SYNTHESIS AND CRYSTAL STRUCTURES OF ION-PAIRS BASED ON ANIONIC IRON-DITHIOLENES AND ALKYLAMMONIUM AS COUNTERCATION

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Abstract

Reactions between $[Fe_2(CO)_6(\mu\text{-}SC_6H_2X_2S)]$ (X= Cl or H) or $FeCl_3 \cdot 6H_2O$ with $HSC_6H_2X_2SH$ and either $ONMe_3$ or $NaOH/Et_4NBr$ give rise to a series of iron dithiolene ion-pairs of formula $[RN]_2[Fe_2(SC_6H_2X_2S)_4]$ [X= Cl or H; R=$(CH_3)_3H$ or $(CH_3CH_2)_4$], or $[(CH_3CH_2)_4N]_2[Fe(SC_6H_2Cl_2S)_3]$. The crystal structures of these iron dithiolates show very intricate crystal structure involving electrostatic interactions and a variety of complex H-bonds, Cl···Cl and aromatic interactions. The use of tetraethylammonium (**4-5**) instead of trimethylammonium (**1-3**) counterions imply less strong supramolecular interactions and compounds more prone to polymorphism as it is the case of **5a** and **5b**.

Keywords: Metal-Dithiolene complexes, Iron-dithiolene ion pairs, Supramolecular Networks, Polymorphs, Crystal Structures.

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1. Introduction

Transition metal dithiolene derivatives have been widely explored due to their structural variety based on the versatility in their coordination modes of dithiolene ligands and their rich redox chemistry among others [1-15]. Substitution reactions of CO by other ligands such as thiolate or dithiolate are well documented in Organometallic Chemistry [16-20] being the ONMe$_3$ an useful reagent in decarbonylation processes. On the other hand, we have previously reported the formation of several coordination polymers (CPs) formed in the reactions of [Fe$_2$(CO)$_6$(SRS)] (R= C$_6$H$_2$Cl$_2$ or C$_6$H$_4$) with the corresponding dithiolenes HSRSH in the presence of alkali bases [21]. In addition, the neutral compound [Fe$_2$(SC$_6$H$_2$Cl$_2$S)$_4$] has been isolated by thermal reaction between [Fe$_2$(CO)$_6$(SC$_6$H$_2$Cl$_2$S)] and HSC$_6$H$_2$Cl$_2$SH [22].

On the other hand, several diiron(tetrakis)dithiolene derivatives containing ammonium cations have been prepared by exchange of Na$^+$ by R$_4$N$^+$ cations in the precursor [Na]$_2$[Fe$_2$(SRS)$_4$] [23] or by reaction of FeCl$_3 \cdot$6H$_2$O with dithiol, NaOH and ammonium halide [24]. Herein we report the syntheses, characterization and crystal structures of the compounds [Me$_3$HN]$_2$[Fe$_2$(SRS)$_4$] (R= C$_6$H$_2$Cl$_2$ or C$_6$H$_4$), [Et$_4$N]$_2$[Fe(SC$_6$H$_2$Cl$_2$S)$_3$] and [Et$_4$N]$_2$[Fe$_2$(SC$_6$H$_4$S)$_4$].

2. Experimental section

2.1. General information

Reagents and solvents are commercial and were used as received without further purification. All reactions were carried out under argon. Elemental analyses were performed on an LECO CHNS-932 Elemental Analyzer. The IR spectra were recorded on a Perkin Elmer spectrum 100 spectrophotometer using a universal ATR sampling accessory.

2.2. Single crystal X-ray diffraction

Single crystals of compounds **1-5** were covered with a layer of an inert mineral oil, mounted on a MiTeGen micromount (**1-3** and **5**) or a cryoloop (**4**) with the aid of a microscope and immediately placed in the low temperature nitrogen stream. The intensity data sets were collected at low temperature on a Bruker Kappa Apex II diffractometer (**1-3** and **5**) or a Bruker-Nonius KappaCCD diffractometer (**4**) both equipped with an Oxford Cryostream 700 unit and with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (SI for detailed information about the data collection and structure refinement). Structures were solved by direct methods (SHELXS-97 for **1-5**) [25] and refined by least-squares against F2 (SHELXL-2014) [26]. Data were corrected for absorption effects using the multi-scan method (SADABS) [27]. All of the non-hydrogen atoms were refined anisotropically. Crystallographic data for compounds **1-4** are summarized in Table 1 (CCDC 1899780 (**1**), 1899781 (**2**), 1899782 (**3**), 1899783 (**4**), 1899784 (**5a**), 1899785 (**5b**).

Table 1. Crystallographic data and structural refinement details.

	1	2	3	4	5a	5b

Formula	$C_{30}H_{28}Cl_8Fe_2N_2S_8$	$C_{38}H_{52}Fe_2N_2O_2S_8$	$C_{30}H_{36}Fe_2N_2S_8$	$C_{35}H_{48}Cl_8FeN_2S_6$	$C_{20}H_{28}FeNS_4$	$C_{20}H_{28}FeNS_4$
Formula weight	1068.32	936.99	792.79	1028.56	466.52	466.52
T (K)	110.(2)	200.(2)	296.(2)	200(2)	175.(2)	175.(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	P 2_1/c	P -1	P bca	P 2_1/c	P 2_1/n	P 2_1/c
Crystal size.mm	0.26x0.04x0.03	0.23x0.06x0.05	0.06x0.06x0.04	0.36x0.30x0.27	0.29x0.23x0.15	0.16x0.08 x 0.07
a (Å)	10.3799(5)	9.1743(5)	12.3307(10)	16.800(4)	12.5628(5)	8.0626(5)
b (Å)	22.5552(11)	9.6778(4)	15.5196(13)	13.7550(6)	11.3369(4)	24.5174(16)
c (Å)	9.0325(4)	12.6851(7)	18.5762(14)	19.8623(15)	16.6758(6)	10.9440(6)
α (°)	90	76.850(2)	90	90	90	90
β (°)	106.138(2)	89.545(2)	90	99.302(11)	108.846(1)	98.127(3)
γ (°)	90	83.188(2)	90	90	90	90
V (Å^3)	2031.37(17)	1088.79(10)	3554.9(5)	4529.5(12)	2247.70(14)	2141.6(2)
Z	2	1	4	4	4	4
ρ_c (g cm^{-3})	1.747	1.429	1.481	1.508	1.379	1.447
μ (mm^{-1})	1.680	1.085	1.310	1.111	1.047	1.099
F (0 0 0)	1076	490	1640	2120	980	980
Θ Range (º)	2.727-25.339	2.753-25.338	2.377-25.034	3.139-27.521	2.212-25.350	2.509-25.348
Index ranges	-12 to 12 -27 to 27 -10 to 10	-11 to 11 -11 to 11 -15 to 15	-11 to 14 -17 to 17 -22 to 17	-21 to 21 -17 to 17 -25 to 25	-15 to 15 -13 to 13 -20 to 20	-9 to 9 -29 to 29 -12 to 13
Reflections collected	18410	17187	27320	84251	38776	32851
Unique reflections	3707	3913	3119	10392	4109	3897
Reflections (I>2σ(I))	2721	3105	1969	7209	3652	2985
[R$_{int}$]	0.0612	0.0430	0.1082	0.0827	0.0409	0.0835
Goodness of fit (S)[a]	1.077	1.075	0.999	1.087	1.023	0.981
R1[b]; wR2[c] (I > 2σ(I))	0.0481; 0.0994	0.0444; 0.1064	0.0445; 0.0968	0.0570; 0.1364	0.0223; 0.0532	0.0416; 0.0994
R1; wR2 (all data)	0.0787; 0.1091	0.0604; 0.1173	0.0959; 0.1174	0.0973; 0.1606	0.0274; 0.0560	0.0623; 0.1105
$\Delta\rho_{max}/\Delta\rho_{min}$ (e.Å^3)	1.447/-0.525	0.801/-0.877	0.497/-0.370	1.374/-1.058	0.284/-0.218	0.554/-0.489

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R1 = \sum ||F_0|-|F_c|| / \sum |F_0|$. [c] $wR2 = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (max(F_0^2,0) + 2Fc^2)/3$ with a = 0.0401 (**1**); a = 0.0489 (**2**); a = 0.0608 (**3**); a = 0.0589 (**4**); a = 0.0224 (**5a**); a = 0.0656 (**5b**), and b = 4.3981 (**1**); b = 1.5707 (**2**); b = 14.8307 (**4**); b = 1.1193 (**5a**).

2.3. Synthesis

2.3.1. Synthesis of [(CH₃)₃HN]₂[Fe₂(SC₆H₂Cl₂S)₄] (1). To a solution of compound [Fe₂(CO)₆(μ-SC₆H₂Cl₂S)] (96 mg, 0.20 mmol) and HSC₆H₂Cl₂SH (124 mg, 0.59 mmol) in THF (15 mL), ONMe₃ (88 mg, 1.17 mmol) was added. The mixture was stirred at room temperature for 1h, then the solvent was removed until dryness and the residue was washed with *n*-hexane. Finally, the solid was crystallized in acetone/*n*-heptane (2:1) at room temperature to yield purple crystals of compound [(CH₃)₃HN]₂[Fe₂(SC₆H₂Cl₂S)₄] **1** (98 mg, 46 %). Anal. Calc. for C₃₀H₂₈N₂Cl₈S₈Fe₂ (**1**): C, 33.73 %; H, 2.64 %; N, 2.62 %; S, 24.01%. Found: C, 34.35%; H, 2.86%; N, 2.52%; S, 23.05%. IR (cm⁻¹): υ(N-H): 3100; υ(C-H): 2988; υ(C=C): 1604, 1598; υ(C-N): 1065; δ(C-H).: 824; υ(C-S): 780.

2.3.2. Synthesis of [(CH₃)₃HN]₂[Fe₂(SC₆H₄S)₄]·2THF (2) and [(CH₃)₃HN]₂[Fe₂(SC₆H₄S)₄] (3). Following the same procedure as for **1** but using the dithiolene HSC₆H₄SH instead, crystals of compound [(CH₃)₃HN]₂[Fe₂(SC₆H₄S)₄]·2THF **2** (38 mg, 34 %) together to a few crystals of [(CH₃)₃HN]₂[Fe₂(SC₆H₄S)₄] **3** were obtained in THF/*n*-heptane. Anal. Calc. for C₃₄H₄₄N₂S₈OFe₂ (**2**-2THF). C, 47.22 %; H, 5.13 %; N, 3.24 %; S, 29.65 %. Found: C, 46.54 %; H, 5.06 %; N, 3.07 %; S, 29.23 %. IR (cm⁻¹): υ(N-H): 3092; υ(C-H): 2963; υ(C=C): 1604, 1598; υ(C-N): 1062; δ (C-H): 823; υ(C-S): 693.

2.3.3. Synthesis of [(CH₃CH₂)₄N]₂[Fe(SC₆H₂Cl₂S)₃]·CH₂Cl₂ (4). To water solution (10 mL) of NaOH (10 mL, 5 wt%) and HSC₆H₂Cl₂SH (235 mg, 1.1 mmol), (CH₃CH₂)₄NBr (11.6 mg, 0.55 mmol) was added. The mixture was stirred for 5 min., and then a solution of FeCl₃.6H₂O (150 mg; 0.55 mmol) in 10 mL of EtOH/H₂O (1/1) was added. The solid obtained after keeping the mixture for 30 min at room temperature, was filtered and washed with H₂O and CH₂Cl₂. Further crystallization in DMF/CH₂Cl₂ at -20 ºC yielded compound [(CH₃CH₂)₄N]₂[Fe(SC₆H₂Cl₂S)₃]·CH₂Cl₂ (**4**) (136 mg, 24 %). Anal. Calc. for C₃₅H₄₈Cl₈FeN₂S₆ (**4**): C, 40.87 %; H, 4.70 %; N, 2.72 %; S, 18.70 %. Found: C, 39.25 %;

H, 4.15 %; N, 2.40 %; S, 19.91 %. IR (cm^{-1}): υ(C-H): 2978, 2945; υ(C=C): 1523; υ(C-N): 1059; δ(C-H): 997, 817; υ(C-S): 675.

2.3.4. Synthesis of [(CH$_3$CH$_2$)$_4$N]$_2$[Fe$_2$(SC$_6$H$_4$S)$_4$] (5). Following the same procedure as for **4** but using the dithiolene HSC$_6$H$_4$SH instead, some crystals of compound [(CH$_3$CH$_2$)$_4$N]$_2$[Fe$_2$(SC$_6$H$_4$S)$_4$] **5** (54 mg, 21 %) were obtained by slow diffusion of CH$_2$Cl$_2$ in a DMF solution. Anal. Calc. for C$_{40}$H$_{56}$Fe$_2$N$_2$S$_8$ **(5)**: C, 51.49 %; H, 6.05 %; N, 3.00 %; S, 27.49 %. Found: C, 49.83 %; H, 5.87 %; N, 2.90 %; S, 26.46 %. IR (cm^{-1}): υ(C-H): 2923, 2853; υ(C=C): 1604, 1508; υ(C-N): 1029; δ (C-H): 1028, 828; υ(C-S): 670.

3. Results and Discussion

In order to evaluate the role of the ONMe$_3$ in the substitution process of carbonyl ligands in the compound [Fe$_2$(CO)$_6$(μ-SC$_6$H$_2$Cl$_2$S)], we initially carried out the reaction between the iron carbonyl complex and the dithiolene HSC$_6$H$_2$Cl$_2$SH in the presence of ONMe$_3$. Diffraction studies carried out on crystals obtained in acetone/*n*-heptane (2:1) at room temperature, confirmed the formation of compound [(CH$_3$)$_3$HN]$_2$[Fe$_2$(SC$_6$H$_2$Cl$_2$S)$_4$] **1** (Scheme 1).

$[Fe_2(CO)_6(\mu\text{-}SC_6H_2X_2S)]$
$+ HSC_6H_2X_2SH$
$+ ONMe_3$

i → $[(CH_3)_3HN]_2[Fe_2(SC_6H_2Cl_2S)_4]$
1

ii → $[(CH_3)_3HN]_2[Fe_2(SC_6H_4S)_4]\cdot2THF$
2

$[(CH_3)_3HN]_2[Fe_2(SC_6H_4S)_4]$
3

$[(CH_3CH_2)_4N]_2[Fe(SC_6H_2Cl_2S)_3]\cdot2CH_2Cl_2$
4

$[(CH_3CH_2)_4N]_2[Fe_2(SC_6H_4S)_4]$
5a/5b

iii ← / ii ←

$FeCl_3\cdot6H_2O +$
$HSC_6H_2X_2SH$
$+ NaOH +$
$(CH_3CH_2)_4NBr$

i: X=Cl; crystallization in acetone/*n*-heptane
ii: X=H; crystallization in THF/*n*-heptane
iii: X=Cl; crystallization in DMF/CH$_2$Cl$_2$
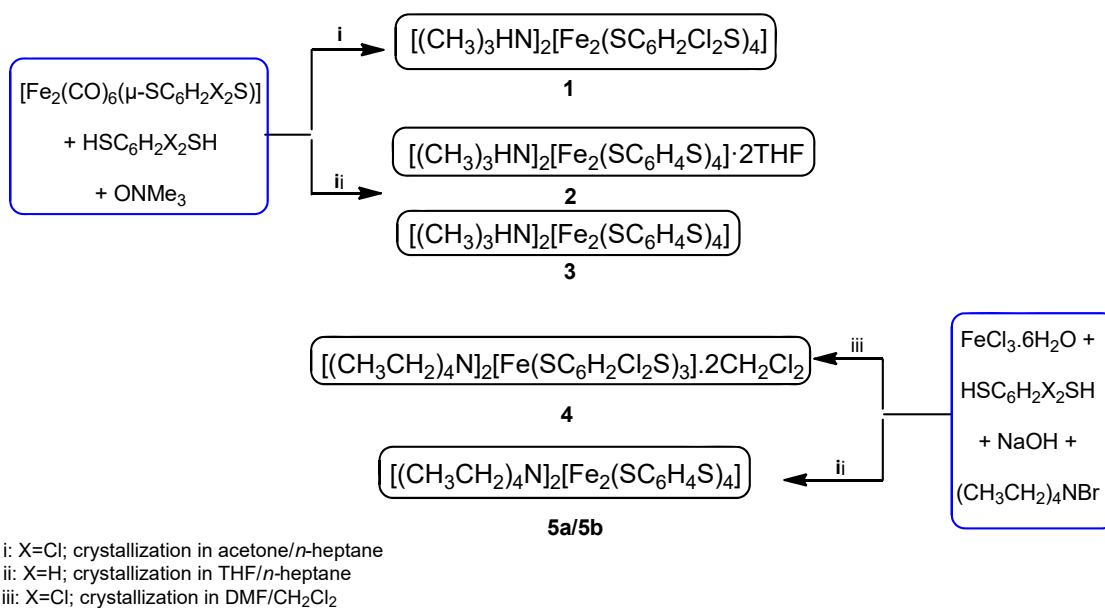
Scheme 1. Schematic representation of the reactions carried out to isolate compounds **1-5**.

Due to is known that the nature of the dithiolene used can also affect to the formation of different compounds, a similar reaction to that before commented has been carried out between $[Fe_2(CO)_6(\mu\text{-}SC_6H_4S)]$ and the unsubstituted dithiol HSC_6H_4SH. It led to a mixture of single crystals of the main compound $[(CH_3)_3HN]_2[Fe_2(SC_6H_4S)_4]\cdot2THF$ **2** together with few crystals of $[(CH_3)_3HN]_2[Fe_2(SC_6H_4S)_4]$ **3**, upon crystallization in THF/*n*-heptane (Scheme 1).

On the other hand, the nature of the employed dithiolene can also help the formation of compounds with a different degree of solvation when the supramolecular interactions are not strong enough to clearly favours a certain crystal structure over others. It happens when a reaction similar to the previous one is carried out between $[Fe_2(CO)_6(\mu\text{-}SC_6H_4S)]$ and the unsubstituted dithiol HSC_6H_4SH.

It is also known that several diiron(tetrakis)dithiolene derivatives containing ammonium cations have been prepared by exchange of Na^+ by R_4N^+ cations in the precursor $[Na]_2[Fe_2(SRS)_4]$ or by reacting $FeCl_3$ with the dithiolene $HSRSH$ and ammonium halide. Therefore, we have decided to evaluate the role of the dithiolene $HSC_6H_2Cl_2SH$ in its reaction with $FeCl_3$ and a mixture of NaOH and Et_4NBr. After crystallization in DMF/CH$_2$Cl$_2$ of the solid obtained in this reaction, compound

[(CH$_3$CH$_2$)$_4$N]$_2$[Fe$_2$(SC$_6$H$_2$Cl$_2$S)$_3$] **4** was isolated (Scheme 1). The unexpected result obtained in this reaction, prompted us to study the role of the unsubstituted dithiol HSC$_6$H$_4$SH. Thus, in a similar reaction to that leading to **4** but using HSC$_6$H$_4$SH and crystallizing the residue in THF/*n*-heptane, compound **5** as two polymorphs, **5a** and **5b**, that show different morphology, needles and prismatic crystals, was obtained.

Fig. 1 shows a summary of building units present in each compound, altogether with the atom labelling scheme. In all cases, except compound **4**, the crystal structure is composed of dianionic entity [Fe$_2$(SC$_6$H$_2$X$_2$S)$_4$]$^{2-}$ (X= Cl or H) and cationic ammonium moieties: (CH$_3$)$_3$HN$^+$ or (CH$_3$CH$_2$)$_4$N$^+$. The dianionic entities can be described as two nearly square planar iron(III) bis(dithiolato) fragments held together through an additional Fe-S bond involving a sulfur atom from a chelating dithiolate ligand from the other iron(III) bis(dithiolato) fragment. It leads to the expected 4+1 square pyramidal geometry typical of these compounds with a FeS$_5$ coordination sphere. The equatorial Fe-S bonds (2.210-2.231 Å) are significantly shorter than the apical one (2.469-2.477 Å). These Fe-S bonds are similar to those found in other Fe(III) dithiolene derivatives [24-28]. The metal center is also displaced from the mean equatorial plane by 0.386-0.417 Å towards the apical position. No metal-metal bond is observed being the Fe···Fe distance of 3.029-3.166 Å. However, there are some evidence of close C···S contacts (3.38-3.50 Å) that could indicate some kind of intradimeric aryl/chelate stacking contacts that would reinforce the molecular structure of the [Fe$_2$(SC$_6$H$_2$X$_2$S)$_4$]$^{2-}$ dimeric entities. Selected bonds and angles are collected in Table 2.
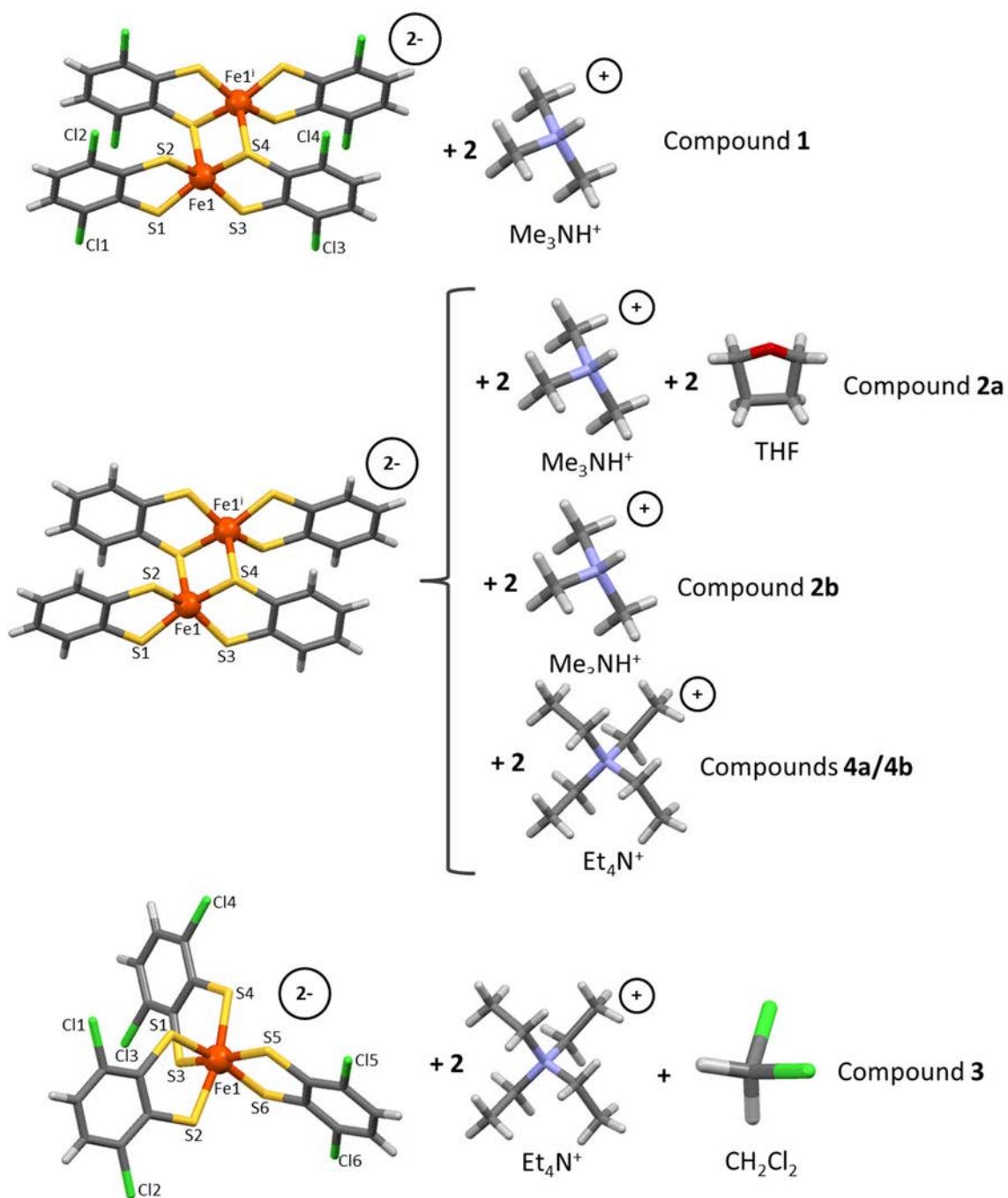
Fig. 1. Molecular building units present in each compound and the atom labelling scheme.

Table 2. Selected bonds (Å) and angles (º) for compounds **1, 2, 3, 5a and 5b**.

Compound	1	2	3	5a	5b

Fe-S1	2.2103(14)	2.2279(10)	2.2267(13)	2.2236(5)	2.2306(9)
Fe-S2	2.2116(14)	2.2215(10)	2.2368(13)	2.2211(5)	2.2230(9)
Fe-S3	2.2240(13)	2.2412(10)	2.2277(13)	2.2309(5)	2.2331(9)
Fe-S4	2.2127(14)	2.2365(10)	2.2324(12)	2.2385(5)	2.2365(9)
Fe-S4^i	2.4691(13)	2.4718(10)	2.4694(13)	2.4773(5)	2.4735(9)
Fe···Fe	3.0291(13)	3.0880(10)	3.0842(12)	3.1655(4)	3.1238(9)
Fe·· S$_4$(eq)^a	0.386	0.398	0.417	0.396	0.386
Dihedral angle^b	12.60	12.03	21.30	15.00	10.33
S1-Fe-S2	88.83(5)	88.71(4)	88.51(5)	88.996(17)	88.64(3)
S1-Fe-S3	88.44(5)	87.92(4)	88.36(5)	88.073(17)	88.16(3)
S2-Fe-S4	86.50(5)	87.28(4)	103.26(5)	87.587(16)	87.77(3)
S3-Fe-S4	89.37(5)	89.20(4)	101.91(5)	89.022(17)	89.26(3)
S1-Fe-S4	162.40(5)	164.39(4)	162.00(5)	166.828(19)	166.40(4)
S2-Fe-S3	157.34(6)	154.44(4)	154.81(5)	152.167(19)	153.69(4)
S$_{eq}$-Fe-S$_{ax}$	99.57(4)-101.86(5)	97.42(4)-101.61(4)	98.18(4)-103.26(5)	95.84(2)-104.91(2)	96.51(3)-103.66(3)
Fe-S4-Fe^i	80.44(5)	81.80(3)	81.82(4)	84.165(15)	82.93(3)

^{a}Deviation of the iron atom from the basal S4 mean plane. ^{b}Dihedral angle between the mean planes of the two dithiolate ligand chelating the same metal center.

The differences between these compounds arise from the supramolecular interactions that direct the final crystal structure. The cohesive forces in these compounds rely mostly on the electrostatic attraction between the ionic components but also on a complex combination of supramolecular interactions [29-32]. The replacement of trimethylammonium (strongly interacting through N-H···S hydrogen bonds) by tetraethylammonium, makes the crystal structure to be build up under less directional

supramolecular interactions. Under these conditions, polymorphism is promoted as it is the case compounds **5a** and **5b**.

In compound **1**, every bis[dithiolateferrate(III)] anionic entity is surrounded by two trimethylammonium cations which establish an asymmetric bifurcated N-H···S hydrogen bond (N1···S2: 3.372 Å and N1-H···S2: 142.0º; N1···S3: 3.542 Å and N1-H···S3: 132.7º). In addition, half of the dithiolate ligands are involved in double C-H···S hydrogen bonds (C···S: 3.709-3.735 Å and C-H···Cl: 141.8-173.2º) to provide 2D supramolecular sheets. These sheets are further connected through Cl···Cl contacts (Cl···Cl: 3.496 Å and C-Cl···Cl: 135.1º) to provide the final 3D supramolecular architecture (Fig. 2). These interactions are consequence of the electrostatic attraction between the positive potential of the sigma holes in Cl atoms and negative electrostatic potential located on the lone electron pairs of adjacent Cl atoms [29].
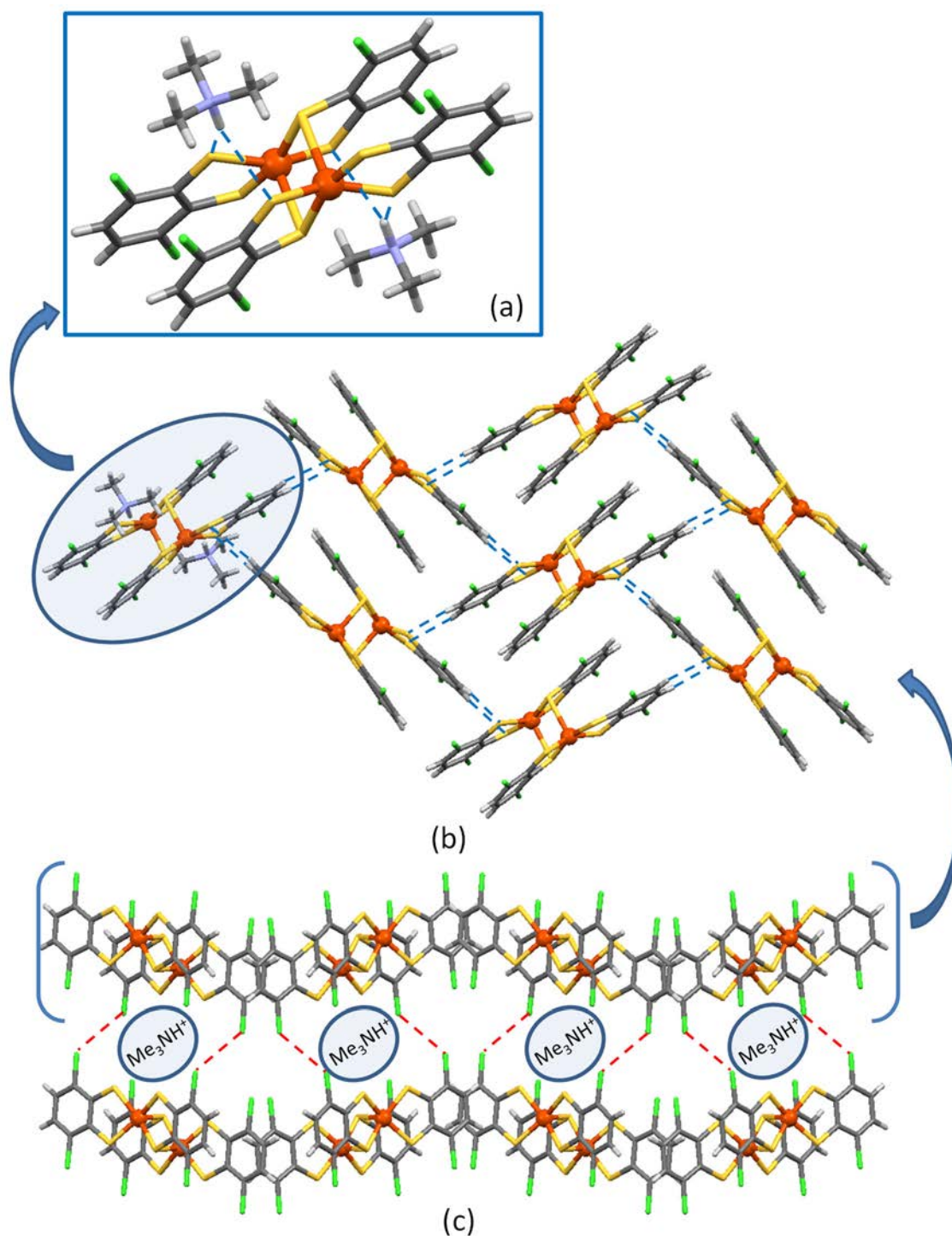
Fig. 2. Supramolecular interactions taking place in compound **1**: (a) N-H···S hydrogen bonds between the trimethylammonium cation and the bis[dithiolateferrate(III)] anionic entity. (b) C-H···S hydrogen bonds to generate a 2D supramolecular sheet, and (c) Cl···Cl contacts to generate the final 3D structure (the trimethylammonium cations have been omitted for clarity).

In compound **2** every bis[dithiolateferrate(III)] anionic entity is also surrounded by two trimethylammonium cations but each establishing a single N-H···S hydrogen bond (N1···S1: 3.278 Å and N1-H···S1: 145.6º). The anionic entities are held together by C-H···S hydrogen bonds among them to generate 1D supramolecular ribbons (Fig. 3), that are connected just by van der Waals dispersive type interactions between the supramolecular ribbons, the trimethylammonium counterions and the disordered inclusion tetrahydrofurane molecules.
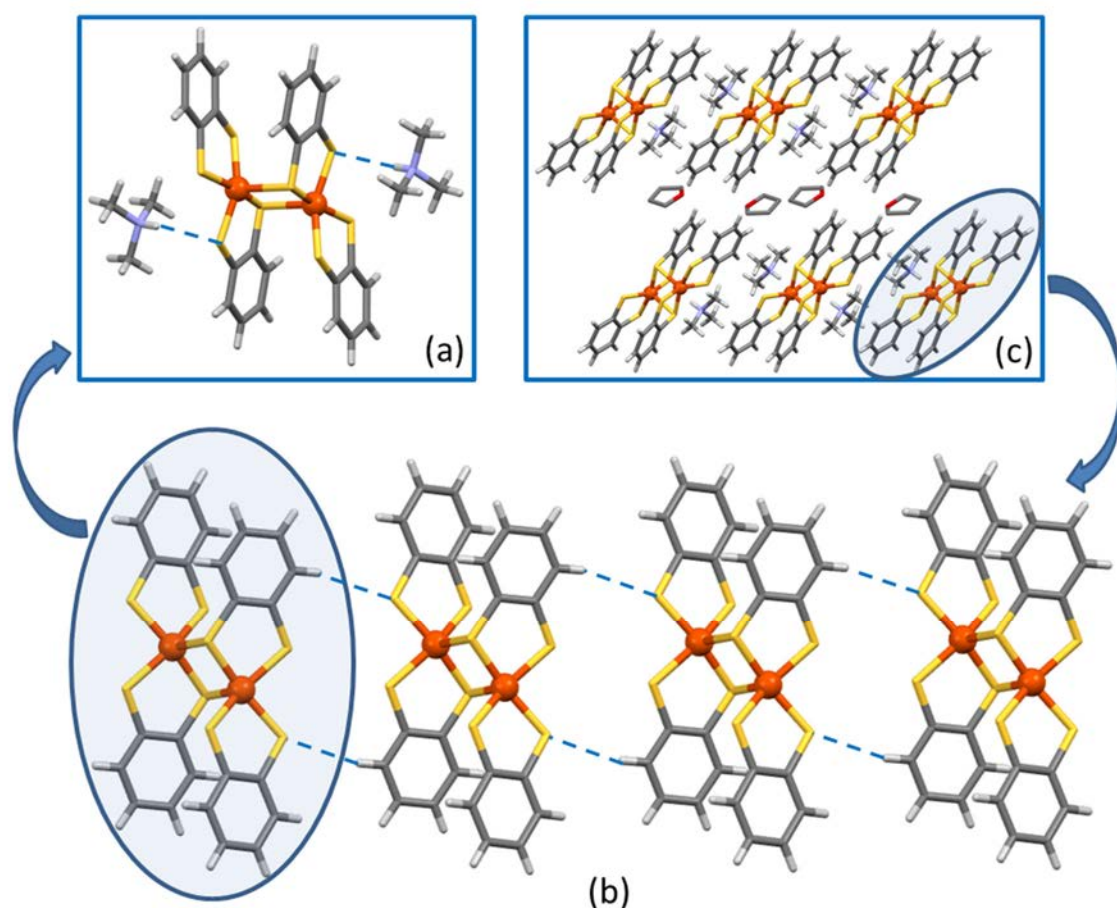

Fig. 3. (a) N-H···S hydrogen bonds between the trimethylammonium cation and the bis[dithiolateferrate(III)] anionic entity taking place in compound **2**. (b) C-H···S hydrogen bonds to generate a 1D supramolecular ribbon (the organic counterions and THF molecules have been omitted for clarity). (c) Perspective view of the crystal packing along the crystallographic *a* axis. The disorder of the tetrahydrofurane inclusion molecules has been omitted for clarity.

In compound **3**, similar N-H···S hydrogen bonds (N1···S1: 3.250 Å and N1-H···S1: 175.2º) are found. However, the anionic entities interact in a different way involving C-H···π interactions (C5···C8: 3.595 Å, C5-H···C8: 143.6º) leading to a 2D supramolecular sheet (Fig. 4). The CH/π interaction is a kind of hydrogen bond operating between a soft acid CH and a soft base π-system which plays a relevant role in the recognition process of carbohydrate-binding proteins and the secondary, tertiary, quaternary structure of proteins and other biomolecules [30, 33-34].
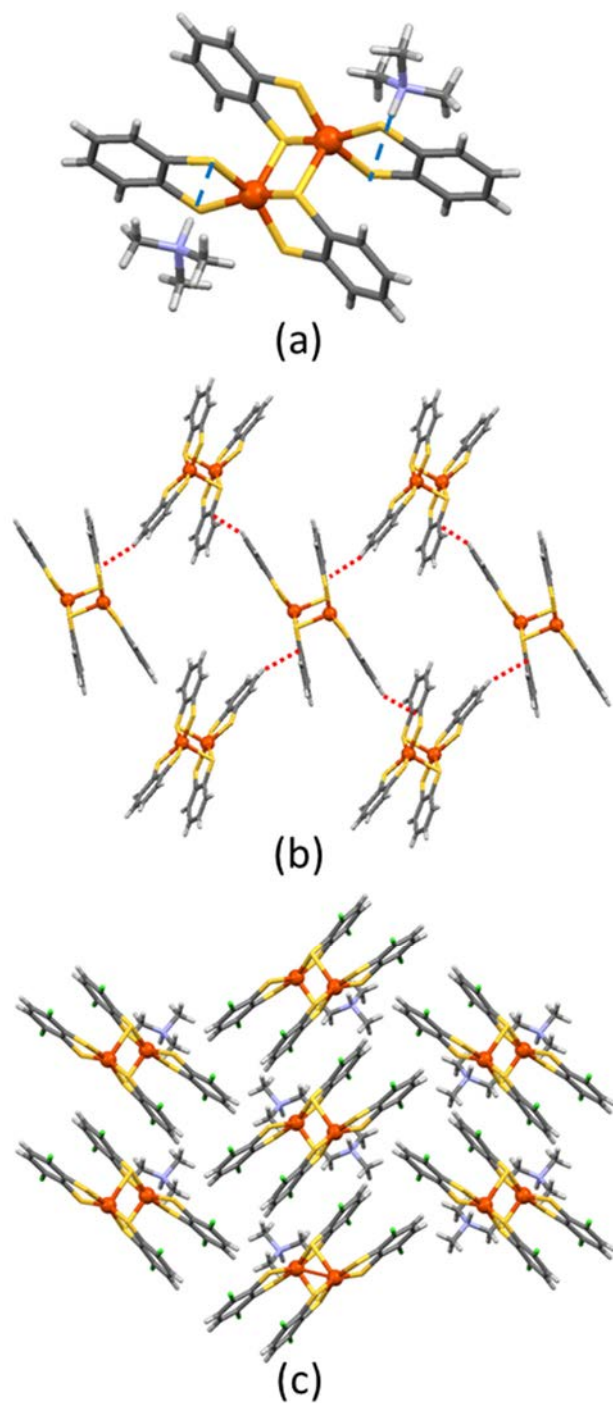
Fig. 4. (a) N-H···S hydrogen bonds (blue dashed lines) between the trimethylammonium cation and the bis[dithiolateferrate(III)] anionic entity in compound **3**, (b) C-H···π interactions (red dotted lines) providing a 2D supramolecular sheet (the organic counterions have been omitted for clarity). (c) Perspective view of the crystal packing along the crystallographic *a* axis.

The crystal structure of polymorphs **5a**/**5b** seems to be dominated by the electrostatic attraction between the ionic components. In this sense, the bis[dithiolateferrate(III)] anionic entity is surrounded by four tetraethylammonium cations in both compounds. It imposes a greater distance among the dimeric anions than in previously described compounds and it precludes any direct supramolecular interaction. Therefore, the exact positioning of the tetraethylammonium cations around the dimers rely on usually unaccounted weaker interactions such as $C_{\alpha\text{-alkyl}}$-H$\cdots$S hydrogen bonds and $C_{\alpha\text{-alkyl}}$-H$\cdots$Fe interactions. The positive charge of ammonium salts is delocalized on the α-hydrogen atoms, which are known to interact with anionic counterions through hydrogen bonding [35-36]. On the other hand, C-H$\cdots$metal interactions can be described as agostic (if H is simultaneously bond to the carbon and metal atoms: three centers two electron bond) or as weak hydrogen bond to an acceptor metal (anagostic interactions) [37]. Structural parameters observed in compound **5b** (H$\cdots$Fe: 3.077 Å, 157.9º) indicate that the observed $C_{\alpha\text{-alkyl}}$-H$\cdots$Fe interaction is best described as a weak hydrogen bonding interaction. In polymorph **5a**, the supramolecular interactions between the tetraethylammonium cation and the bis[dithiolateferrate(III)] anion comes from the $C_{\alpha\text{-alkyl}}$-H$\cdots$S hydrogen bonds. In the crystal structure of **5b**, it can be observed both $C_{\alpha\text{-alkyl}}$-H$\cdots$S and $C_{\alpha\text{-alkyl}}$-H$\cdots$Fe hydrogen bonds. It implies a slightly different arrangement of the organic cations around the anionic complex entity that gives rise to the observed polymorphism (Fig. 5). It is worthy to note that $C_{\alpha\text{-alkyl}}$-H$\cdots$S interactions can be also found in compounds **1**, **2** and **3** but due to the presence of stronger interactions they play a less relevant role on the building up of the crystal structure.
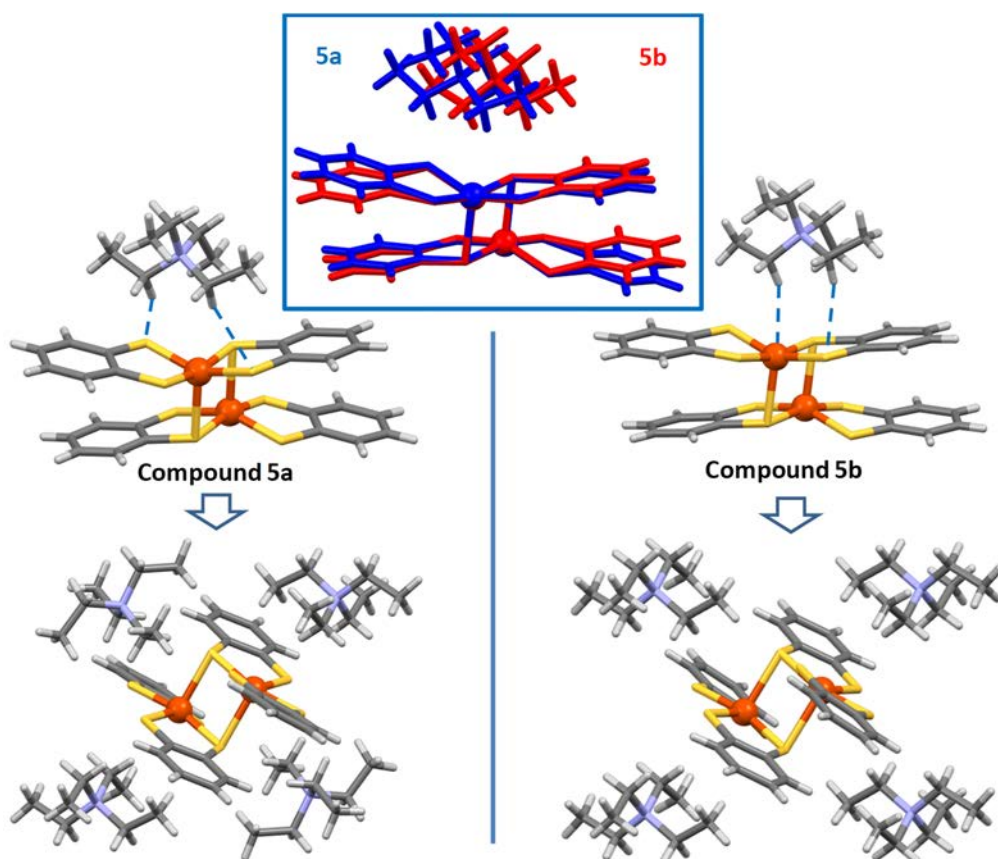
Fig. 5. Different supramolecular interactions ($C_{\alpha\text{-alkyl}}$-H$\cdots$S and $C_{\alpha\text{-alkyl}}$-H$\cdots$Fe hydrogen bonds) taking place in polymorphs **5a** and **5b**.

Finally, the X-ray diffraction studies of compound **4** confirmed the formation of an ionic compound in which the cationic charge of the tetraethylammonium cations is counter balanced by dianionic $[Fe(SC_6H_2Cl_2S)_3]^{2-}$ monomeric complex entities (Fig. 6). In the latter, the iron atom is coordinated to six sulfur atoms from three chelating dithiolate ligands yielding a distorted octahedral geometry. The formation of this entity, implying a formal IV oxidation state for the iron metal center, is not very common in the iron dithiolene chemistry, although similar compounds such as $[PPh_4]_2[Fe(mnt)_3]$ [38-40], $[PPh_3Me]_2[Fe(mnt)_3]$ [41], $[AsPh_4]_2[Fe(mnt)_3]$ [42] and $[NEt_4]_2[Fe(mnt)_3]$ [43] has been reported. Table 3 lists the Fe-S bond lengths and angles in compound **4**, which are within the range found in the above-mentioned analogous compounds.

Table 3. Selected bonds (Å) and angles (º) for compound **4**.

Fe-S1	2.2862(12)	S1-Fe-S2	85.92(4)	S2-Fe-S4	167.33(5)	S4-Fe-S5	85.96(4)
Fe-S2	2.2940(12)	S1-Fe-S3	99.73(5)	S2-Fe-S5	101.82(5)	S4-Fe-S6	106.00(5)
Fe-S3	2.2707(12)	S1-Fe-S4	84.05(4)	S2-Fe-S6	84.57(4)	S5-Fe-S6	87.05(4)
Fe-S4	2.2856(13)	S1-Fe-S5	90.22(4)	S3-Fe-S4	87.02(5)		
Fe-S5	2.2747(12)	S1-Fe-S6	169.35(5)	S3-Fe-S5	167.17(5)		
Fe-S6	2.2619(12)	S2-Fe-S3	87.06(4)	S3-Fe-S6	84.57(4)		

As in polymorphs **5a/5b** the use of the tetraethylammonium cations limits the presence of strong supramolecular interactions, relaying the crystal building on a complex mixture of $C_{aromatic}$-H···Cl, $C_{\alpha\text{-alkyl}}$-H···S, $C_{\alpha\text{-alkyl}}$-H···Cl hydrogen bonds and Cl···Cl contacts (Fig. 6). The monomeric complex anion is surrounded by four organic cations ($C_{\alpha\text{-alkyl}}$-H···S, $C_{\alpha\text{-alkyl}}$-H···Cl hydrogen bonds) but it is able to establish additional $C_{aromatic}$-H···Cl hydrogen bonds and Cl···Cl contacts with adjacent tris(dithiolate)ferrate(IV) entities. Dichloromethane molecules are also incorporated to the crystal structure interacting with the organic cations through weak $C_{\alpha\text{-alkyl}}$-H···Cl hydrogen bonds.
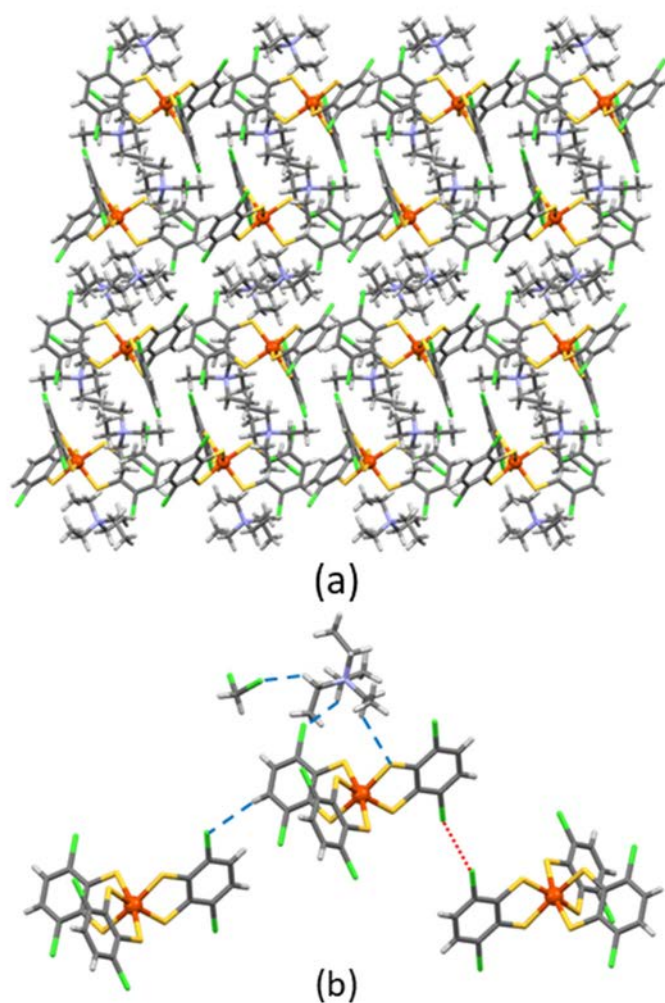
Fig. 6. (a) Crystal packing of compound **4** viewed along the crystallographic b axis. (b) Weak supramolecular interactions present in this compound: $C_{\alpha\text{-alkyl}}$-H$\cdots$S, $C_{aromatic}$-H$\cdots$Cl and $C_{\alpha\text{-alkyl}}$-H$\cdots$Cl hydrogen bonds (blue dashed lines) and Cl$\cdots$Cl contacts (red dotted line).

4. Conclusions

The complete substitution of CO by $^-$SRS$^-$ (R= $C_6H_2Cl_2$ or C_6H_4) ligands in the precursor $[Fe_2(CO)_6(\mu\text{-}SC_6H_2X_2S)]$ (X = Cl or H) complex give rises to the dithiolene derivatives $[(CH_3)_3HN]_2[Fe_2(SC_6H_2X_2S)_4]$. Additionally, two different compounds $[(CH_3CH_2)_4N]_2[Fe(SC_6H_2Cl_2S)_3]\cdot CH_2Cl_2$ or $[(CH_3CH_2)_4N]_2[Fe_2(SC_6H_4S)_4]$ have been obtained in the reactions of $HSC_6H_2X_2SH$ (X=Cl or H), NaOH, $(CH_3CH_2)_4NBr$ and

FeCl$_3$·6H$_2$O depending on the presence or absence of donor substituent atoms in the dithiolene ring used.

The analysis of the crystal structures of these novel compounds show that they consist of dimeric dianionic entities [Fe$_2$(SC$_6$H$_2$X$_2$S)$_4$]$^{2-}$ (X= Cl or H) and (CH$_3$)$_3$HN$^+$ or (CH$_3$CH$_2$)$_4$N$^+$. The dimeric entities show two nearly square planar iron(III) bis(dithiolato) fragments held together through by apical Fe-S bonds. The differences between these compounds arise from the supramolecular interactions. These networks are mainly based on the electrostatic attraction between the ionic components but also a complex combination of supramolecular interactions, such as C-H···π interactions, C$_{α-alkyl}$-H···S and C$_{α-alkyl}$-H···Fe hydrogen bonds, Cl···Cl interactions; but in which N-H···S hydrogen bonds play a key role. Thus, the replacement of trimethylammonium (strongly interacting *via* N-H···S bonds) by tetraethylammonium, produces a remarkable effect in the crystal structure to be build up under less directional supramolecular interactions then giving rise to polymorphism as it is the case compounds **5a** and **5b**.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/******

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Appendix A. Supplementary data

Table S1. Hydrogen bonds in compounds **2**, **5a** and **5b**.

Compound	D	H	A	dDH(Ǻ)	dHA(Ǻ)	dDA(Ǻ)	aDHA(º)
	C13	H13B	S1	0.98	2.89	3.549(7)	125.1
	C2	H2	S4	0.95	2.90	3.827(6)	164.3
	N1	H1	S4	1.00	2.94	3.681(6)	131.8
	N1	H1	S1	1.00	2.96	3.528(5)	117.0
	N1	H1	S1	1.00	2.43	3.276(5)	141.7
	C13	H13B	S3	0.98	2.99	3.894(8)	153.2
	C13	H13B	S1	0.98	2.89	3.549(7)	125.1
2	C2	H2	S4	0.95	2.90	3.827(6)	164.3
	C13	H13B	S3	0.98	2.99	3.894(8)	153.2
	C13	H13B	S1	0.98	2.89	3.549(7)	125.1
	C2	H2	S4	0.95	2.90	3.827(6)	164.3
	N1	H1	S4	1.00	2.94	3.681(6)	131.8
	N1	H1	S1	1.00	2.96	3.528(5)	117.0
	N1	H1	S1	1.00	2.43	3.276(5)	141.7
	C14	H14C	S1	0.98	3.02	3.652(8)	123.3
	C13	H13A	S2	0.99	2.91	3.849(2)	158.8
	C15	H15A	S3	0.99	2.96	3.878(2)	154.8
5a	C17	H17A	S2	0.99	2.79	3.564(3)	135.9
	C17	H17B	S4	0.99	2.87	3.595(3)	130.9
	C18	H18C	S2	0.98	2.97	3.892(3)	156.5
	C19	H19A	S4	0.99	2.97	3.902(2)	157.6
5b	C19	H19A	S1	0.99	2.91	3.834(4)	155.5
	C20	H20B	S2	0.98	2.92	3.877(4)	166.2