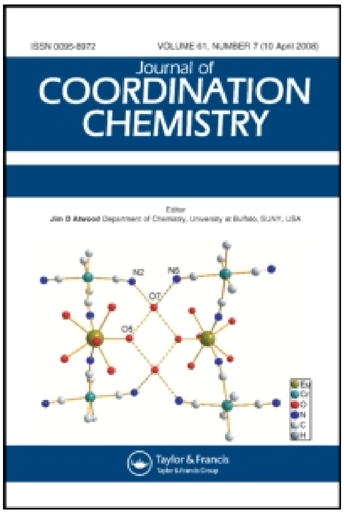

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NOVEL MIXED VALENCE IRON COMPOUND, $[(\eta^5$-CYCLOPENTADIENYL$)(\eta^6$-TETRALIN$)$ $Fe(II)]_3[Fe(III)(NCS)_6]$

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The title compound was encountered in the course of preparing $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]SCN$ from $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]PF_6$. The mixed valence iron compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell. There are three crystallographically independent cations and two anions (each residing on a center of inversion) in the asymmetric unit. Lattice constants are a = 17.231(7), b = 18.167(6), c = 16.572(7) Å, and β = 97.86(4)°.

Keywords: Iron, mixed-valence, crystal structure, arene, isothiocyanate

INTRODUCTION

Our group has been interested for some time in the dissolution and upgrading of coal.[1] The method of effecting the former involves the use of a "solvent" with special properties, one of which is the combination of an ionic substance in the presence of an aromatic compound.[2] Simple systems such as $K[Al_2Me_6N_3]\cdot$ *aromatic* have long been studied.[3,4] More recently, our attention turned to parent compounds in which the cation is more complex and potentially offers more interesting chemistry. Arene–metal cations in conjunction with small anions, *e.g.*, I^- or SCN^-, form salts which react with $AlMe_3$ to give the desired "solvents."[5] However, arene–metal compounds in general are synthesized as the salts of large anions, *e.g.*, PF_6^-, BF_4^-, or BPh_4^-.[6] In the course of preparing $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]SCN$ from $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]PF_6$ we encountered a novel mixed valence iron salt which is the subject of this report.

EXPERIMENTAL

Preparation of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]_3[Fe(NCS)_6]$, (I)

Under an N_2 atmosphere a suspension of $(\eta^5\text{-}C_5H_5)_2Fe$ (18.6 g, 0.1 mol), $AlCl_3$ (40.6 g, 0.3 mol) and Al (2.7 g, 0.1 mol) in tetralin (500 cm^3) was refluxed for 4 h. The resultant brown, viscous solution was hydrolysed carefully with water (1 dm^3). The aqueous phase solution was separated and to this was added an excess of a saturated aqueous solution of KSCN. The resultant yellow precipitate was filtered in air, but

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†Deceased November 5, 1986. * Author for correspondence.

rapidly turned red in the solid state. The solid was extracted with acetone (50 cm^3) to yield a deep-red solution and careful addition of diethylether (100 cm^3) afforded crystals of (**I**) (yield 3 g, 10%). ^{1}H nmr measurements showed a badly broadened spectrum because of the paramagnetic species present.

X-ray Structure Determination of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]_3[Fe(NCS)_6]$

Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 25 reflections ($2\theta > 30°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Data were collected by the θ–2θ scan technique as described previously.[7] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects.

TABLE I
Crystal data and summary of data collection for **I**.

Cmpd.	$[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]_3Fe(NCS)_6$
Mol wt.	1163.2
Space group	$P2_1/c$
Cell constants	
a, Å	17.231(7)
b, Å	18.167(6)
c, Å	16.572(7)
β, deg	97.86(4)
Cell vol, Å^3	5125
Molecules/unit cell	4
ρ(calc), gcm^{-3}	1.51
μ(calc), cm^{-1}	14.2
Radiation	Mo$K\alpha$
Max crystal dimensions, mm	$0.10 \times 0.10 \times 0.10$
Scan width	$0.80 + 0.20 \tan\theta$
Standard reflections	040,004,400
Variation of standards	<2%
Reflections measured	4937
2θ range, deg	1–18
Reflections considered observed	1925
No. of parameters varied	322
GOF	1.0
R	0.059
R_w	0.059

Calculations were carried out using the SHELX system of computer programs.[8] Neutral atom scattering factors for Fe, S, N, and C were taken from Cromer and Waber,[9] and those stored within the SHELX program were used for H. The scattering for all atoms was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[10] Structure solution was accomplished by means of the direct methods program MULTAN80,[11] which gave the location of the Fe and S atoms. Difference Fourier maps phased on these atoms readily revealed the positions of the remaining non-hydrogen atoms. Because of the paucity of observed data, only the Fe and S atoms were refined with anisotropic thermal parameters. Hydrogen atoms were positioned at locations determined by geometry, and were not varied. A final difference Fourier showed no feature greater than 0.3e/Å^3. The weighting scheme was based upon unit weights and no systematic variation of $w(|F_o| - |F_c|)^2$ *vs* $|F_o|$ or $(\sin\theta/\lambda)$ was observed. The final values of the positional parameters of the non-hydrogen atoms are given in Table II. Table of positional parameters for all atoms, anisotropic thermal parameters, and structure factors are available from the Editor.

TABLE II

Final fractional coordinates for **I**, with estimated standard deviations in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Fe(1)	0.2103(1)	0.1654(2)	0.3174(2)
Fe(2)	0.5622(2)	0.1601(1)	0.9249(2)
Fe(3)	0.1823(2)	0.6242(1)	0.2375(2)
Fe(4)	0.0000	0.5000	0.5000
Fe(5)	0.5000	0.0000	0.5000
S(1)	0.2626(4)	0.4023(4)	0.5361(4)
S(2)	0.0868(4)	0.7429(3)	0.4428(4)
S(3)	0.0195(4)	0.6046(3)	0.7685(4)
S(4)	0.4072(4)	0.2204(3)	0.6140(4)
S(5)	0.4984(3)	0.0856(3)	0.2268(3)
S(6)	0.2440(3)	−0.1097(4)	0.4360(4)
N(1)	0.114(1)	0.4633(8)	0.518(1)
N(2)	0.038(1)	0.602(1)	0.467(1)
N(3)	0.011(1)	0.5343(9)	0.621(1)
N(4)	0.4593(9)	0.0970(8)	0.5397(9)
N(5)	0.4927(9)	0.0426(8)	0.385(1)
N(6)	0.387(1)	−0.0408(8)	0.4741(9)
C(1)	0.179(1)	0.436(1)	0.525(1)
C(2)	0.057(1)	0.659(1)	0.456(1)
C(3)	0.015(1)	0.564(1)	0.684(1)
C(4)	0.436(1)	0.148(1)	0.573(1)
C(5)	0.498(1)	0.0586(9)	0.317(1)
C(6)	0.327(1)	−0.070(1)	0.458(1)
C(11)	0.109(1)	0.221(1)	0.282(1)
C(12)	0.124(1)	0.172(1)	0.219(1)
C(13)	0.138(1)	0.099(1)	0.232(1)
C(14)	0.136(1)	0.073(1)	0.308(1)
C(15)	0.121(1)	0.117(1)	0.375(1)
C(16)	0.118(2)	0.082(1)	0.455(2)
C(17)	0.087(2)	0.135(2)	0.519(2)
C(18)	0.112(2)	0.209(2)	0.507(2)
C(19)	0.093(2)	0.243(1)	0.431(2)
C(20)	0.109(1)	0.193(1)	0.364(1)
Cp(1)	0.317(1)	0.148(1)	0.280(2)
Cp(2)	0.304(1)	0.223(1)	0.288(1)
Cp(3)	0.294(1)	0.242(1)	0.361(1)
Cp(4)	0.300(1)	0.183(1)	0.408(1)
Cp(5)	0.316(1)	0.123(1)	0.358(1)
C(21)	0.657(1)	0.229(1)	0.945(1)
C(22)	0.591(1)	0.269(1)	0.940(1)
C(23)	0.531(1)	0.262(1)	0.872(1)
C(24)	0.544(1)	0.212(1)	0.812(1)
C(25)	0.613(1)	0.172(1)	0.817(1)
C(26)	0.624(1)	0.115(1)	0.753(1)
C(27)	0.688(1)	0.064(1)	0.775(1)
C(28)	0.762(1)	0.097(1)	0.818(1)
C(29)	0.747(1)	0.133(1)	0.893(1)
C(30)	0.672(1)	0.180(1)	0.882(1)

Table II cont.

Atom	*x/a*	*y/b*	*z/c*
Cp(6)	0.526(1)	0.133(1)	1.030(1)
Cp(7)	0.463(1)	0.130(1)	0.972(1)
Cp(8)	0.480(1)	0.079(1)	0.915(1)
Cp(9)	0.554(1)	0.047(1)	0.937(1)
Cp(10)	0.579(1)	0.082(1)	1.013(1)
C(31)	0.300(1)	0.631(1)	0.224(1)
C(32)	0.281(1)	0.682(1)	0.286(1)
C(33)	0.244(1)	0.663(1)	0.344(1)
C(34)	0.222(1)	0.589(1)	0.354(1)
C(35)	0.241(1)	0.535(1)	0.298(1)
C(36)	0.212(2)	0.456(1)	0.308(2)
C(37)	0.228(2)	0.414(2)	0.239(2)
C(38)	0.271(2)	0.433(2)	0.180(2)
C(39)	0.299(1)	0.502(1)	0.164(1)
C(40)	0.280(1)	0.557(1)	0.232(1)
Cp(11)	0.118(1)	0.617(1)	0.122(1)
Cp(12)	0.082(1)	0.578(1)	0.177(1)
Cp(13)	0.064(1)	0.621(1)	0.236(1)
Cp(14)	0.087(1)	0.693(1)	0.224(1)
Cp(15)	0.121(1)	0.689(1)	0.150(1)

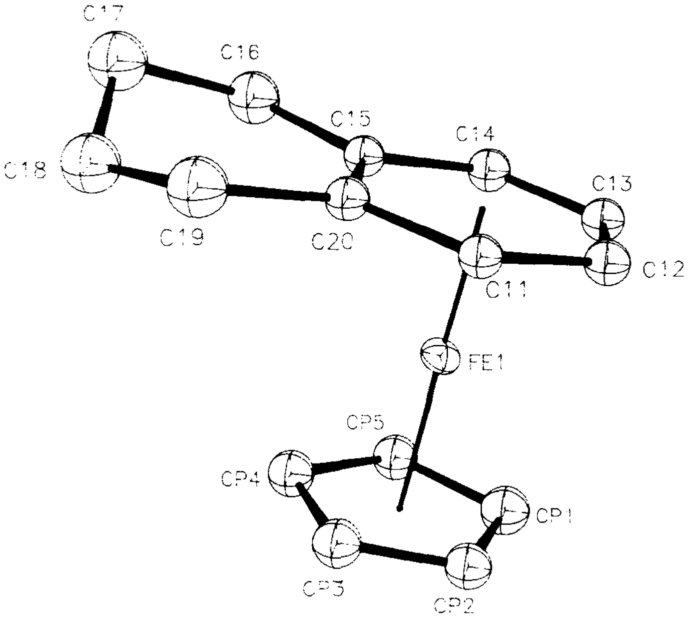

FIGURE 1 View of one of the independent cations of **I**.

RESULTS AND DISCUSSION

Even though the complex crystallizes in the most common of space groups, $P2_1/c$, it displays crystallographic complexities. There are three independent cations and two independent half-anions in the asymmetric unit. Each of the $\mathrm{Fe(NCS)_6}^{3-}$ units is positioned on a crystallographic center of inversion. Nevertheless, there are no significant differences in bonding parameters among the cations or anions. Figure 1 shows one of the $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]^+$ cations.

There are several reports of neutral [(cyclopentadienyl)(arene)iron] molecules in the literature,[12–16] but those of cationic species are more rare.[17,18] In the title compound the Fe–C(η^5-) distances range from 1.99(2) to 2.08(2)Å, and average 2.04(3)Å (Table III). These values are near the norm when compared to $[(\eta^5\text{-}C_5H_5)(\text{arene})Fe]^+$,[17,18] neutral molecules,[12–16] or ferrocene itself.[19] For the (η^6-tetralin) ligand, one might expect longer Fe–C lengths associated with the carbon in common to both ring systems. Careful scrutiny of Table II shows that this is not the case. The average Fe–C distance for the most sterically hindered carbon atoms, 2.10(3)Å, is not significantly different from that for the most accessible ones, 2.09(3)Å.

TABLE III

Selected bond distances (Å) in the $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})Fe]^+$ cations with estimated standard deviations in parentheses.

Atoms	Distance	Atoms	Distance
Fe(1)–C(11)	2.04(2)	Fe(1)–C(12)	2.05(2)
Fe(1)–C(13)	2.12(2)	Fe(1)–C(14)	2.11(2)
Fe(1)–C(15)	2.10(2)	Fe(1)–C(20)	2.07(2)
Fe(1)–Cp(1)	2.03(3)	Fe(1)–Cp(2)	2.04(2)
Fe(1)–Cp(3)	2.07(2)	Fe(1)–Cp(4)	2.03(2)
Fe(1)–Cp(5)	2.02(2)		
Fe(2)–C(21)	2.05(2)	Fe(2)–C(22)	2.04(2)
Fe(2)–C(23)	2.08(2)	Fe(2)–C(24)	2.08(2)
Fe(2)–C(25)	2.10(2)	Fe(2)–C(30)	2.13(2)
Fe(2)–Cp(6)	1.99(2)	Fe(2)–Cp(7)	2.04(2)
Fe(2)–Cp(8)	2.04(2)	Fe(2)–Cp(9)	2.06(2)
Fe(2)–Cp(10)	2.03(2)		
Fe(3)–C(31)	2.07(2)	Fe(3)–C(32)	2.07(2)
Fe(3)–C(33)	2.06(2)	Fe(3)–C(34)	2.05(2)
Fe(3)–C(35)	2.10(2)	Fe(3)–C(40)	2.09(2)
Fe(3)–Cp(11)	2.08(2)	Fe(3)–Cp(12)	2.05(2)
Fe(3)–Cp(13)	2.04(2)	Fe(3)–Cp(14)	2.06(2)
Fe(3)–Cp(15)	2.04(2)		

The iron atom resides 1.53–1.55Å from the centroid of the η^6-portion of the tetralin molecules, and 1.66–1.68Å from that of the cyclopentadienyl groups. The (η^5-centroid)–Fe–(η^6-centroid) angles range from 178 to 179°.

The parameters within the anions (Table IV) compare favourably with those found for $[N(CH_3)_4]_3[Fe(NCS)_6]$,[20] as can be seen from the following (those for the tetramethylammonium salt are given in square brackets: Fe–N, 2.04–2.08Å [2.03–2.06Å]; Fe–N–C, 169–174° [170–179°];[21] N–C–S, 174–179° [178–179°]; N–C, 1.11–1.22Å [1.11–1.15Å]; C–S, 1.54–1.63Å [1.57–1,66Å].

In an effort to further characterize the mixed-valence nature of the complex, a Mössbauer study was performed.[22] The spectrum was expected to show three peaks, one from Fe^{3+} and two from Fe^{2+}. However, only the two from Fe^{2+} were observed (isomer shift, 0.593 mm/s, and quadrupole splitting, 1.723 mm/s). It is believed that the single peak from Fe^{3+} lies under one of the peaks of Fe^{2+}. A similar coincidence of peaks has been observed in Fe^{2+}/Fe^{3+} cyanide complexes.[23]

TABLE IV

Bond distances (Å) and angles (°) in the $[Fe(NCS)_6]^{3-}$ anions, with estimated standard deviations in parentheses.

Atoms	Distance	Atoms	Distance
Fe(4)–N(1)	2.06(2)	Fe(4)–N(2)	2.06(2)
Fe(4)–N(3)	2.08(2)	Fe(5)–N(4)	2.04(2)
Fe(5)–N(5)	2.04(2)	Fe(5)–N(6)	2.08(2)
C(1)–N(1)	1.22(2)	C(1)–S(1)	1.54(2)
C(2)–N(2)	1.11(2)	C(2)–S(2)	1.63(2)
C(3)–N(3)	1.18(2)	C(3)–S(3)	1.57(2)
C(4)–N(4)	1.17(2)	C(4)–S(4)	1.60(2)
C(5)–N(5)	1.19(2)	C(5)–S(5)	1.57(2)
C(6)–N(6)	1.15(2)	C(6)–S(6)	1.60(2)

Atoms	Angle	Atoms	Angle
N(1)–Fe(4)–N(2)	90.0(6)	N(1)–Fe(4)–N(3)	90.2(6)
N(2)–Fe(4)–N(3)	89.8(6)	N(4)–Fe(5)–N(5)	89.6(6)
N(4)–Fe(5)–N(6)	91.1(6)	N(5)–Fe(5)–N(6)	90.4(6)
N(1)–C(1)–S(1)	179(2)	N(2)–C(2)–S(2)	179(2)
N(3)–C(3)–S(3)	179(2)	N(4)–C(4)–S(4)	176(2)
N(5)–C(5)–S(5)	174(2)	N(6)–C(6)–S(6)	178(2)
Fe(4)–N(1)–C(1)	174(2)	Fe(4)–N(2)–C(2)	173(2)
Fe(4)–N(3)–C(3)	170(2)	Fe(5)–N(4)–C(4)	170(2)
Fe(5)–N(5)–C(5)	169(1)	Fe(5)–N(6)–C(6)	173(2)

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