483(2) Å; α 96.524(11), β 110.484(11), γ 101.836(9)°, $V = 826.1(3)$ Å^3; $Z = 2$, 4218 reflections were refined to $R = 0.046$. The 2-methylthianthrene complex crystallizes in the orthorhombic space group $P2_12_12_1$, a 11.526(2), b 11.940(10), c 13.701(10) Å, V 1886(2) Å^3; $Z = 4$, 2278 reflections were refined to an $R = 0.056$. Both complexed heterocycles are bent and have dihedral angles between the planes of the phenyl rings of 176.71(9)° (xanthene) and 127.4(3)° (2-methylthianthrene). The stereochemistry of the double S_NAr reaction leading to the formation of 2-methylthianthrene complex is discussed.

Introduction

Studies of the synthesis and properties of (η^6-arene)(cyclopentadienyl)iron(II) salts and related complexes have attracted considerable attention recently. However, only a relatively small number of the structures have been confirmed by X-ray diffraction methods: bridged (1,1′-trimethylenebenzene)(Cp)Fe PF_6 salt (Nesmeyanov et al. [1]); (hexaethylbenzene)(Cp)Fe PF_6 salt (Astruc and coworkers [2]); ([2.2]paracyclophane)(Cp)Fe BF_4, (bis[2′,5′-dimethyl-3′,4′-cyclobutabenzo]-1,5-cyclooctadienyl)(Cp)Fe PF_6 and $[2_5]$(1,2,3,4,5-cyclophane)(Cp)Fe PF_6 (Hanson [3–5]); and (3*a*-7*a*[hexahydro-2,2′,3,3′,5′,6′-spiro(1*H*-indene-1:4′-pyrane])(Cp)Fe PF_6

(Precigoux et al. [6]). In addition, the *exo*-position of the methyl substituent in (*exo*-9-methylfluorene)(Cp)Fe PF_6 has been confirmed by Johnson and Treichel [7] and preliminary data on (tetraphenylborato)(Cp)Fe have been presented by Owen et al. [8].

Our earlier studies on the complexation of heterocycles related to anthracene by the (Cp)Fe moiety [9–11], and our interest in the parent heterocycles [12] prompted us to examine the structures of the title compounds. These heterocycles are of interest, in part, because of their structural similarity to the phenothiazines which have a wide pharmacologic applicability. The activities of some members of the phenothiazine series have been related to their dihedral angle [13]. In this paper we report the results of crystallographic studies on the structures of xanthene (I) and 2-methylthianthrene (II) complexes of (Cp)Fe salts as well as the implication of the structure of II as it relates to the double S_NAr reaction [11] which is the likely pathway involved in its formation.

Experimental

The synthesis and physical properties of both complexes have been previously described. Complex I was obtained in 45% yield via a ligand exchange reaction between ferrocene and xanthene in decalin in the presence of $AlCl_3$ and Al [9]. Complex II was obtained in very high yield (82%) by a nucleophilic substitution reaction of the (*o*-dichlorobenzene)(Cp)Fe complex with 3,4-dimercaptotoluene under mild conditions [11]. Crystals of both complexes were grown at ca. $-18°$C from dilute acetone/diethyl ether/methylene chloride solutions.

X-ray

Details of crystal data, data collection and structure refinement are included in the crystallographic summary (Table 1). The least-squares planes program was supplied by Cordes [17]; other computer programs are listed in reference 11 of Gadol and Davis work [18].

The structure of I was solved by the heavy atom method from which the position of the Fe atom was obtained. All other non-hydrogen atoms were obtained from subsequent Fourier maps. After several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms, the H atoms were located from a difference Fourier map; the H atoms were refined isotropically.

The structure of II was solved by direct methods using MULTAN 78 [19] which afforded the positions of the Fe atom and all the atoms of the heterocycle. The other non-H atoms were located from an electron density map. After several cycles of full-matrix least-squares refinement with isotropic thermal parameters, there was significant electron density in the region of the F atoms indicating disorder, which is not uncommon for this group. The F atoms of the PF_6^- group were found to be disordered with two principal orientations. Starting positions for the F atoms of the second orientation were obtained from a difference map in the following manner. Positions of three of the largest peaks near P with F–P–F angles near 90° were used as F atom positions. These positions were subsequently inverted through the P atom to generate the complete set of six F atoms of this second orientation. This approximate starting set was refined to fix the P–F distance at 1.54 Å with an idealized octahedral arrangement around the P atom. The two orientations were

TABLE 1

CRYSTALLOGRAPHIC SUMMARY: (η^6-XANTHENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE (I) AND (η^6-2-METHYLTHIANTHRENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE (II)

	I	II
A. Crystal data (− 110°C) [14]		
a, Å	8.585(2)	11.526(2)
b, Å	10.224(2)	11.940(10)
c, Å	10.483(2)	13.701(10)
α, deg	96.524(11)	90.0
β, deg	110.484(11)	90.0
γ, deg	101.836(9)	90.0
V, Å^3	826.1(3)	1886(2)
d_{calcd}, g cm^{-3}(-110°C)	1.801	1.748
Empirical formula	$C_{18}H_{15}OFePF_6$	$C_{18}H_{15}S_2FePF_6$
Form. wt.	448.14	496.28
Crystal system	TRICLINIC	ORTHORHOMBIC
Space group	$P\bar{1}$	$P2_12_12_1$
Z	2	4
F(000), electrons	452	1000
B. Data collection (− 110°C) [15]		
Radiation, λ (Å)	Mo-K_α, 0.71069	
Mode	ω scan	
Scan range	symmetrically over 1.0° about $K_{\alpha_{1,2}}$ maximum	
Background	offset 1.0 and −1.0° in omega from $K_{\alpha_{1,2}}$ maximum	
	I	II
Scan rate, deg min^{-1}	3.0–6.0	3.0–6.0
Exposure time, h	39.4	39.8
Stability analysis		
Computed s, t (×10^6)	−1131, 22	not applied
Correction range (on I)	0.991–1.014	
2θ, range, deg	4.0–60.0	4.0–60.0
Total reflections measd	4813	3091
Absorption coeff, μ(Mo-K_α), cm^{-1}	11.10	11.81
C. Structure refinement [16]		
Ignorance factor p	0.04	0.04
Reflections used, $I > 3\sigma(I)$	4218	2278
No. of variables	304	226
R_1, R_2	0.046, 0.065	0.056, 0.069
R_1 for all data	0.052	0.080
S, Goodness of Fit	2.445	1.907
Max shift/esd	−0.026	0.014
Max peak in diff map (e Å^{-3})	0.80	0.84
Min peak in diff map (e Å^{-3})	−0.59	−0.98

refined as rigid groups while the occupancy factor was varied resulting in an occupancy of 0.67(2) for the first group and 0.33(2) for the second. The F atoms of both orientations were refined isotropically while all other non-H atoms were refined anisotropically. Positions for all H atoms were calculated with a C–H bond distance of 1.0 Å and idealized angles and were tied to their respective C atoms and refined with isotropic thermal parameters. Anomalous dispersion corrections were applied to I and II, no absorption corrections were made. The enantiomorph of II was refined to an R_2 of 0.074, as compared to 0.069 for the reported configuration. According to the Hamilton test [21] this difference is highly significant at the 0.005 level.

Discussion

ORTEP diagrams of I and II with the atom labelling scheme are shown in Fig. 1 and 3, respectively, while views of the unit cell packing are shown in Fig. 2 and 4. Positional and thermal parameters for I and II are listed in Tables 2 and 3, respectively. Table 4 lists the bond distances and angles for both complexes, while Tables 5 and 6 list the least-squares planes and dihedral angles for I and II, respectively [22].

Complexation by the (Cp)Fe moiety results in a flattening of xanthene but has little effect on the dihedral angle of 2-methylthianthrene. The dihedral angle of xanthene in I is 176.71(9)°, while that of uncomplexed xanthene has been estimated to be 160(6)° by Aroney et al. [23] on the basis of molecular polarizability measurements in the solution. The dihedral angle of 2-methylthianthrene in II is 127.4(3)°. Uncomplexed 2-methylthianthrene was first synthesized by Sutherland et

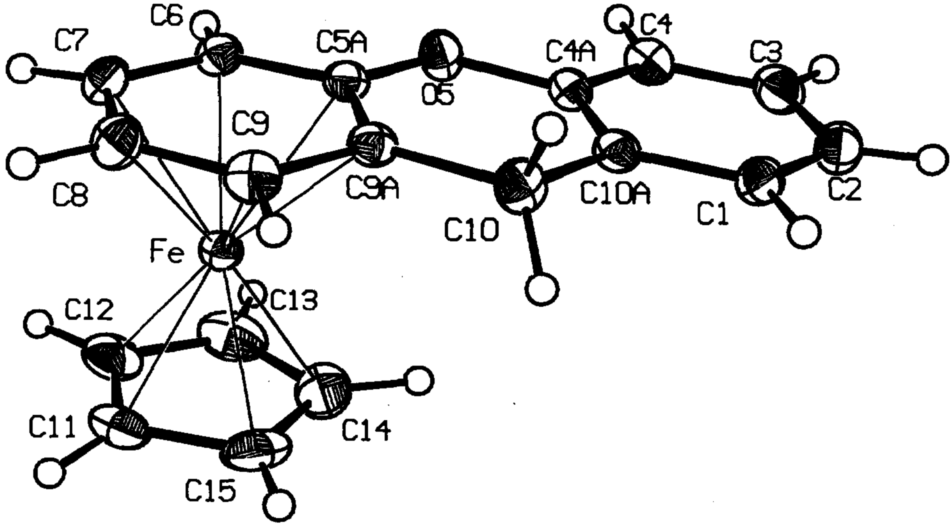


Fig. 1. ORTEP drawing of xanthene complex (I) and numbering system.

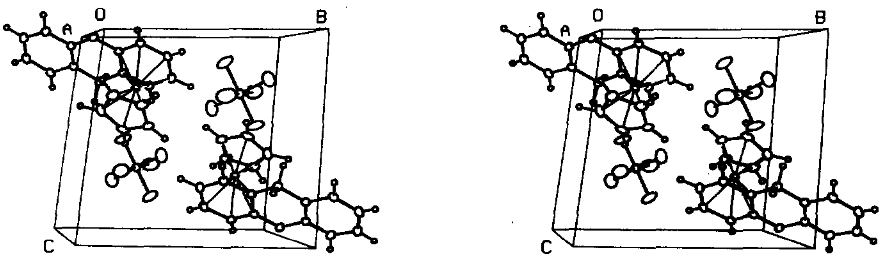


Fig. 2. Stereodrawing showing the packing arrangement in I.

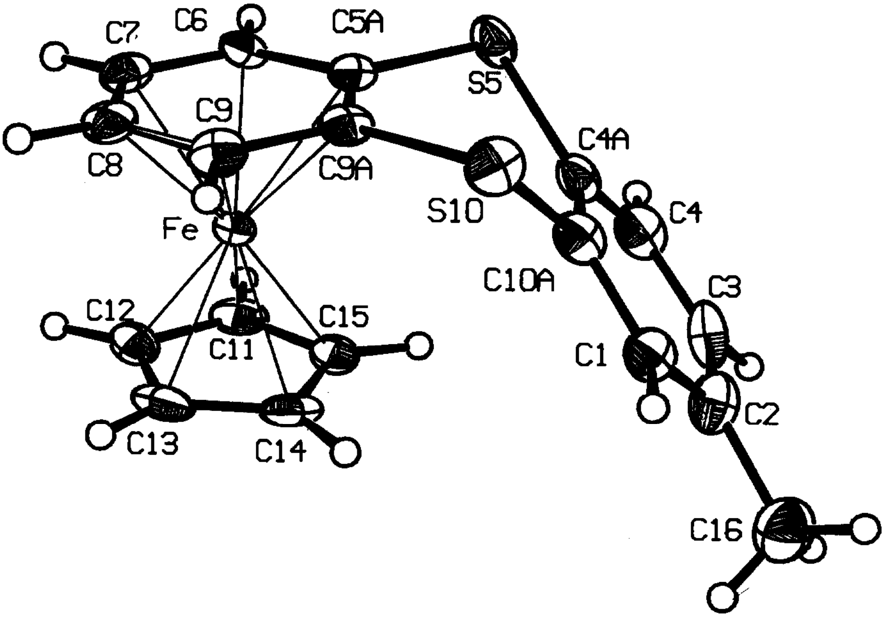


Fig. 3. ORTEP drawing of 2-methylthianthrene complex II and numbering system.

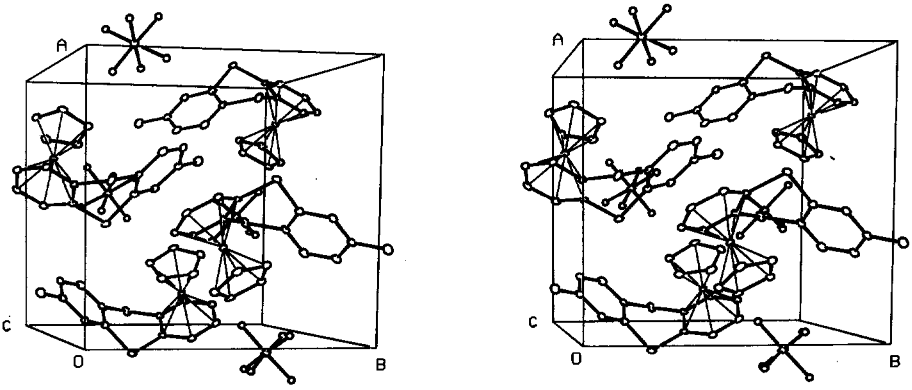


Fig. 4. Stereodrawing showing the packing arrangement in II.

al. [11]. The dihedral angle is unknown but should be close to that of thianthrene and 2,7-dimethylthianthrene which have values of 128.28(7)° [24] and 131.1° [25], respectively. The dihedral angle of thianthrenes appears to be insensitive to changes in substituents in or on the aromatic rings [12,26].

For both I and II, the (Cp)Fe moiety is situated inside the fold of the heterocyle. Surprisingly, although 2-methylthianthrene is substantially folded in II, there appears to be only minor steric interactions between the uncomplexed phenyl ring and the Cp ring. For example, the dihedral angle between the Cp ring and the complexed ring is 3.4(3)° in II, while for I it is 1.22(14)°. Dihedral angles of this magnitude are commonly observed in unstrained ferrocenes [27]. In addition, the relative orientations of the complexed rings are only slightly different. In I, C(14) is approximately equidistant from C(9A) and C(5A), 3.274(5) and 3.320(5) Å, respectively. In II,

TABLE 2

POSITIONAL PARAMETERS WITH EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS OF (η^6-XANTHENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE

Atom	x	y	z	U_{eq}/U_{iso} [20]
Fe	0.29050(4)	0.21531(3)	0.27922(3)	0.02146(12)
C(1)	0.6105(3)	−0.1624(3)	0.1980(3)	0.0297(8)
C(2)	0.5397(4)	−0.2961(3)	0.1279(3)	0.0344(10)
C(3)	0.3715(4)	−0.3369(3)	0.0279(3)	0.0341(9)
C(4)	0.2765(3)	−0.2421(2)	−0.0008(3)	0.0298(8)
C(4A)	0.3513(3)	−0.1071(2)	0.0703(2)	0.0245(7)
O(5)	0.2459(2)	−0.0187(2)	0.0321(2)	0.0282(6)
C(5A)	0.3078(3)	0.1158(2)	0.0978(2)	0.0234(7)
C(6)	0.1886(3)	0.1953(2)	0.0627(2)	0.0267(8)
C(7)	0.2377(3)	0.3342(2)	0.1272(3)	0.0306(8)
C(8)	0.4062(3)	0.3914(2)	0.2295(3)	0.0328(9)
C(9)	0.5231(3)	0.3097(2)	0.2679(3)	0.0287(8)
C(9A)	0.4746(3)	0.1695(2)	0.2024(2)	0.0238(7)
C(10A)	0.5162(3)	−0.0643(2)	0.1708(2)	0.0247(7)
C(10)	0.5952(3)	0.0817(3)	0.2461(3)	0.0291(8)
C(11)	0.2736(4)	0.2902(3)	0.4636(3)	0.0390(10)
C(12)	0.1073(4)	0.2289(3)	0.3627(3)	0.0401(10)
C(13)	0.0964(4)	0.0922(3)	0.3167(3)	0.0451(11)
C(14)	0.2563(5)	0.0667(3)	0.3898(4)	0.0494(14)
C(15)	0.3679(4)	0.1901(4)	0.4818(3)	0.0445(11)
P	0.93586(8)	0.35462(6)	0.68934(7)	0.0308(2)
F(1)	0.7712(3)	0.2597(3)	0.7007(3)	0.0842(12)
F(2)	0.8805(3)	0.2646(3)	0.5411(2)	0.0808(11)
F(3)	0.9853(4)	0.4434(3)	0.8398(3)	0.0843(12)
F(4)	1.1015(4)	0.4437(4)	0.6803(3)	0.111(2)
F(5)	1.0418(4)	0.2566(3)	0.7594(3)	0.0956(14)
F(6)	0.8210(5)	0.4500(3)	0.6246(4)	0.124(2)
H(1)	0.733(4)	−0.131(3)	0.271(3)	0.030(7)
H(2)	0.625(6)	−0.343(4)	0.146(5)	0.073(13)
H(3)	0.317(4)	−0.427(3)	−0.022(3)	0.026(7)
H(4)	0.157(4)	−0.274(3)	−0.078(3)	0.030(7)
H(6)	0.079(4)	0.162(3)	0.003(3)	0.035(8)
H(7)	0.147(4)	0.382(3)	0.106(3)	0.032(8)
H(8)	0.423(3)	0.486(3)	0.270(3)	0.018(6)
H(9)	0.643(4)	0.344(3)	0.342(3)	0.032(8)
H(101)	0.647(5)	0.076(4)	0.346(4)	0.066(12)
H(102)	0.690(5)	0.119(4)	0.219(4)	0.061(11)
H(11)	0.323(5)	0.379(4)	0.527(4)	0.046(9)
H(12)	0.002(5)	0.268(4)	0.320(4)	0.055(10)
H(13)	−0.009(8)	0.022(5)	0.244(6)	0.11(2)
H(14)	0.278(6)	−0.027(5)	0.368(5)	0.09(2)
H(15)	0.496(6)	0.225(4)	0.552(5)	0.072(13)

however, the equivalent Cp carbon, C(15) is closer to C(9A) than to C(5A), with distances of 3.286(19) and 3.455(10) Å, respectively. The closest C...H and C...C contacts between the Cp ring and the uncomplexed phenyl ring in II are 2.718(11) and 3.372(11) Å between C(4A) and H(15) and C(4A) and C(15), respectively. Both distances are only slightly shorter than the sums of the Van der Waals radii of the

(Continued on p. 396)

TABLE 3

POSITIONAL PARAMETERS WITH EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS OF (η^6-2-METHYLTHIANTHRENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE

Atom	x	y	z	U_{eq}/U_{iso} [20]
Fe	0.15733(8)	0.51113(8)	0.57326(7)	0.0207(2)
S(5)	0.0716(2)	0.3568(2)	0.78267(13)	0.0354(6)
S(10)	−0.0790(2)	0.3240(2)	0.5865(2)	0.0351(6)
C(1)	0.0543(7)	0.1361(6)	0.5576(6)	0.033(2)
C(2)	0.1372(6)	0.0568(7)	0.5817(7)	0.039(2)
C(3)	0.1979(7)	0.0691(7)	0.6697(7)	0.042(3)
C(4)	0.1784(7)	0.1610(7)	0.7279(6)	0.041(3)
C(4A)	0.0958(7)	0.2398(6)	0.7057(5)	0.030(2)
C(5A)	0.0599(6)	0.4652(6)	0.6968(5)	0.024(2)
C(6)	0.1189(6)	0.5676(6)	0.7122(5)	0.025(2)
C(7)	0.1088(6)	0.6554(6)	0.6440(5)	0.031(2)
C(8)	0.0418(7)	0.6420(7)	0.5612(6)	0.035(2)
C(9)	−0.0145(6)	0.5413(7)	0.5424(6)	0.032(2)
C(9A)	−0.0088(6)	0.5414(7)	0.6109(6)	0.027(2)
C(10A)	0.0313(7)	0.2281(7)	0.6178(5)	0.032(2)
C(11)	0.3331(6)	0.4814(7)	0.5825(6)	0.034(2)
C(12)	0.3097(7)	0.5609(7)	0.5106(6)	0.037(3)
C(13)	0.2359(7)	0.5106(8)	0.4405(5)	0.039(3)
C(14)	0.2162(7)	0.4017(8)	0.4691(6)	0.037(3)
C(15)	0.2753(6)	0.3833(7)	0.5568(6)	0.034(2)
C(16)	0.1606(9)	−0.0388(8)	0.5130(8)	0.054(3)
P	0.0441(2)	0.2230(2)	0.2301(2)	0.0367(8)
F(1)	0.115138	0.177914	0.138598	0.074(3)
F(2)	0.144376	0.310378	0.251682	0.056(2)
F(3)	−0.02694	0.271327	0.320292	0.078(3)
F(4)	−0.012299	0.312494	0.159120	0.067(3)
F(5)	0.103464	0.139882	0.302894	0.085(3)
F(6)	−0.055667	0.141068	0.207229	0.087(3)
F(11)	−0.00923	0.1072	0.208863	0.068(5)
F(12)	0.138479	0.167271	0.293270	0.087(7)
F(13)	−0.034175	0.234709	0.320756	0.065(6)
F(14)	0.097421	0.338863	0.251386	0.057(5)
F(15)	−0.050290	0.278791	0.166977	0.063(5)
F(16)	0.122364	0.211354	0.139492	0.081(8)
H(1)	0.0109(7)	0.1270(6)	0.4949(6)	0.05(3)
H(3)	0.2580(7)	0.0125(7)	0.6881(7)	0.03(2)
H(4)	0.2253(7)	0.1698(7)	0.7888(6)	0.06(3)
H(6)	0.1679(6)	0.5770(6)	0.7719(5)	0.03(2)
H(7)	0.1505(6)	0.7277(6)	0.6555(5)	0.02(2)
H(8)	0.0335(7)	0.7050(7)	0.5136(6)	0.04(2)
H(9)	−0.0597(6)	0.5305(7)	0.4808(6)	0.04(2)
H(11)	0.3836(6)	0.4918(7)	0.6412(6)	0.05(3)
H(12)	0.3392(7)	0.6396(7)	0.5099(6)	0.06(3)
H(13)	0.2029(7)	0.5483(8)	0.3815(5)	0.06(3)
H(14)	0.1686(7)	0.3448(8)	0.4335(6)	0.05(3)
H(15)	0.2770(6)	0.3123(7)	0.5955(6)	0.04(2)
H(161)	0.2282(9)	−0.0828(8)	0.5381(8)	0.06(3)
H(162)	0.1779(9)	−0.0078(8)	0.4472(8)	0.15(6)
H(163)	0.0913(9)	−0.0888(8)	0.5079(8)	0.05(3)

TABLE 4

BOND DISTANCES AND ANGLES WITH ESD'S FOR THE HYDROGEN ATOMS OF (η^6-XANTHENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE

1	2	3	1–2	1–2–3
H(1)	C(1)	C(2)	1.02(3)	121.(2)
H(1)	C(1)	C(10A)		118.(2)
H(2)	C(2)	C(3)	0.93(5)	129.(2)
H(2)	C(2)	C(1)		110.(2)
H(3)	C(3)	C(4)	0.94(3)	117.(2)
H(3)	C(3)	C(2)		124.(2)
H(4)	C(4)	C(4A)	1.02(3)	123.(2)
H(4)	C(4)	C(3)		118.(2)
H(6)	C(6)	C(7)	0.89(3)	116.(2)
H(6)	C(6)	C(5A)		124.(2)
H(7)	C(7)	C(8)	0.98(3)	124.0(15)
H(7)	C(7)	C(6)		116.3(15)
H(8)	C(8)	C(9)	0.98(3)	127.5(15)
H(8)	C(8)	C(7)		112.(2)
H(9)	C(9)	C(9A)	1.01(3)	116.(2)
H(9)	C(9)	C(8)		124.(2)
H(101)	C(10)	H(102)	1.00(4)	107.(3)
H(101)	C(10)	C(9A)		120.(3)
H(101)	C(10)	C(10A)		104.(2)
H(102)	C(10)	C(9A)	0.97(5)	105.(3)
H(102)	C(10)	C(10A)		108.(2)
H(11)	C(11)	C(12)	0.98(3)	131.(2)
H(11)	C(11)	C(15)		120.(2)
H(12)	C(12)	C(13)	1.04(4)	120.(2)
H(12)	C(12)	C(11)		132.(2)
H(13)	C(13)	C(14)	1.02(5)	126.(4)
H(13)	C(13)	C(12)		126.(4)
H(14)	C(14)	C(15)	1.03(6)	131.(2)
H(14)	C(14)	C(13)		121.(2)
H(15)	C(15)	C(11)	1.04(4)	115.(3)
H(15)	C(15)	C(14)		138.(3)
C(5A)	Fe		2.119(2)	
C(6)	Fe		2.095(2)	
C(7)	Fe		2.094(3)	
C(8)	Fe		2.084(3)	
C(9)	Fe		2.082(3)	
C(9A)	Fe		2.115(3)	
C(11)	Fe		2.061(3)	
C(12)	Fe		2.070(4)	
C(13)	Fe		2.056(4)	
C(14)	Fe		2.048(4)	
C(15)	Fe		2.055(3)	
C(2)	C(1)	C(10A)	1.378(3)	121.1(2)
C(10A)	C(1)		1.406(4)	
C(3)	C(2)	C(1)	1.397(4)	120.2(3)
C(4)	C(3)	C(2)	1.383(4)	119.7(2)
C(4A)	C(4)	C(3)	1.394(3)	119.1(2)
O(5)	C(4A)	C(10A)	1.400(3)	122.8(2)
O(5)	C(4A)	C(4)		114.8(2)
C(10A)	C(4A)	C(4)	1.379(3)	122.4(2)
C(5A)	O(5)	C(4A)	1.370(3)	118.9(2)

TABLE 4 (continued)

1	2	3	1–2	1–2–3
C(6)	C(5A)	C(9A)	1.410(4)	121.7(2)
C(6)	C(5A)	O(5)		115.4(2)
C(9A)	C(5A)	O(5)	1.413(3)	122.6(2)
C(7)	C(6)	C(5A)	1.410(3)	120.0(2)
C(8)	C(7)	C(6)	1.417(3)	119.2(3)
C(9)	C(8)	C(7)	1.416(4)	120.4(2)
C(9A)	C(9)	C(8)	1.425(3)	120.6(2)
C(10)	C(9A)	C(5A)	1.493(4)	121.3(2)
C(10)	C(9A)	C(9)		120.8(2)
C(5A)	C(9A)	C(9)		117.9(2)
C(10)	C(10A)	C(1)	1.501(3)	120.8(2)
C(10)	C(10A)	C(4A)		121.8(2)
C(1)	C(10A)	C(4A)		117.4(2)
C(9A)	C(10)	C(10A)		112.6(2)
C(12)	C(11)	C(15)	1.406(3)	108.3(3)
C(15)	C(11)		1.420(5)	
C(13)	C(12)	C(11)	1.399(5)	108.4(3)
C(14)	C(13)	C(12)	1.412(5)	108.3(2)
C(15)	C(14)	C(13)	1.422(4)	108.0(3)
C(11)	C(15)	C(14)		107.1(3)
F(1)	P	F(2)	1.592(3)	87.48(15)
F(1)	P	F(3)		90.5(2)
F(1)	P	F(4)		177.8(2)
F(1)	P	F(5)		88.0(2)
F(2)	P	F(3)	1.570(2)	177.9(2)
F(2)	P	F(4)		92.3(2)
F(2)	P	F(5)		91.4(2)
F(2)	P	F(6)		90.3(2)
F(3)	P	F(4)	1.594(3)	89.7(2)
F(3)	P	F(5)		89.0(2)
F(3)	P	F(6)		89.2(2)
F(4)	P	F(5)	1.563(4)	89.7(2)
F(4)	P	F(6)		93.8(2)
F(5)	P	F(6)	1.563(3)	176.0(2)
F(6)	P	F(1)	1.569(4)	88.4(2)

BOND DISTANCES AND ANGLES WITH ESD'S FOR THE NON-HYDROGEN ATOMS OF (η^6-2-METHYLTHIANTHRENE)(η^5-CYCLOPENTADIENY)-IRON-HEXAFLUOROPHOSPHATE

1	2	3	1–2	1–2–3
C(5A)	Fe		2.104(7)	
C(6)	Fe		2.068(7)	
C(7)	Fe		2.055(8)	
C(8)	Fe		2.060(8)	
C(9)	Fe		2.057(7)	
C(9A)	Fe		2.108(7)	
C(11)	Fe		2.061(7)	
C(12)	Fe		2.043(8)	
C(13)	Fe		2.033(7)	
C(14)	Fe		2.050(9)	
C(15)	Fe		2.056(8)	
C(4A)	S(5)	C(5A)	1.772(8)	101.2(3)
C(5A)	S(5)		1.754(7)	
C(9A)	S(10)	C(10A)	1.755(8)	100.6(4)
C(10A)	S(10)		1.764(8)	

TABLE 4 (continued)

1	2	3	1–2	1–2–3
C(2)	C(1)	C(10A)	1.385(11)	121.8(7)
C(10A)	C(1)		1.399(11)	
C(3)	C(2)	C(16)	1.401(13)	121.9(8)
C(3)	C(2)	C(1)		118.6(8)
C(16)	C(2)	C(1)	1.505(13)	119.5(8)
C(4)	C(3)	C(2)	1.375(12)	120.0(8)
C(4A)	C(4)	C(3)	1.373(11)	122.2(8)
C(10A)	C(4A)	S(5)	1.422(11)	119.9(6)
C(10A)	C(4A)	C(4)		118.9(7)
S(5)	C(4A)	C(4)		121.2(6)
C(6)	C(5A)	C(9A)	1.414(10)	119.3(6)
C(6)	C(5A)	S(5)		120.1(5)
C(9A)	C(5A)	S(5)	1.428(10)	120.7(5)
C(7)	C(6)	C(5A)	1.410(10)	120.3(6)
C(8)	C(7)	C(6)	1.381(11)	120.3(7)
C(9)	C(8)	C(7)	1.391(11)	120.9(7)
C(9A)	C(9)	C(8)	1.427(11)	120.4(7)
S(10)	C(9A)	C(5A)		120.9(6)
S(10)	C(9A)	C(9)		120.3(6)
C(5A)	C(9A)	C(9)		118.7(7)
S(10)	C(10A)	C(1)		120.2(6)
S(10)	C(10A)	C(4A)		121.2(6)
C(1)	C(10A)	C(4A)		118.5(7)
C(12)	C(11)	C(15)	1.395(12)	107.5(7)
C(15)	C(11)		1.392(11)	
C(13)	C(12)	C(11)	1.416(11)	107.9(7)
C(14)	C(13)	C(12)	1.377(13)	107.8(7)
C(15)	C(14)	C(13)	1.399(11)	108.2(7)
C(11)	C(15)	C(14)		108.6(7)
F(1)	P	F(2)	1.592(3)	89.67(14)
F(1)	P	F(3)		178.5(2)
F(1)	P	F(4)		87.45(13)
F(1)	P	F(5)		93.6(2)
F(2)	P	F(3)	1.585(3)	89.55(14)
F(2)	P	F(4)		88.28(15)
F(2)	P	F(5)		88.82(14)
F(2)	P	F(6)		178.1(2)
F(3)	P	F(4)	1.590(3)	91.22(15)
F(3)	P	F(5)		87.72(13)
F(3)	P	F(6)		90.24(14)
F(4)	P	F(5)	1.584(3)	176.9(2)
F(4)	P	F(6)		89.83(14)
F(5)	P	F(6)	1.565(3)	93.0(2)
F(6)	P	F(1)	1.542(3)	90.49(14)

atoms involved. Because of the near planarity of xanthene, there are no close contacts of this type in I.

Coordination by (Cp)Fe to the heterocycle is unsymmetrical in both I and II resulting in 4 short and 2 slightly longer Fe–C bond distances. In both complexes the longer distances involve the quaternary carbon atoms, C(5A) and C(9A). Since the asymmetry is observed with both the flat xanthene and the highly folded 2-methylthianthrene, it is unlikely to be the result of steric effects. The distances of

TABLE 5

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES FOR (η^6-XANTHENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE

Plane 1

$-0.70293x - 0.22723y + 0.67399z + 0.97918 = 0$

Distances of selected atoms from plane in Å (* indicates atom not used in plane calculation).

C(1) −0.004(3)	C(2) −0.013(4)	C(3) −0.002(4)	C(4) 0.011(3)	C(4A) 0.004(3)
C(10A) 0.0012(3)	O(5) −0.006(2)	C(10) −0.0015(31)	Fe* 1.7005(4)	

Plane 2

Equation of plane

$0.69916x + 0.23334y - 0.67582z - 0.94602 = 0$

Distances of selected atoms from plane

C(1) 0.0008(32)	C(2) 0.004(4)	C(3) −0.0013(36)	C(4) −0.005(3)	C(4A) 0.007(3)
C(10A) −0.005(3)	O(5)* 0.028(2)	C(10)* 0.014(3)	Fe* −1.6670(4)	

Plane 3

Equation of plane

$0.68651x + 0.27336y - 0.67378z - 0.92901 = 0$

Distances of selected atoms from plane

C(5A) 0.037(3)	C(6) −0.018(3)	C(7) −0.018(3)	C(8) 0.002(3)	C(9) 0.006(3)
C(9A) 0.016(3)	O(5) −0.005(2)	C(10) −0.031(3)	Fe* −1.6020(4)	

Plane 4

Equation of plane

$0.67872x + 0.28695y - 0.67602z - 0.93748 = 0$

Distances of selected atoms from plane

C(5A) 0.018(3)	C(6) −0.015(3)	C(7) −0.0005(32)	C(8) 0.014(3)	C(9) −0.005(3)
C(9A) −0.010(3)	O(5)* −0.038(2)	C(10)* −0.080(3)	Fe* −1.6046(4)	

Plane 5

Equation of plane

$0.66314x + 0.28909y - 0.69042z + 2.44180 = 0$

Distances of selected atoms from plane

C(11) 0.002(3)	C(12) −0.002(4)	C(13) 0.003(4)	C(14) −0.002(5)	C(15) −0.0006(38)
Fe* 1.7281(4)				

Dihedral angle

Planes		(°)
1	2	0.42(8)
1	3	177.19(6)
1	4	176.31(7)
1	5	4.32(11)
2	3	177.59(7)
2	4	176.71(9)
2	5	3.89(13)
3	4	0.91(7)
3	5	1.87(12)
4	5	1.22(14)

iron to the complexed phenyl ring and Cp ring are 1.6046(4) and 1.7281(4) Å, respectively, for I and 1.5239(9) and 1.6688(9) Å, respectively, for II. The distances for II are normal while those for I are slightly longer than the distances observed for similar complexes [1–6]. Additionally, there results an asymmetry in the bonding, in I, between O(5) and C(10) and the quaternary carbon atoms, with the shorter bonds being to the carbon atoms of the complexed ring. Such asymmetry is not observed in

TABLE 6

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES FOR (η^6-2-METHYLTHIANTHRENE)(η^5-CYCLOPENTADIENYL)IRON HEXAFLUOROPHOSPHATE

Plane 1

Equation of plane

$-0.67541x - 0.53147y + 0.51123z - 2.66350 = 0$

Distances of selected atoms from plane in Å (* indicates atoms not used in plane calculation).

S(5) −0.003(2) S(10) 0.004(2) C(1) −0.045(8) C(2) −0.018(8) C(3) 0.048(8)
C(4) 0.024(8) C(4A) 0.011(8) C(10A) −0.027(8) Fe* −3.1165(9)

Plane 2

Equation of plane

$0.69540x + 0.52709y - 0.48846z + 2.44284 = 0$

Distances of selected atoms from plane

S(5)* 0.024(2) S(10)* −0.077(2) C(1) 0.003(8) C(2) 0.007(8) C(3) −0.018(9)
C(4) 0.015(8) C(4A) −0.002(8) C(10A) −0.006(8) Fe* 3.0841(9)

Plane 3

Equation of plane

$0.80962x - 0.34590y - 0.47421z + 5.88865 = 0$

Distances of selected atoms from plane

S(5) −0.002(2) S(10) 0.002(2) C(5A) −0.0005(67) C(6) 0.026(7) C(7) 0.013(7)
C(8) −0.019(8) C(9) −0.006(8) C(9A) −0.027(7) Fe* 1.5215(9)

Plane 4

Equation of plane

$0.80021x - 0.35245y - 0.48523z + 6.0466 = 0$

Distances of selected atoms from plane

S(5)* −0.010(2) C(10)* 0.043(2) C(5A) −0.003(7) C(6) 0.008(8) C(7) −0.0015(74)
C(8) −0.013(8) C(9) 0.017(8) C(9A) −0.008(7) Fe* 1.5239(9)

Plane 5

Equation of plane

$0.80265x - 0.30174y - 0.51450z + 2.75793 = 0$

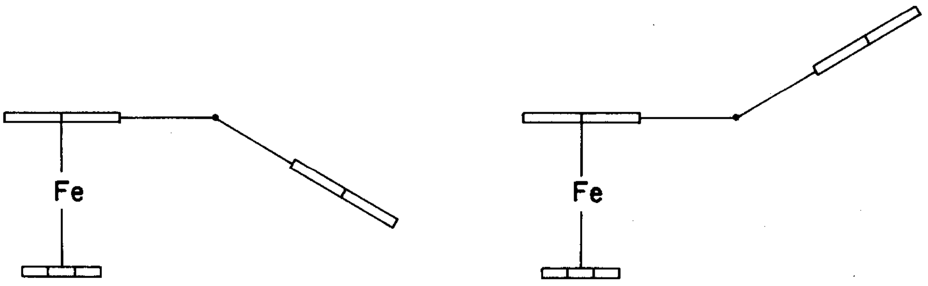
Distances of selected atoms from plane

C(11) −0.0009(72) C(12) 0.003(8) C(13) −0.004(8) C(14) 0.004(8) C(15) −0.0012(76)
Fe* −1.6688(9)

Dihedral angles

Planes		(°)
1	2	1.8 (2)
1	3	127.26(10)
1	4	127.0 (2)
1	5	49.9 (3)
2	3	127.8 (2)
2	4	127.4 (3)
2	5	49.4 (3)
3	4	0.9 (2)
3	5	3.5 (3)
4	5	3.4 (3)

II. Interestingly, in aza-substituted phenoxathiins and thianthrenes a similar pattern is observed. With the phenoxathiins, the shorter O–C and S–C distances are to the aza-substituted ring, while for the analogous thianthrenes, such asymmetry is not normally observed. The aromatic rings in both complexes are planar. The C–C bond



I a (II a)   I b (II b)

Fig. 5.

distances for the atoms in the complexed phenyl ring in I and II are generally slightly longer than those of the uncomplexed ring. The C–C bond distances of the Cp rings are normal.

Synthesis of I via a ligand exchange reaction described elsewhere [9], should lead to two possible isomeric cations, Ia and Ib, shown in Fig. 5. Because of the nearly planar geometry of xanthene in I, the conformational energy barrier separating Ia from Ib will be very small making the two isomers practically indistinguishable. Although the structure in the solid state was confirmed to be Ia, we cannot show that this was the only conformer formed in the reaction. In II, however, 2-methylthianthrene is substantially bent with the (Cp)Fe moiety lying inside the fold of the heterocycle. We are currently involved in attempting to ascertain whether both IIa and IIb are present in solution and, if possible, to determine the energy barrier separating the two conformers.

The mechanism of this reaction seems to involve a double S_NAr substitution leading to the formation of II from reaction of the *o*-dichlorobenzene complex with 3,4-dimercaptotoluene in two subsequent steps. The first step would involve attack of the SH group in position four (electronic effects would increase its nucleophilicity over that of position three) from the *exo* side of the *o*-dichlorobenzene complex [28–30] followed by attack of the second SH group on the second chlorine atom resulting in the formation of the heterocyclic complex II.

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Function minimized was $w(|F_0|-|F_c|)^2$, where $w=(\sigma(F))^{-2}$
$R_1=\Sigma(||F_0|-|F_c||)/\Sigma|F_0|$
$R_2=[\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$
$S=[\Sigma w(|F_0|-|F_c|)^2/(m-n)]^{1/2}$
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