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Synthesis and crystal structure of a novel mixed valence tri-iron complex salt: [hexakis(thiazole)iron(II)][μ-oxo-bis(trichloroiron(III))]

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Abstract—The title compound, $[Fe(tz)_6][Fe_2OCl_6]$ (**1**) (tz = thiazole) has been synthesised under argon by the reaction of anhydrous $FeCl_3$ with thiazole in ethanol. **1** crystallises in the cubic space group $Pa\bar{3}$ (no. 205) with $a = 15.001(5)$ Å, $V = 3375(2)$ Å^3, $Z = 4$, $R = 0.061$ and $R_w = 0.073$. **1** consists of a face-centred cubic array of $[Fe(tz)_6]^{2+}$ cations, with the oxo-bridged $[Fe_2OCl_6]^{2-}$ anion occupying the cell and edge centres. © 1997 Elsevier Science Ltd

Keywords: mixed valence; oxo-bridged; face-centred cubic; tri-metallic.

Polymeric systems of Cu and Co containing thiazole and di-bridging chloro ligands have been known for some time; however, until recently only the structure of dichloro-bis(thiazole)copper(II) has been reported [1]. Our previous study of the reactivity of thiazole and iron(II) chloride has indicated that an analogous compound is formed, although at that time no conclusive structural data had been reported [2]. As part of the continuing investigation into the structure and chemistry of polymeric bis(thiazole)iron(II) and iron/thiazole reactions in general, we have isolated the new compound $[Fe(tz)_6][Fe_2OCl_6]$ (**1**). This paper details the synthesis and structural characterisation of **1** by single crystal techniques.

EXPERIMENTAL

Infrared spectra were recorded (Nujol mull) in 350–5200 cm^{-1} range on a Perkin-Elmer FT-IR 2000 spectrophotometer. Elemental analyses were carried out on a LECO CHNS-900 elemental analyser. Anhydrous $FeCl_3$ and thiazole were obtained from commercial sources and used as received. Ethanol was of A.R. grade and was used when freshly distilled. All syntheses were carried-out under argon using Schlenk techniques.

Reaction of $FeCl_3$ *with thiazole*

To an ethanolic solution of $FeCl_3$ (4 mmol, 16 ml) was added thiazole (12 mmol, 2 ml) with stirring. A clear yellow-orange solution was obtained. The volume of this solution was reduced to ~8 ml under vacuum. After allowing to stand in a sealed vessel for four weeks, small yellow-brown single crystals of **1** of sufficient quality for structural determination were obtained; as well as very fine needle crystals which we believe to be the previously characterised 1-D polymeric compound $Fe(tz)_2Cl_2$ (**2**) [2,3]. Both **1** and **2** are formed in low yield. Upon filtering, and allowing the filtrate stand for 24 hours in a refrigerator orange polycrystals (**3**) were formed. Found for **3**: C, 26.0; H, 2.2; N, 9.9; S, 22.8. Calc.: C, 25.9; H, 2.2; N, 10.1; S, 23.0%. IR (Nujol): ν(ligand) 609(s), 823(s), 876(m), 911(m), 1048(s), 1111(m), 1235(m), 1311(m), 1496(m) cm^{-1}. These results agree with our previous observations in regard to $Fe(tz)_3Cl_3$ [2].

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Crystal structure determination

Measurements were made on a Rigaku AFC7R diffractometer at ambient temperature using monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). A yellow-brown single crystal of **1** was sealed in a glass capillary. Cell constants were obtained by least-squares analysis of 25 strong reflections in the range $22.19° < 2\theta < 24.93°$. Details of crystal data, data collection and structure refinement are summarised in Table 1.

The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction based on azimuthal scans of several reflections was also applied. The structure of **1** was solved by direct methods and developed by alternating cycles of difference Fourier syntheses and full matrix least-squares refinements. The positions of the non-hydrogen atoms were determined unequivocally. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined isotropically. Hydrogen atoms were placed at calculated positions for the final refinement. Neutral atom scattering factors were taken from [4] and anamalous dispersion corrections were taken from [5]. Crystallographic calculations were carried out with a teXsan crystallographic software package of Molecular Structure corporation (1985 & 1992).

Table 1. Summary of crystallographic data for **1**

Chemical formula	$Fe_3O(NSC_3H_3)_6Cl_6$
Formula weight	907.00
Crystal system	cubic
Space group	Pa-3 (No. 205)
a (Å)	15.001(5)
b (Å)	15.001(5)
c (Å)	15.001(5)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3375(2)
Z	4
Cryst. size (mm)	0.25 × 0.10 × 0.20
D_c (g cm^{-3})	1.785
Radiation (Å)	0.71069
μ (Mo-K_α) (cm^{-1})	21.43
$2\theta_{max}$ (°)	50.0
No. of reflns	1127
No. of reflns used	365 ($I > 3\sigma(I)$)
No. of variables	62
$(\Delta/\sigma)_{max}$	0.01
ρ_{max}/ρ_{min} (e Å^{-3})	0.42/−0.47
R^a	0.061
$R_w{}^b$	0.073
GOF^c	1.97

$^a R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

$^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

$^c \mathrm{GOF} = [\Sigma(|F_o| - |F_c|)^2/\Sigma(N_{reflns} - N_{params})]^{1/2}$.

RESULTS AND DISCUSSION

The crystal structure of **1** is shown in Fig. 1; while selected bond lengths and bond angles are presented in Table 2. **1** is comprised of a face-centred cubic array of $[Fe(tz)_6]^{2+}$ cations, with the oxo-bridged $[Fe_2OCl_6]^{2-}$ anions occupying the cell and edge centres. Thus, a mixed-valence complex salt is formed containing iron in both 2+ and 3+ oxidation states. There is no crystallographic evidence for charge transfer between the high-spin Fe^{II} cationic sites and the high-spin Fe^{III} anionic sites. The thiazole and chloro ligands sufficiently insulate the iron sites from each other; the nearest intermolecular Fe(1)—Fe(2) distance being 6.64(1) Å.

Cation structure

In contrast to the vast number of chelating and macrocyclic species formed by iron(II) and six N-donors, very few complexes have been characterised that have 6 monodentate N-donors; some examples being $[Fe(methylcyanato)_6][I_3]_2$ [6], $[Fe(isoxazole)_6][ClO_4]_2$ [7] and trans-$FeL_4(NCS)_2$ (L = pyridine [8], 4-styrylpiridine [9]). To our knowledge, **1** is the first $[Fe_2OCl_6]$ complex salt to be formed with a cation containing iron(II) octahedrally coordinated to six monodentate N-donors; indeed the first complex salt of any kind to bear six thiazole ligands in such an arrangement. Complex salts of μ-oxo-bis(trichloroiron(III)) containing iron(II) and chelating bidentate N-donors have however been reported for $[Fe(bpy)_3][Fe_2OCl_6]$ (bpy = 2,2′-bipyridine) [10,11] and $[Fe(phen)_3][Fe_2OCl_6]$ (phen = *o*-phenanthroline) [12]. The chelating compound $[Fe(bith)_3][ClO_4]_2$ (bith = 4,4′-bithiazole) has also been prepared [13].

The six thiazxole ligands of **1** form an almost regular octahedron about the Fe^{2+} centre, with Fe(1)—N distances of 2.21(1) Å and N—Fe(1)—N bond angles of 90.2(4)°, 89.8(4)° and 180°. These bond lengths are substantially longer than those low-spin Fe^{2+}—N bond lengths of 1.97(1) Å, 1.96(2) Å and 1.972(2) Å, observed for $[Fe(bpy)_3][Fe_2OCl_6]$ [11], $[Fe(phen)_3][Fe_2OCl_6]$ [12] and $[Fe(bith)_3][ClO_4]_2$ [13] respectively. While other high-spin thiazole containing complexes such as $Fe_2(tz)_4OCl_4$ (2.178 (5) Å) [2] and $Fe(tz)_2Cl_2$ (2.173(7) Å) [3] show slightly shorter average Fe—N bond lengths compared to **1**, this value is comparable to those found in other high-spin pseudo-octahedral iron(II) complexes [14,15].

The bond lengths and bond angles of the tz ligands are typical of other thiazole-containing species [1–3]. Several previous structure studies of thiazole-containing complexes have detected orientational disorder between the sulfur and an adjacent carbon atoms, due to 180° rotations about the M—N bonds [2,3,16]. While the thermal parameters for the S atom of **1** might be indicative of such orientational disorder, the corresponding thermal parameter for C(2) does

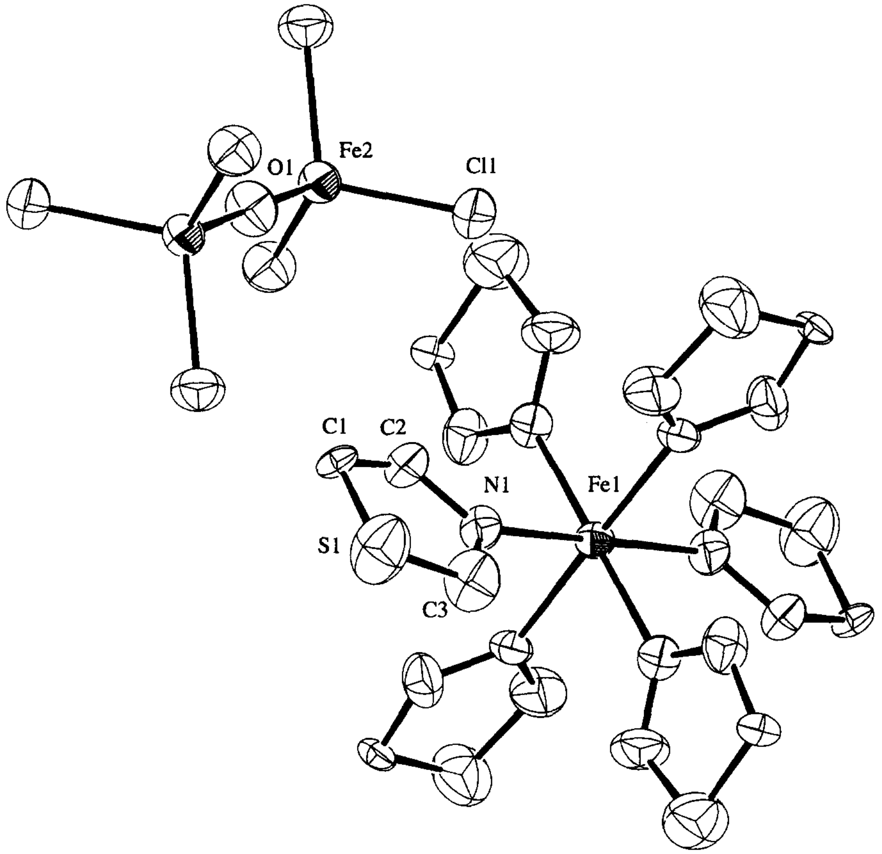

Fig. 1. An ORTEP drawing of $[Fe(thiazole)_6][Fe_2OCl_6]$ (**1**). All atoms are represented by the thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Fe(1)—N(1)	2.21(1)	Fe(2)—O(1)	1.756(4)
N(1)—C(1)	1.30(2)	Fe(2)—Cl(1)	2.239(5)
C(1)—S(1)	1.66(2)	C(1)—H(1)	0.981
S(1)—C(2)	1.69(1)	C(2)—H(2)	0.973
C(2)—C(3)	1.42(2)	C(3)—H(3)	0.978
N(1)—C(3)	1.35(2)		
N(1)—Fe(1)—N(1)	90.2(4)	Fe(2)—O(1)—Fe(2)	180.00
N(1)—Fe(1)—N(1)	89.8(4)	Cl(1)—Fe(2)—O(1)	110.3(2)
N(1)—Fe(1)—N(1)	180.00	Cl(1)—Fe(2)—Cl(1)	108.7(2)
Fe(1)—N(1)—C(1)	127(1)	Fe(1),N(1)—C(3)	126(1)
N(1)—C(1)—S(1)	116(1)	C(1)—S(1)—C(2)	94.1(8)
S(1)—C(2)—C(3)	102(1)	C(2)—C(3)—N(1)	121(1)
C(1)—N(1)—C(3)	107(1)		

not indicate any significant level of disorder. Indeed, attempts to refine the occupancy of the S site away from unity did not lead to any significant improvement in the fit to the observed data.

Anion structure

The Fe(2) atoms in **1** appear to have C_{3v} site symmetry such that the anion adopts a staggered conformation. Figure 1 shows this conformation when viewed down the ⟨111⟩ axis of the unit cell (i.e. along the Fe—O—Fe bond). The bond lengths and angles of $[Fe_2OCl_6]^{2-}$ in **1** are typical of those found in other complex salts containing this complex anion. Previous studies have shown that the Fe^{III} centres of these anions tend to have almost tetrahedral coordination, with Fe—O distances (within experimental error) almost identical at 1.756 Å and Fe—Cl distances ranging between 2.201 Å and 2.238 Å [17]. The Fe(2)—O(1) distance in **1** was found to be 1.756(4) Å while the Fe(2)—Cl(1) distance was observed to be 2.239(5) Å. The Cl—Fe—Cl and Cl—Fe—O bond angles were found to be 108.7(2)° and 110.3(2)° respectively.

The Fe—O—Fe bond angle of other complex salts containing the $[Fe_2OCl_6]^{2-}$ anion have been reported to vary between 146.5° and 180° [17]. According to Haselhorst *et al.* however, there has been no definitive evidence for linear Fe—O—Fe bond angles [17]. In cases where authors have reported linear Fe—O—Fe bond angles [18–20]. It has been suggested that crystallographically imposed site symmetry masks an orientational disorder of the anion, which may be detected by inspection of the thermal displacement parameters of the chlorine and oxygen atoms. Examination of the anisotropic thermal parameters of the bridging oxygen atom of **1**, indicates a relatively large contribution ($\langle u^2 \rangle = 0.089(8)$ Å^2) perpendicular to the direction of the Fe—O—Fe bond; while that along the bond (i.e. the $\langle 111 \rangle$ direction) is essentially zero. Given this root-mean squared displacement of ~0.30 Å and an interatomic Fe(2)—O distance of 1.756(4) Å, one could envisage a maximum angular displacement of approximately 9.6°. Attempts to refine the oxygen coordinates off the special *4b* $(\frac{1}{2}, 0, 0)$ position were unsuccessful, suggesting that this atom might be disordered in a ring about this position. Thus, it seems likely that the true Fe—O—Fe bond angle in **1** is not linear, but rather occurs between the limits of 160.8° and 180°.

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