Cyclopentadienylcarbonyl Complexes of Iron with Azoles.
III. The Structure of Iron 1-N-(1,2,3-triazole)cyclopentadienyldicarbonyl Bisulphate and Proton Exchange Reactions in its Solutions

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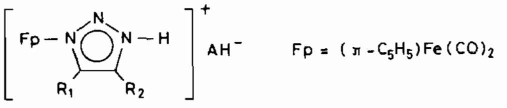
On the basis of the X-ray study of iron 1-N(1,2,3-triazole)cyclopentadienyldicarbonyl bisulphate and NMR investigations of sulphate salts of 1,2,3-triazole complexes, a mechanism of the proton transfer in these compounds is proposed. Crystals of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_3N_3)]^+HSO_4^-$ *are rhombic,* $a = 8.159(1)$, $b = 11.813(2)$, $c = 13.107(2)$ Å, $\rho(calc) = 1.80$ $g \cdot cm^{-3}$, $z = 4$, *space group* $P2_12_12_1$. *The structure was deciphered by the heavy-atom method and refined by the least-squares method in anisotropic full-matrix approximation for non-hydrogen and isotropic for hydrogen atoms to* $R = 0.042$, $R_w = 0.046$ *for 1568 reflections.*

Introduction

This paper is a sequel of the study of cyclopentadienylcarbonyl complexes of iron and azoles [1, 2] and proton transfer reactions in azoles and their complexes with metals [3, 4].

We have reported [2] that the rate of proton exchange *via* N–H–O-bonding in salts of dibasic acids with 1-substituted cyclopentadienylcarbonyl complexes of 1,2,3-triazoles is high.



$Fp = (\pi\text{-}C_5H_5)Fe(CO)_2$

a) $R_1 = R_2 = H$; b) $R_1 = H$, $R_2 = Ph$; c) $R_1\text{-}R_2 = \text{-}(CH)_4$ (benzotriazole) $AH^- = HSO_4^-, HC_2O_4^-$.

This fact was suggested to be related to an aggregation of molecules of sulphate salts in solutions of polar solvents.

To obtain reliable information on the nature of intermolecular interactions in such salts, an X-ray study of iron 1-N-(1,2,3-triazole)cyclopentadienyldicarbonyl bisulphate (1a) was carried out.

X-ray Study

The structure of iron 1-N-(1,2,3-triazole)cyclopentadienyldicarbonyl bisulphate involves helical chains of HSO_4^- ions linked by O–H···O hydrogen bridges. Complex cations $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_3N_3)]^+$ branch away from the chains and are linked to HSO_4^- anions by the single hydrogen bond N(3)–H···O(5). The structure of the complex is presented in Fig. 1; bond lengths and angles are listed in Tables I and II, respectively. The cation geometry is found to be practically identical with that established for $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_7H_6N_2)]^+B(C_6H_5)_4^- \cdot (CH_3)_2CO$ salt [1]. The iron atom is linked to the η^5-cyclopentadienyl ligand, to a pair of CO-groups and to the N(1) atom of triazole ligand. Mean lengths for Fe–C(C_5H_5), Fe–CO and Fe–N(1) bonds are 2.10(1), 1.787(6), and 1.961(4) Å, respectively, and are close to values determined in [1] (2,107(9), 1.77(1), and 1.970(7) Å).

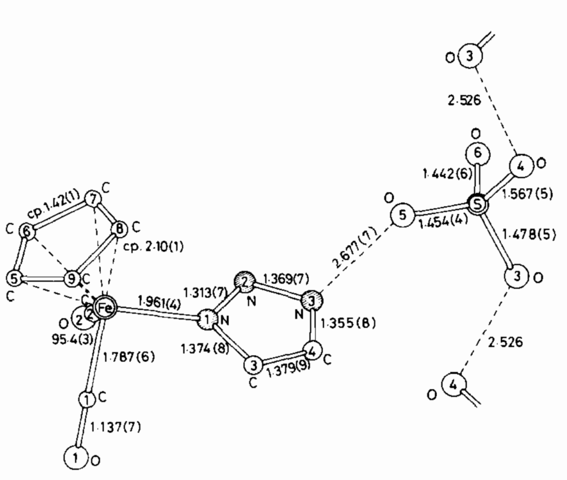


Fig. 1. The structure of iron 1-N-(1,2,3-triazole)cyclopentadienyldicarbonyl bisulphate.

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TABLE I. Bond Lengths d (Å).

Bond	(Å)	Bond	(Å)	Bond	(Å)
Fe–N(1)	1.961(4)	C(1)–O(1)	1.147(8)	N(2)–N(3)	1.359(7)
Fe–C(1)	1.785(7)	C(2)–O(2)	1.127(7)	N(1)–C(3)	1.374(8)
Fe–C(2)	1.788(6)	mean	1.137	N(3)–C(4)	1.355(8)
mean	1.787	C(5)–C(6)	1.418(10)	C(3)–C(4)	1.379(9)
Fe–C(5)	2.081(7)	C(6)–C(7)	1.430(10)	S–O(3)	1.478(5)
Fe–C(6)	2.090(7)	C(7)–C(8)	1.419(12)	S–O(4)	1.567(5)
Fe–C(7)	2.106(7)	C(8)–C(9)	1.402(10)	S–O(5)	1.454(4)
Fe–C(8)	2.124(8)	C(9)–C(5)	1.418(9)	S–O(6)	1.442(5)
Fe–C(9)	2.107(6)	mean	1.417		
mean	2.101	N(1)–N(2)	1.313(7)		

TABLE II. Bond Angles ω(°).

Angle	ω°	Angle	ω°
FeN(1)N(2)	119.5(4)	C(5)C(6)C(7)	106.8(6)
FeN(1)C(3)	129.7(4)	C(6)C(7)C(8)	107.6(7)
FeC(1)O(1)	176.7(6)	C(7)C(8)C(9)	109.2(7)
FeC(2)O(2)	178.7(6)	C(8)C(9)C(5)	107.2(6)
N(1)FeC(1)	94.6(3)	C(9)C(5)C(6)	109.2(6)
N(1)FeC(2)	93.3(2)	mean	108.0
C(1)FeC(2)	95.4(3)	O(3)SO(4)	101.9(3)
N(1)N(2)N(3)	106.9(5)	O(3)SO(5)	112.6(3)
N(2)N(1)C(3)	110.8(5)	O(3)SO(6)	112.8(3)
N(2)N(3)C(4)	109.7(5)	O(4)SO(5)	117.1(3)
N(1)C(3)C(4)	105.9(5)	O(4)SO(6)	108.0(3)
N(3)C(4)C(3)	106.8(6)	O(5)SO(6)	113.5(3)

Triazole ligand is planar and the dihedral angle between the ligand and cyclopentadienyl ring planes is 33.7° (in [1] the analogous angle was found to be 32°). The structure of the HSO_4^- anion is usual: the S atom coordination geometry is distorted tetrahedral, S–O bond lengths are between 1.442 and 1.478 Å and are comparable to those found for $(C_6H_7N_5O)Cu(H_2O)_3SO_4 \cdot 3H_2O$ [5] (1.466–1.474 Å). The S–O(4) bond length is 1.567(5) Å and corresponds to the S–OH normal bond.

The HSO_4^- anion is bound to the complex cation by just the single hydrogen bond N(3)H•••O(5) of 2.677(7) Å (similar $H \cdots O(SO_4)^{2-}$ bond lengths in $(C_6H_7N_5O)_2Cu(H_2O)_3SO_4 \cdot 3H_2O$ [5] are 2.714(7) and 2.890(9) Å). The hydrogen atom of the HSO_4^- anion is not involved in hydrogen bond formation with the N(2) atom of the triazole ligand: inter- and intramolecular distances N(2)•••O(4) are all greater than 4.0 Å. On the other hand, the structure contains a short H-bond O(4)•••O(3) (–1/2 + x, 3/2 – y, z) of 2.526(7) Å, *i.e.* the hydrogen atom* bonded to O(4) participates in the formation of the H-bond between HSO_4^- ions, joining them into helical chains oriented along the X axis (the second H-bond with the O(3) atom of the original anion is formed by O(4) (1/2 + x, 3/2 – y, z)). Thus, both protons capable of H-bonding participate in H-bonds in the complex under study.

A similar structural organization for the anion is observed in imidazolium phosphate $[C_3H_5N_2]^+H_2PO_4^-$. Its structure also involves chains of $H_2PO_4^-$ anions stretched along the strong O–H•••O bonds (2.578 Å), and the other proton of the anion forms the H-bond with the heterocycle [6].

Discussion

The study of the temperature dependence of the 1-N-Fp-benzotriazole sulphate (1c) ^{13}C-NMR spectrum (Fig. 2) showed that with a decrease in temperature down to –125 °C the spectral picture becomes complicated, although we failed to obtain the boundary ^{13}C-NMR spectrum. At –80 °C the broadening of ^{13}C nuclei signals takes place for all ligands; at –125 °C additional signals appear in the region corresponding to ^{13}C-atoms of carbonyl and cyclopentadienyl ligands.

Literature data on the association of azoles and their derivatives in solutions and the results on intermolecular aggregation in the crystalline state reveal a strong analogy between these phenomena. For instance, the 1,3-association of benzotriazole in a crystal [7] corresponds to the 1,3-association in the inert solvents [8]. This leads to the prototropic tautomerism in the THF solution [9], so that at low temperatures it becomes possible to observe the corresponding asymmetric tautomer. Prototropic tautomerism is a degenerate process because self-association of benzotriazole in solution also results from intermolecular N–H•••N-bonds in 1,3-positions. Thus, in this case, we based our analysis of exchange processes in salts on the

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*The $H(O_4)$ atom was not localized during difference synthesis; however, its location near O(4) is evident from the analysis of bond lengths in HSO_4^- anion.

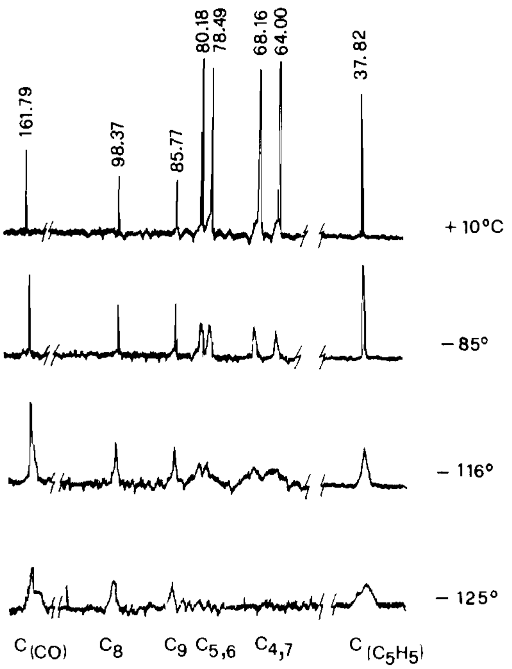
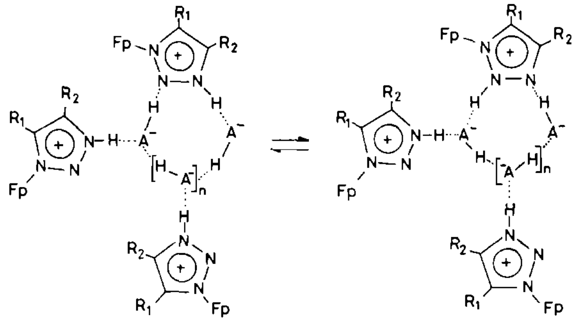


Fig. 2. ^{13}C-NMR spectra. The temperature dependence of iron 1-N-benzotriazolecyclopentadienyldicarbonyl bisulphate (solvent CH_3OH/iso-C_3H_7OH, 10:1).

assumption that intermolecular aggregation of these compounds both in solution and in crystalline state is of a similar nature. Proton exchange in such associates is complex since it involves sulphate and azole fragments as well as solvent molecules. Fast proton exchange with participation of alcohol and anionic self-associates (HSO_4^-) (but without organometallic cations) cannot change the ^{13}C-NMR spectra of the whole organo-metallic part of the system (azole, cyclopentadienyl and carbonyl ligands), since the parameters of ^{13}C-NMR spectra of azoles and their complexes are low sensitive to the intermolecular interactions in the outer coordination sphere [10]. Likewise, it could hardly be possible that the fast single-proton transfer between cation and anion takes place since Fp-Az complexes are strong bases [11]. In fact, it was shown in a series of papers that proton exchange in azoles in the presence of H_2SO_4 or CH_3COOH either does not takes place at all, or proceeds at low rates [12, 13].

A similar situation is realized when H_2SO_4 is added to 2-N-Fp-benzotriazole solution in tetrahydrofuran. The symmetry of the AA′BB′-system in the proton spectrum of benzene grouping is immediately broken and no changes in the spectrum are observed with the temperature decreasing to −100 °C.

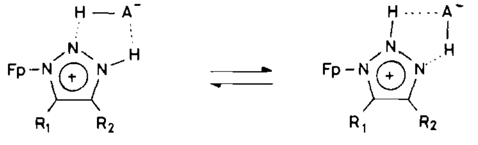
Basicity measured in nitromethane [11] has, however, shown that the 2-isomers of Fp-complexes of 1,2,3-triazoles are 5 orders of magnitude less basic than the 1-isomers and, consequently, deprotonation and proton exchange reactions for the former compounds must proceed more readily. Therefore, the salts of the 1-N-isomer are somewhat peculiar. The foregoing suggests that the proton exchange in such salts is of a bifunctional concerted character. If HSO_4^- chains are arranged helically as in the crystalline state, then the formation of a N(2)•••H–O hydrogen bond appears to be quite real.



The proton exchange in this case is prototropic tautomerism, the form with the N-2-localized proton being thermodynamically less advantageous. This form plays the role of the short-lived intermediate. A fast exchange takes place with respect to which the azole ligands in self-associates of HSO_4^--ions are bifunctional catalysts.

Moreover, ^{1}H-NMR spectral data show that in the temperature region $+60 \div -100°$ the protons of NH and OH (of HSO_4^-) do not produce separate signals. This points to fast proton exchange reactions involving azole and sulphate fragments.

The X-ray study indicates that the second proton, able to form H-bonds, belongs to the HSO_4^--ion and participates in the formation of helical H-bond chains (HSO_4^-). Then it may be supposed that terminal HSO_4^--ions form bonds with N(2) atoms in solutions. Aggregate rearrangement (even at a low extent) into cyclic and insular-like aggregates is also possible and proton exchange in the framework of such structures may take place:



Similar structures in which the 1,2,3-triazole ring forms the two H-bonds and the third nitrogen atom is coordinated to the metal, are described in the literature [14]. It should be noted that azoles, involving the 1,2-arrangement of amino- and imino-groups, frequently give rise to cyclic associates in solutions. This is the case, *e.g.*, of pyrazole when in place of chains of H-bonded molecules in a crystal [15], the cyclic three-membered structures [16]

TABLE IIIa. Coordinates of Atoms ($\times 10^4$) and their Anisotropic Thermal Parameter Values. Thermal Factor $T = \exp[-10^{-1}/4\,(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	1844(1)	1408(1)	1301(1)	4(0)	8(0)	10(0)	0(0)	−1(0)	0(0)
S	−688(2)	7278(1)	−700(1)	9(1)	9(1)	17(1)	0(1)	−3(1)	−3(1)
O(1)	5307(5)	934(4)	1715(4)	5(2)	34(2)	23(2)	5(2)	−3(2)	0(2)
O(2)	2052(7)	1110(4)	−903(3)	27(2)	40(3)	16(2)	2(2)	1(2)	−8(2)
O(3)	857(5)	7911(4)	−845(4)	8(2)	20(2)	31(2)	5(2)	2(2)	−10(2)
O(4)	−1530(6)	7965(4)	177(4)	18(2)	20(2)	36(2)	3(2)	7(2)	10(2)
O(5)	−419(5)	6137(3)	−318(3)	19(2)	8(2)	27(2)	−2(2)	−7(2)	−5(2)
O(6)	−1742(7)	7321(4)	−1583(3)	31(2)	24(2)	26(2)	6(2)	−20(2)	−8(2)
N(1)	2088(6)	3057(4)	1223(4)	9(2)	8(2)	14(2)	−1(2)	4(2)	4(2)
N(2)	1181(6)	3635(5)	581(4)	8(2)	13(2)	18(2)	3(2)	−2(2)	3(2)
N(3)	1588(6)	4743(4)	698(4)	10(2)	9(2)	20(2)	−3(2)	2(2)	−4(2)
C(1)	3964(8)	1151(6)	1544(5)	17(3)	21(3)	16(3)	−3(2)	5(2)	4(2)
C(2)	1987(8)	1233(5)	−51(5)	12(2)	16(3)	16(3)	0(2)	−3(2)	−4(2)
C(3)	3101(9)	3765(5)	1765(5)	17(3)	14(3)	17(2)	−3(2)	−5(3)	0(2)
C(4)	2761(8)	4844(6)	1424(5)	15(3)	12(3)	19(3)	−2(2)	−3(2)	0(2)
C(5)	1217(8)	−47(5)	2106(5)	13(3)	9(3)	22(3)	−1(2)	4(2)	7(2)
C(6)	64(8)	135(6)	1314(6)	22(3)	18(3)	27(3)	−16(3)	5(3)	5(3)
C(7)	−698(8)	1203(7)	1512(7)	5(2)	32(4)	48(5)	−4(3)	4(3)	20(4)
C(8)	−5(9)	1643(6)	2422(6)	20(3)	17(3)	34(4)	−2(3)	22(3)	0(3)
C(9)	1188(8)	889(6)	2784(5)	14(3)	16(3)	13(3)	−3(2)	7(2)	1(2)

TABLE IIIb. Coordinates ($\times 10^3$) and Isotropic Thermal Factors for Hydrogen Atoms[a].

Atom	X	Y	Z	β_{iso}(Å^2)
H(N3)	110(9)	539(5)	31(5)	3.5(15)
H(3)	392(9)	356(5)	230(5)	3.0(20)
H(4)	297(9)	556(5)	161(5)	1.7(16)
H(5)	180(8)	−68(5)	213(5)	1.1(13)
H(6)	−23(9)	−53(6)	−73(7)	5.4(23)
H(7)	−156(9)	157(6)	109(6)	3.3(21)
H(8)	−29(9)	226(6)	273(5)	2.7(18)
H(9)	189(9)	99(6)	340(6)	4.5(19)

[a] Hydrogen atoms' numbers are those of carbon atoms to which they are linked.

turn out to be the most advantageous in a solution. They are important in proton exchange reactions [3, 10].

Experimental

Complex (1a) was obtained following the procedure described in [2] and recrystallized from methanol/THF mixture (1:1). Crystals of (1a) are rhombic, $a = 8.159(1)$, $b = 11.813(2)$, $c = 13.107(2)$ Å; ρ(calc) = 1.80 g·cm^{-3}, $z = 4$, space group-$P2_12_12_1$. The experiments were performed on 'Syntex-P2$_1$' diffractometer, λMoK$_\alpha$, $2\theta \leqslant 50°$, exposure t = −100 °C. The structure was deciphered by the heavy-atom method and refined by the least-square method in anisotropic full-matrix approximation for non-hydrogen and isotropic for hydrogen atoms to $R = 0.042$, $R_w = 0.046$ for 1568 reflections with $F^2 \geqslant 1.96\ \sigma$. Atomic coordinates and thermal factors are presented in Tables IIIa and IIIb.

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