



Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:
This is an **author produced version** of a paper published in:

Crystal Growth and Design 16.9 (2016): 5466-5478

DOI: <https://doi.org/10.1021/acs.cgd.6b00921>

Copyright: © 2016 American Chemical Society

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription

Structural Diversity of Compounds Based on Iron-Dithiolene with Sodium or Potassium Complexes

Oscar Castillo,[‡] Esther Delgado,^{#,} Diego Hernández,[#] Elisa Hernández,[#] Avelino
Martín,[§] Ignacio Martín,[#] Félix Zamora[#]*

[‡]Departamento de Química Inorgánica. Universidad del País Vasco. Apartado 644, e-48080 Bilbao (Spain). [#]Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049 Madrid (Spain). [§]Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871, Alcalá de Henares (Spain).

KEYWORDS: dithiolene, iron dithiolene, coordination polymers, sodium complexes, potassium complexes.

ABSTRACT

A series of iron dithiolene compounds with sodium or potassium complexes have been prepared by direct reactions. Their structures consist of coordination polymers (CPs) of different dimensionalities or molecular compounds depending on the nature of the iron precursor, the presence or not of a donor substituent in the aromatic ring of the dithiolene ligand and the amount of water molecules present during the crystallization. Since all these compounds are based on the combination of cationic alkaline and anionic iron-dithiolene entities that connect each other by coordination bonds, in order to favor local electroneutrality the structures obtained show that charged entities with similar charge/size ratio pack more effectively. The flexibility of the potassium coordination environment seems to facilitate the structural diversity found for this family of compounds.

Introduction

1,2-dithiolene transition metal derivatives are a subject of research interest from different points of view, such as catalysis, biology, material science and crystal engineering among others.¹⁻¹⁶ Coordination polymers (CPs) of Group 10 metal dithiolene containing Na or K complexes as counter cations bearing bulky ligands such as crown ethers, are known.¹⁷⁻²⁰ It has also been reported the synthesis of copper and gold-dithiolene polymers with different dimensionality depending on the nature of the coordinative solvents^{13,21} around the Na or K cations.²² However, to the best of our knowledge examples with thf as ligands have only been previously reported by us.²³⁻²⁴ Thus, we have described the preparation of the monodimensional coordination polymer

(1D-CP) $\{[K_2(\mu-H_2O)_2(thf)_4][Fe_2(SC_6H_2Cl_2S)_4]\}_n$ from the reaction between $[Fe_2(CO)_6(\mu-SC_6H_2Cl_2S)]$ and K_2CO_3 in the presence of $HSC_6H_2Cl_2SH$.²³ This compound represents the first CP containing dithiolene entities bridging by “s” group metal complexes. Remarkable this new material shows interesting electrical properties including two electrical reversible transitions and electrical bi-stability.²³ Following this research project, we have recently reported a series of 1D-CPs containing $[Fe_2(SC_6H_2Cl_2S)_4]^{2-}$ entities connected through alkaline metal complexes formed by reaction between $FeCl_3 \cdot 6H_2O$ and $HSC_6H_2Cl_2SH$ in the presence of alkaline bases.²⁴ We have observed that in the potassium case, two 1D-CPs containing different cation complexes are obtained, depending on the iron precursor used.²³⁻²⁴ On the base of these results, we have carried out studies in order to know if this behavior is also observed in other alkali metal such as sodium. On the other hand, in the CPs before commented, the alkaline cations are linked towards the chloride substituents of the aromatic rings of the dithiolene ligands of the $[Fe_2(SC_6H_2Cl_2S)_4]^{2-}$ entities to afford to 1D-CPs. Taking into account this fact, we have evaluated if the absence of donor substituents in the ring of the dithiolene $-SC_6H_4S-$ may favor the formation of 2D- or 3D-CP instead by coordination of the alkaline metals to sulfur atoms of the $[Fe_2(SC_6H_4S)_4]^{2-}$ entities of different chains. Therefore, in this work we report the synthesis of the coordination polymers $\{[Na(thf)_6][Na_2(\mu-H_2O)_2(H_2O)_2][Fe_3(SC_6H_2Cl_2S)_6] \cdot (C_4H_8O)\}_n$ **1**, $\{[M_2(thf)_4][Fe_2(SC_6H_4S)_4]\}_n$ [$M = Na$ (**4**), K (**5**)], $\{[Na_2(\mu-H_2O)_4(H_2O)_2(thf)_2][Fe_2(SC_6H_4S)_4] \cdot H_2O\}_n$ **7**, $\{[K_2(thf)_2(\mu-H_2O)_2][Fe_2(SC_6H_4S)_4]\}_n$ **8**, the neutral tetrametallic molecules $[(thf)_4Na][Fe_2(SC_6H_2Cl_2S)_4][Na(thf)_4]$ **3** and $[(thf)_3Na][Fe_2(SC_6H_4S)_4][Na(thf)_3]$ **6a** and **6b**, as well as the ion pair derivative $[Na(thf)_6][Fe(SC_6H_2Cl_2S)_2]$ **2**.

Experimental Section

Materials and Methods

All manipulations were carried out under argon atmosphere. Solvents are commercial available, and dried, when they were required, using standard methods. $\text{HSC}_6\text{H}_2\text{Cl}_2\text{SH}$ and $\text{HSC}_6\text{H}_4\text{SH}$ supplied by Aldrich Co., $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, K_2CO_3 by Scharlau, KOH and NaOH by Panreac and Carlo Erba respectively. $[\text{Fe}_2(\text{CO})_6(\mu\text{-SRS})]$ ($\text{R}=\text{C}_6\text{H}_2\text{Cl}_2$ or C_6H_4) were prepared according to the modified published procedure.²⁵ Elemental analyses were performed on an LECO CHNS-932 Elemental Analyzer.

X-ray structure analysis of 1-8. Single crystals of compounds **1-8** were covered with a layer of a viscous perfluoropolyether (Fomblin®Y), mounted on a cryoloop (**2, 8**) or a MicroMount (**1, 3-7**) with the aid of a microscope, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets for complexes **2** and **8** were collected at 200 K on a Bruker-Nonius Kappa CCD diffractometer, while the data sets for compounds **1, 3** and **6a** were collected at 100 K, **6b** and **7** at 110 K and **4** and **5** at 200K on a Bruker Kappa Apex II diffractometer. All the diffractometers were equipped with Oxford Cryostream units and with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using the SIR92 program²⁶ and refined by full-matrix least-squares on F^2 for all reflections (SHELXL97).²⁷ All calculations were performed with the WINGX crystallographic software package.²⁸ All non-hydrogen atoms, except those involved in the disorder of the thf molecules in compounds **1** and **2**, were refined anisotropically. The hydrogen atoms were included in geometrically calculated positions and refined isotropically according to the riding model, except those belonging to the water molecules of compound **7** whose coordinates were freely refined but using a thermal isotropic displacement parameters related to that of the

parent oxygen atom. Crystal data and details of the refinement parameters of the compounds are given in Table 1. CCDC 1485047-1485055 contain the supplementary crystallographic data for this paper.

Synthesis

$\{[Na(thf)_6][Na_2(\mu-H_2O)_2(H_2O)_2][Fe_3(SC_6H_2Cl_2S)_6] \cdot (C_4H_8O)\}_n$ **1**. $[Fe_2(CO)_6(\mu-SC_6H_2Cl_2S)]$ (100 mg, 0.2 mmol) and $HSC_6H_2Cl_2SH$ (130 mg, 0.6 mmol) were added to a suspension of $Na_2CO_3 \cdot 10H_2O$ (58 mg, 0.2 mmol) in thf (10 mL) and the mixture kept under stirring for 16 h at room temperature. Then, a change from red to dark brown was observed. Afterwards, the solvent was removed under vacuum and the residue washed with hexane. Suitable crystals of compound **1** were formed by crystallization in wet thf/*n*-heptane (2:3) (120 mg; 44.1 %). Additionally, a few crystals of compound $[Na(thf)_6][Fe(SC_6H_2Cl_2S)_2]$ **2** were obtained after kept the filtrate at -20 ° C for a few days. Anal. Calcd. (Found) for $C_{44}H_{28}Cl_{12}Fe_3Na_3O_6S_{12}$ (**1**-5thf): C, 30.95 (31.10); H, 2.13 (1.66); S, 22.54 (22.64). Anal. Calcd. (Found) for $C_{36}H_{52}Cl_4FeNaO_6S_4$ (**2**): C, 46.51 (46.66); H, 5.64 (5.31) and S, 13.77 (13.89).

$[(thf)_4Na][Fe_2(SC_6H_2Cl_2S)_4][Na(thf)_4]$ **3**. The reaction was carried out following the above procedure, but using dried thf/*n*-heptane (1/1) in the crystallization process. In these conditions crystals of compound **3** were obtained (170 mg, 35.0 %). Anal. Calcd. (Found) for $C_{48}H_{56}Cl_8Fe_2Na_2O_6S_8$ (**3**- 2thf): C, 39.60 (40.41); H, 3.72 (3.96); S, 17.42 (17.98).

$\{[M_2(thf)_4][Fe_2(SC_6H_4S)_4]\}_n$ [$M = Na$ (**4**), $M = K$ (**5**)]. The reactions were carried out following the procedure used for preparing compound **1** but using $[Fe_2(CO)_6(\mu-SC_6H_4S)]$ instead and K_2CO_3 for compound **5**. Polymers **4** and **5** were obtained by crystallization in wet thf/*n*- heptane (1/1). Compound **4** (trace amounts) and compound

5 (170 mg, 45.4 %). Anal. Calcd. (Found) for $C_{40}H_{48}Fe_2K_2O_4S_8$, **5**: C, 46.23 (46.64); H, 4.66 (4.62) and S, 24.68 (23.70).

$[(thf)_3Na][Fe_2(SC_6H_4S)_4][Na(thf)_3]$ **6a** and **6b**. The reaction was carried out following the same procedure above indicated for compound **4**, but using dried thf/*n*-heptane (1/1) instead. Then, a mixture of two polymorphs $[(thf)_3Na][Fe_2(SC_6H_4S)_4][Na(thf)_3]$ **6a** and **6b** were obtained. Compound **6a** (188 mg, 34.1 %) and compound **6b** (40 mg, 7.2 %). Anal. Calcd. (Found) for $C_{48}H_{64}Fe_2Na_2O_6S_8$, **6**: C, 50.08 (49.22); H, 5.60 (5.00); S, 22.28 (21.01).

$\{[Na_2(\mu-H_2O)_4(H_2O)_2(thf)_2][Fe_2(SC_6H_4S)_4] \cdot H_2O\}_n$ **7**. The reaction was carried out following the same procedure above indicated for compound **4**, but using wet thf/*n*-heptane (1/1) and some additional drops of water. Then, crystals of polymer $\{[Na_2(\mu-H_2O)_4(H_2O)_2(thf)_2][Fe_2(SC_6H_4S)_4] \cdot H_2O\}_n$ **7** were obtained (130 mg, 53.1 %). Anal. Calcd. (Found) for $C_{32}H_{46}Fe_2Na_2O_9S_8$, **7**: C, 38.87 (37.50); H, 4.69 (4.49); S, 25.94 (24.32).

$\{[K_2(thf)_2(\mu-H_2O)_2][Fe_2(SC_6H_4S)_4]\}_n$ **8**. 1,2-HSC₆H₄SH (157 mg, 127 μ l, 1.10 mmol) was treated with an aqueous solution (10 mL) of KOH, Then, FeCl₃·6H₂O (150 mg, 0.55 mmol) in 10 mL of ethanol/water (1:1) was slowly added. The mixture was stirred at room temperature for 30 min. The solvent was removed in vacuum, yielding a solid residue which was washed several times with water and *n*-heptane. Suitable crystals for X-ray analysis of compound $\{[K_2(thf)_2(\mu-H_2O)_2][Fe_2(SC_6H_4S)_4]\}_n$ **8** (230 mg, 55.8%) were obtained from a solution of wet thf/*n*-heptane (1:1). Anal. Calcd. (Found) for $C_{35.5}H_{44}Fe_2K_4O_4S_8$, (**8** + $\frac{1}{2}$ heptane): C, 43.46 (42.96); H, 4.52 (4.23); S, 26.15 (24.32).

Results and Discussion

We have previously reported on a series of different CPs based on dithiolenes with iron and potassium that have been isolated depending on the iron precursors and experimental crystallization conditions. These CPs show interesting structures and physical properties.^{23, 24} In order to know whether this behavior is also exhibited for another alkaline cations, we have now carried out the reaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{H}_2\text{Cl}_2\text{S})]$ in the presence of $\text{HSC}_6\text{H}_2\text{Cl}_2\text{SH}$ and Na_2CO_3 (Scheme 1). Further crystallization of the residue by diffusion of wet *n*-heptane in a thf solution, yielded to suitable crystals for X-ray diffraction studies. The crystal structure of compound $\{[\text{Na}(\text{thf})_6][\text{Na}_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2][\text{Fe}_3(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_6] \cdot (\text{C}_4\text{H}_8\text{O})\}_n$ **1** (Figure 1) confirms the formation of a Na-Fe 1D-CP which is different in structure to that obtained in the similar reaction but using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ instead.²⁴

Interestingly, the crystal structure of all compounds share the common basic structural building block feature of square planar $[\text{Fe}(\text{SC}_6\text{H}_x\text{Cl}_{4-x}\text{S})_2]^-$ ($X=2$ or $X=4$) entities that can pile up through additional somewhat longer Fe-S bonds to generate different nuclearity complex entities (monomers, dimers and trimers). The negative charge of these anionic complexes is counterbalanced by means of alkaline ions coordinated to a variable number of thf and/or water molecules. Depending on the saturation of the coordination sphere around the alkaline cation, we can get the cationic entities coordinatively bonded to the anionic $[\text{Fe}(\text{SC}_6\text{H}_x\text{Cl}_{4-x}\text{S})_2]_n^{n-}$ ($X=2$ or $X=4$) core or as independent entities.

The crystal structure of compound **1** consists of trianionic entities $[\text{Fe}_3(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_6]^{3-}$ linked by disodium species $[\text{Na}_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]^{2+}$ through Na-Cl and Na-S bonds

yielding to a mononegative chain in which sodium complexes $[\text{Na}(\text{thf})_6]^+$ act as counterions (Figure 1). The packing of these entities left space for the inclusion of a non-coordinated thf molecule. Each iron atom shows the expected 4+1 square pyramidal geometry typical of most of the iron bis(dithiolato) compounds. In fact, a search at the CSD²⁹ on iron complexes involving S,S'-chelating ligands showed a preference for a square pyramid geometry (46 hits) over coordination numbers 6 (7 hits) or 4 (9 hits). At this point, it is worthy to note that the central iron of the trinuclear fragment, instead of adopting a 4+2 elongated octahedral geometry, is disordered into two symmetry related position with its more common 4+1 square pyramid geometry. As usually for square pyramid coordination geometries, the metal center is significantly displaced from the equatorial mean plane towards the apical position: 0.357 Å for Fe1 and 0.338 Å for Fe2. The metal...metal distance is 3.146 Å. The dihedral angle between the mean planes of the dithiolene ligands chelated to the metal centers placed at the end of the trimer is 6.9°, but the two dithiolene ligands coordinated to the central one adopt a non-coplanar parallel arrangement with a distance between the mean planes of 0.643 Å. There are some close S...C contacts between adjacent dithiolenes that could also play a relevant role in stabilizing the trinuclear $[\text{Fe}_3(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_6]^{3-}$ core.

All the Fe-S distances and angles are in the range found in other similar compounds (Fe-S_{equatorial}: 2.20-2.25 Å and Fe-S_{apical}: 2.45-2.50 Å (Table 2).^{25, 30-34} On the other hand, the dicationic Na_2^{2+} entities linked to the anionic ones as well as the outer monocationic $[\text{Na}(\text{thf})_6]^+$ exhibit a pseudo-octahedral geometry. The Na-O distances agree with similar complexes previously reported.^{23, 24}

In the same reaction a few crystals of compound $[\text{Na}(\text{thf})_6][\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]$ **2** were also isolated and X-ray characterized. As can see in Figure 2, compound **2** consists of

discrete $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ anions and $[\text{Na}(\text{thf})_6]^+$ cations. In the anion, the iron atom exhibits a square-planar coordination environment with four very similar Fe-S bonds (2.17-2.19 Å). This geometry is rather unusual for the iron dithiolene compounds due to the high tendency of the anionic $[\text{Fe}(\text{SRS})_2]^-$ species to dimerize to yield to $[\text{Fe}_2(\text{SRS})_4]^{2-}$ entities which exhibit a square-planar pyramidal geometry. In the cation, the sodium atom shows an octahedral geometry by coordination to the oxygen atoms of six thf ligands.

When we compared the crystal structure of the previously reported 1D-CP $\{[\text{Na}_2(\mu\text{-H}_2\text{O})_2(\text{THF})_2][\text{Fe}_2(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_4]\}_n$ ²⁴ with those exhibit for compounds $\{[\text{Na}(\text{thf})_6][\text{Na}_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2][\text{Fe}_3(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_6]\cdot(\text{C}_4\text{H}_8\text{O})\}_n$ **1** and $[\text{Na}(\text{thf})_6][\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]$ **2**, we considered that compound **2** could be an intermediate in the reaction formation of **1**. In order to get more inside this process we wanted to evaluate the crystallization process of a mixture of compound **2** and $\{[\text{Na}_2(\mu\text{-H}_2\text{O})_2(\text{THF})_2][\text{Fe}_2(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_4]\}_n$ ²⁴ in wet THF/n-heptane in order to verify the formation of compound **1**. However since this evaluation needs compound **2** and the latter reaction produces only few crystals of this material, we have first tried to find an alternative way to isolate **2** in higher yield. Then, taking into account that compound **2** does not contain H_2O , we changed the crystallization conditions using dried solvents instead. Surprisingly, a new tetrametallic compound $[(\text{thf})_4\text{Na}][\text{Fe}_2(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_4][\text{Na}(\text{thf})_4]$ **3** is obtained instead (Figure 3).

This new entity consist of a central $[\text{Fe}_2(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_4]^{2-}$ core showing the common 4+1 square pyramid coordination geometry for iron(III) dithiolene complexes. The equatorial Fe-S distances are significantly shorter (2.21-2.24 Å) than the apical one (2.50 Å). The metal center is also displaced 0.38 Å from the mean equatorial plane in

the direction of apical ligand. The metal...metal distance inside the iron dinuclear fragment is 3.110 Å. The mean planes of the dithiolene ligands coordinated to the same metal center are not completely parallel, being the dihedral angle 4.9°. There are also some evidence of weak π - π stacking interactions (C...S distance: 3.400 Å).

Two sodium cations are attached to the edges of the iron dinuclear fragment through its linkage to S2 sulfur atom. The coordination sphere of the sodium is completed by four thf molecules, leading to a bipyramid trigonal geometry. This geometry is not the more usual octahedral one for sodium cations, although some examples with five coordination number have been reported^{21,35} but it can be explained on the basis of the greater steric hindrance of the sulphur atom. The overall crystal packing of these neutral entities is achieved by means of unspecific weak van der Waals interactions and relatively short Cl...Cl intermolecular contacts (3.471 Å).

At this point, we decided to employ the carbonyl compound $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{H}_4\text{S})]$ as precursor in the synthesis of analogous alkali-iron entities. In compound **1**, as in similar 1D-CPs alkali-iron previously reported by us,²⁴ the chloro substituent of the aromatic ring play a crucial role anchoring the sodium cations to the iron-dithiolene core. Therefore, we expect that its absence would lead to new structural motifs for the alkali-iron-dithiolene system. We assume that the lack of chloro substituents would make necessary to employ more dithiolene groups to complete the coordination sphere of the cations and as a consequence an increase of the alkali-iron-dithiolene system dimensionality is expected. In this sense, the reactions carried out between $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{H}_4\text{S})]$ and M_2CO_3 (M=Na or K) in the presence of $\text{HSC}_6\text{H}_4\text{SH}$ followed by further crystallization of the residue in wet thf/*n*-heptane gave rise to the isolation of the new CPs **4** and **5**, respectively.

The crystal structure of compound **4** is based on an 1D-CP of $\{[\text{Na}_2(\text{thf})_4][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]\}_n$ chains in which $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]^{2-}$ fragments are held together through sodium cations coordinated to the sulfur atoms of consecutive diiron entities (Figure 4). The dinuclear iron fragments show a close resemblance to that described for compound **3**: elongated square pyramid geometry with apical Fe-S distances (2.44 Å) longer than those of the equatorial plane (2.22-2.23 Å), metal center displaced 0.385 Å from the equatorial mean plane, dihedral angle between the dithiolene ligands coordinated to the same metal center of 8.0 °, Fe...Fe distance of 3.149 Å and π - π stacking contacts (C...S: 3.433 Å). Every consecutive diiron fragments are connected by means of two sodium cations showing a distorted octahedral coordination geometry sphere that involves four sulfur atoms from two $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]^{2-}$ fragments and two thf molecules, in a *cis* arrangement.

Compound **5** consist also of 1D-CP $\{[\text{K}_2(\text{thf})_4][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]\}_n$ with similar structural features of those found for compound **4**, but replacing sodium atoms by potassium ones (Figure 5). However, the bigger size of potassium makes the cations and the thf molecules coordinated to them to be more separated from the central axis of the 1D CP chain and also to exhibit a slightly different external shape (Figure 6). It implies that the thf molecules are less hindrance and more available to establish supramolecular interactions. In fact, the relative displacement between adjacent chains that leads to a different 3D crystal structure in **4** and **5** are due to the contacts involving the thf molecules and dithiolene ligands which are present in **4** but not in **5**.

The same synthetic procedure but using dried solvents in the crystallization process, yield to a mixture of two polymorphs of a new tetrametallic compounds $[(\text{thf})_3\text{Na}][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4][\text{Na}(\text{thf})_3]$ (**6a** and **6b**). Both polymorphs consist of Na_2Fe_2

tetrametallic entities similar to those found in compound **3**. The differences come basically from the sodium coordination environment. Although the Na⁺ are five coordinated in both compounds, **6a** and **6b** show just three thf ligands coordinated to the sodium (O₃S₂ donor set) while in **3** the coordination environment is completed with four thf molecules (O₄S donor set). This difference is attributed to the absence of substituents in the aromatic ring of the dithiolenes that allow a stronger interaction of the cations with these sulfur containing ligands.

The weakness and less directional supramolecular interactions between these Na₂Fe₂ tetrametallic discrete entities allow the presence of two different packing schemes that correspond to the polymorphs **6a** and **6b** (Figure 8). In compound **6a**, the [(thf)₃Na][Fe₂(SC₆H₄S)₄][Na(thf)₃] entities are held together just by weak van der Waals interactions involving the thf and dithiolene ligands. However, in compound **6b** they form infinite supramolecular chains based on slightly stronger hydrogen bonding interactions between the aromatic hydrogen atoms and the sulphur substituent of adjacent dithiolenes. In fact, polymorph **6b** is slightly denser than **6a** (1.463 g/cm³ vs 1.441 g/cm³).

As far as we isolated different Na-Fe compounds depending on the crystallization conditions, we decided to modulate the amount of water to test its effect on the coordination environment around the sodium. Thus, {[Na₂(μ-H₂O)₄(H₂O)₂(thf)₂][Fe₂(SC₆H₄S)₄]·H₂O}_n **7** was isolated from a diffusion of *n*-heptane into a thf solution of the residue of the reaction between [Fe₂(CO)₆(μ-SC₆H₄S)], Na₂CO₃ and HSC₆H₄SH, that contains a few H₂O drops (*ca.* 2 %). The crystal structure of compound **7** indicates that the coordination environment around the sodium cation is now dominated by the presence of a considerable amount of water molecules that

determines the formation of a new 1D-CP in which the Na^+ cations are joined by double bridging H_2O ligands yielding to a positively charged *zig-zag* chain (Figure 9). The octahedral environment of the sodium cations is completed by a terminal water molecule and a thf molecule. The positive charge of the 1D-CP of Na^+ cations is counterbalanced by the previously described dianionic $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]^{2-}$ discrete entities. The water molecules play also a key role in the final 3D crystal structure of this compound as the most relevant supramolecular interactions, apart from the electrostatic interactions between the cationic and anionic entities, are the hydrogen bonds involving the coordination and crystallization water molecules and the sulfur atoms of the dithiolene ligands.

Finally, the reaction carried out between $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HSC}_6\text{H}_4\text{SH}$ in the presence of KOH leads to the 2D-CP $\{[\text{K}_2(\text{thf})_2(\mu\text{-H}_2\text{O})_2][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]\}_n$ **8** (Figure 10). The 2D-CP layer contains the usual $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]^{2-}$ entities that are held together through centrosymmetric $[\text{K}_2(\mu\text{-OH}_2)_2(\text{thf})_2]^{2+}$ fragments in which the octahedral K^+ cations are also coordinated to three sulfur atoms from three adjacent iron dinuclear fragments in *mer*-arrangement. In this sense, there are two crystallographically independent dithiolene ligands with the same $\mu_3\text{-}\kappa\text{S},\kappa\text{S}'_2:\kappa\text{S}:\kappa\text{S}'$ coordination mode but linking $2\text{Fe}+1\text{K}$ and $1\text{Fe}+2\text{K}$, respectively (Figure 11).

Unfortunately, we have not been able to grow suitable crystals for X-ray diffraction studies of the compound obtained from a similar reaction using NaOH instead.

Conclusions

In summary, the results herein reported suggest that the nature of the iron precursor affects to the structural type of these compounds, however, it is worth to note that the

amount of water molecules present during the crystallization of these compounds plays a key role on the final crystal structure. All these compounds are built up by the combination of alkaline cations and anionic iron-dithiolene entities that connect each other by coordination bonds to form coordination polymers of different dimensionalities. Therefore, it is reasonable to assume, in order to favor local electroneutrality, which charged entities with similar charge/size (van der Waals) ratio would pack more effectively. This reasoning can be exemplified in compound **2**, as it contains both monomeric $[\text{Na}(\text{thf})_6]^+$ cations and $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ anions. The remaining compounds containing dimeric or trimeric Fe-dithiolene entities/fragments contain alkaline dimeric entities or are coordinatively bound to the Fe-dithiolene fragment. It provides high positive charge density entities that rapidly counterbalance the relatively high negative charge of the iron-dithiolene polynuclear entities. In order to provide these highly charged alkaline entities/fragments water molecules are an easy tool as they usually act as bridging ligands when interacting with alkaline cations.

On the other hand, compound **1** shows an unprecedented structure based on a trimeric $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]_3^{3-}$ moieties being a clear example that iron-dithiolene entities with nuclearities higher than two are also attainable. In this sense, the use of other metal cations with larger charge/size ratio seems to be a good option to generate more extended anionic iron-dithiolene entities. In order to better understand this fact, we have to notice that the $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]_n^{n-}$ anionic entities grow in a linear fashion and, due to the ionic nature of most of the resulting compounds, it implies that the positive charge density of the s-block complexes must match that of the $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]_n^{n-}$ anionic complexes, but it applies not only to volume but also to every direction within the crystal including the growing direction of the iron-dithiolene polynuclear complexes. Having in mind the final goal of achieving an infinite chain of iron-dithiolene complexes, it would imply a great

positive charge density along the growing direction of the chain to counterbalance its negative charge. It is quite difficult to achieve through monovalent alkaline complexes as it would require a pile up of cationic complexes of repulsive nature, but it can be easier achieved by means of high charge density divalent metal complexes, as depicted in Scheme 2.

As a result we may conclude that the alkaline metals are suitable linkers to held together iron dithiolene derivatives bearing or not donor substituent in the aromatic ring, in order to prepare CPs of different dimensionality and large structural variety.

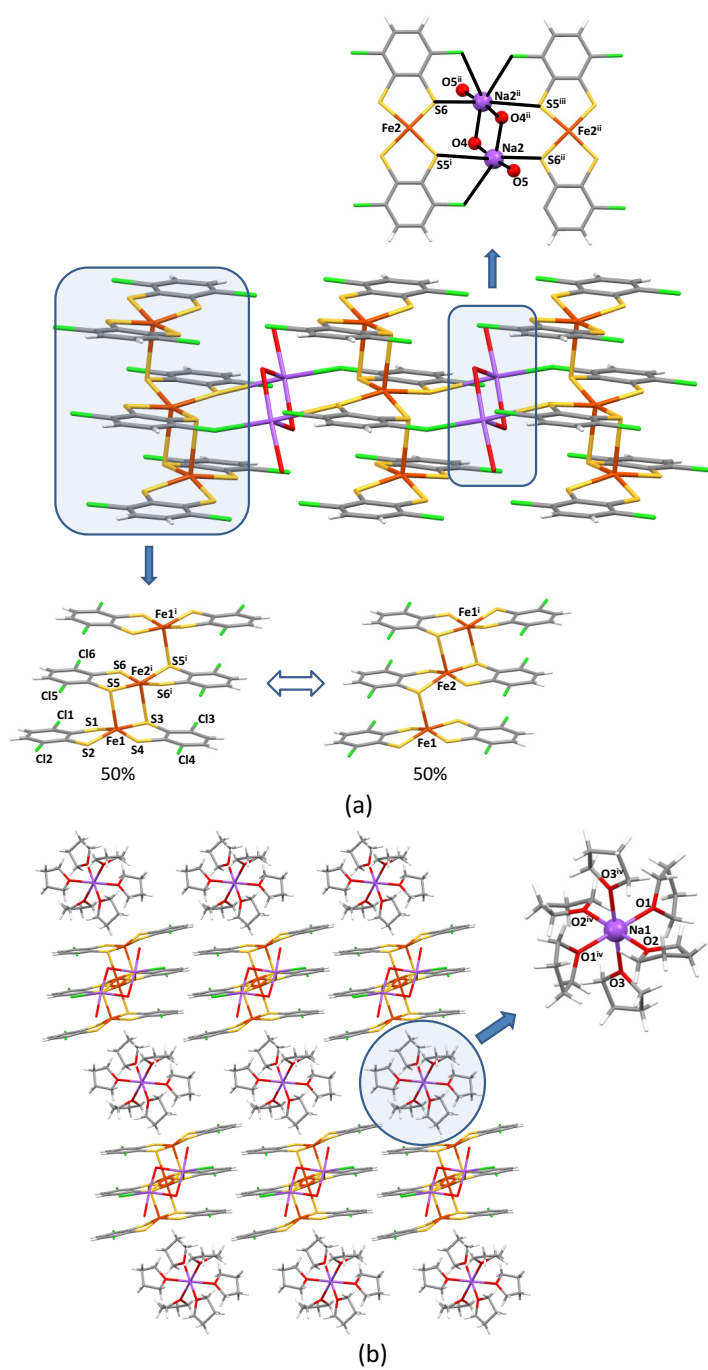


Figure 1. Crystal structure of compound **1**: a) [Fe₃(SC₆H₄Cl₂S)₆] fragments present in the anionic {Na₂(μ-H₂O)₂(H₂O)₂[Fe₃(SC₆H₄Cl₂S)₆]}ⁿ⁻ 1D-CP and b) their packing with [Na(thf)₆]⁺ isolated entities.

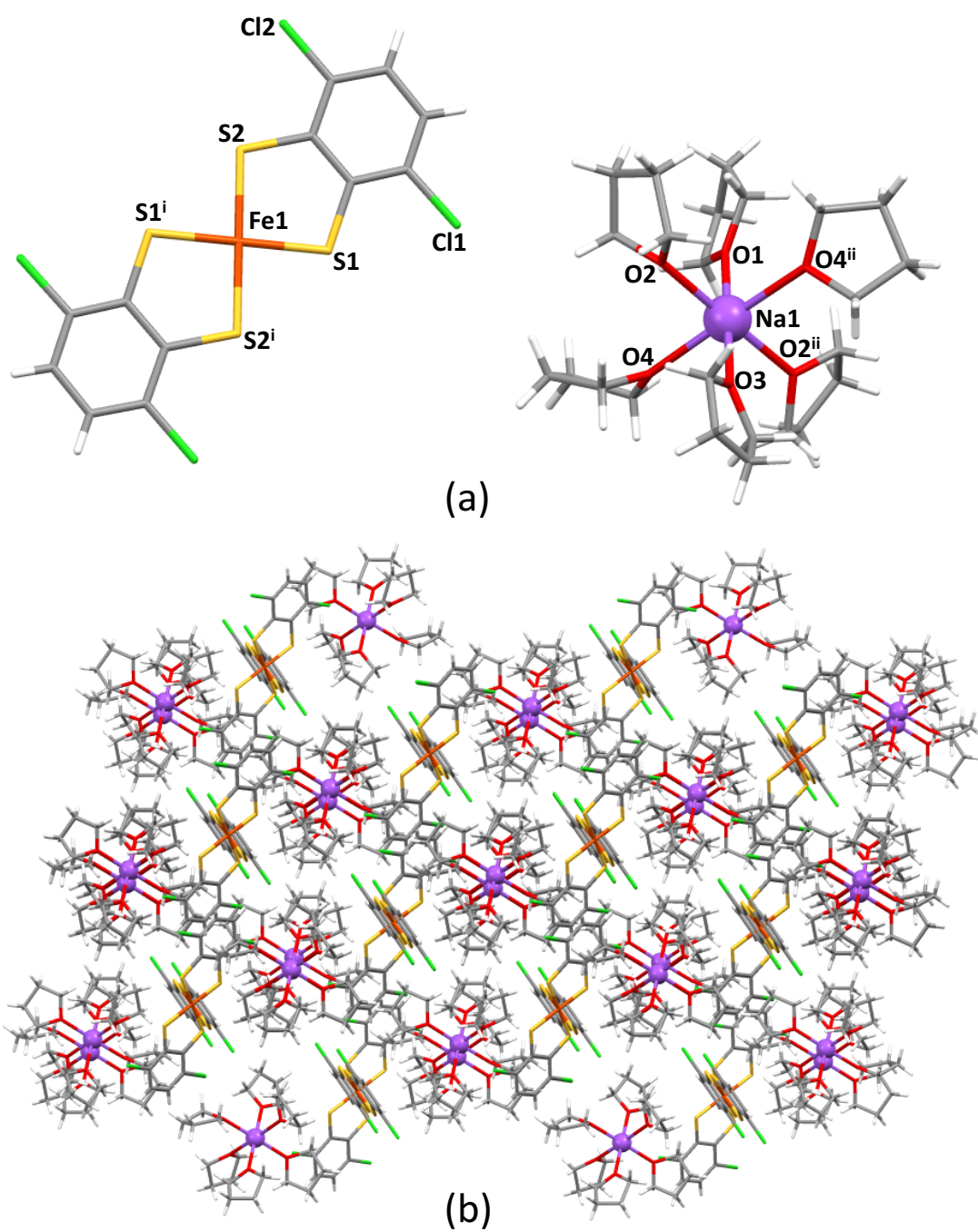


Figure 2. a) Discrete $[\text{Na}(\text{thf})_6]^+$ and $[\text{Fe}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ entities and b) crystal packing found in compound **2**.

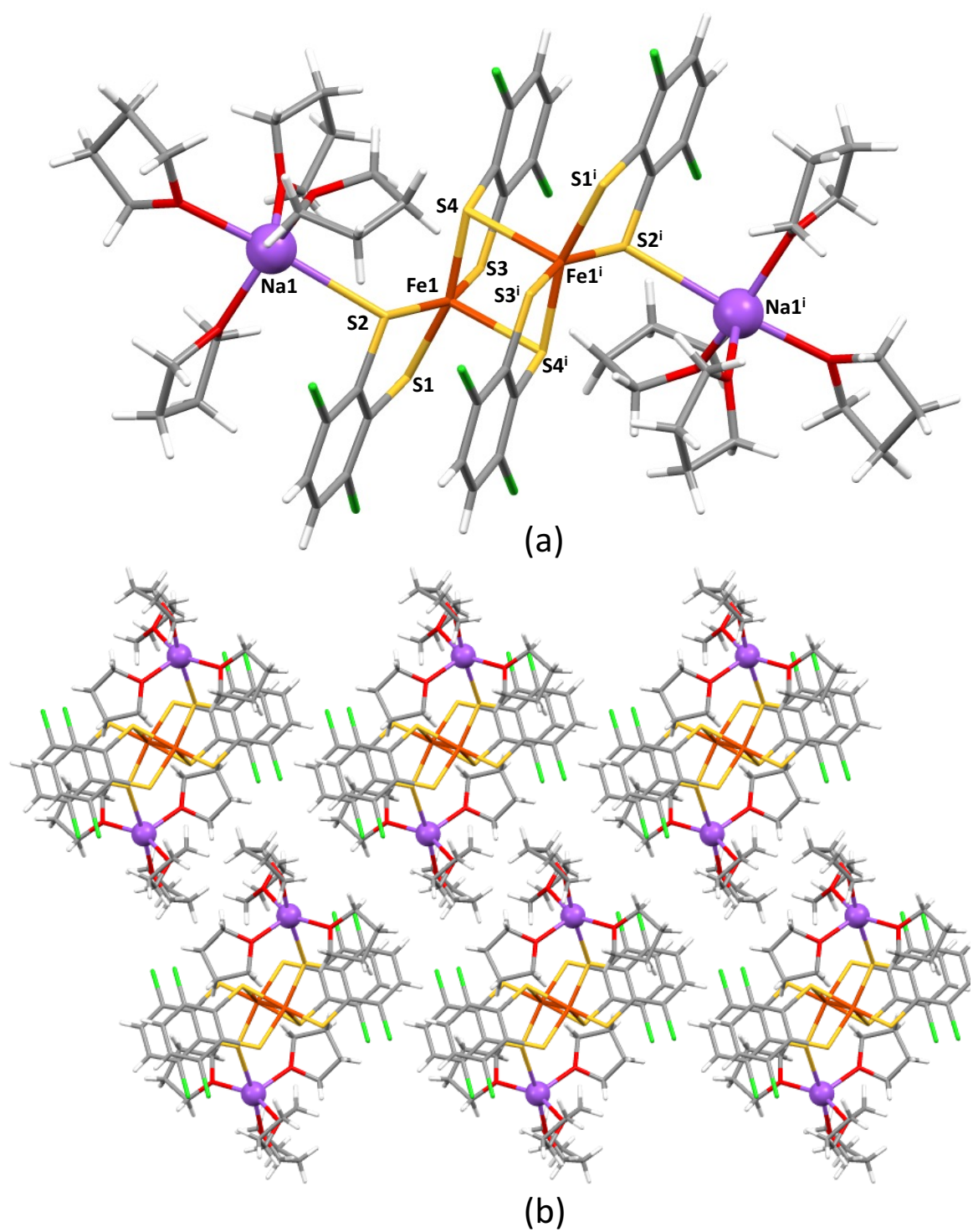


Figure 3. Molecular structure (a) and crystal packing (b) of compound **3**.

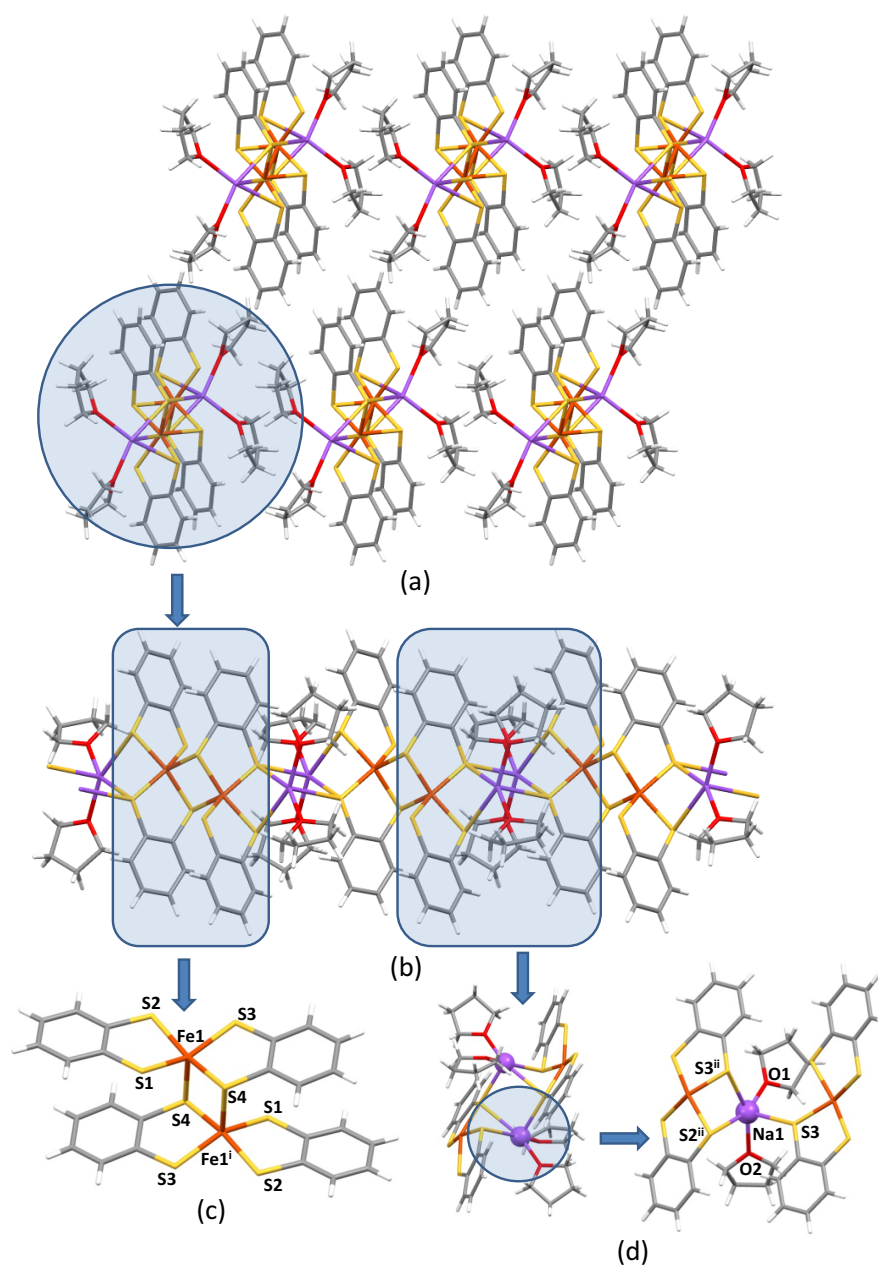


Figure 4. Crystal packing (a) of compound **4** showing the 1D nature of the sodium-iron-dithiolene entity (b) together with the dinuclear iron (c) sodium cation coordination sphere (d).

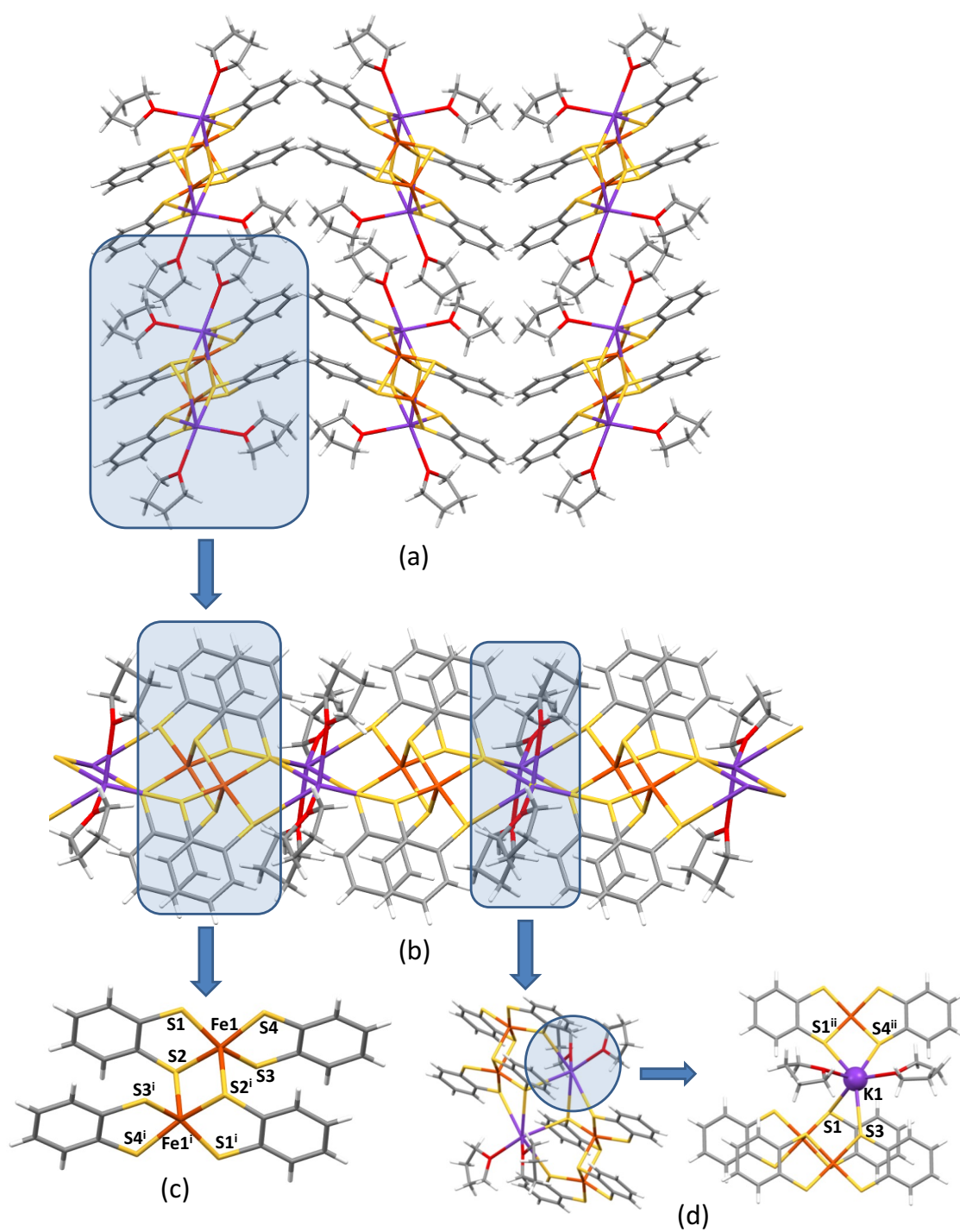


Figure 5. Crystal packing (a) of compound **5**, showing the 1D nature of the potassium-iron-dithiolene entity (b) together with the dinuclear iron (c) potassium cation coordination sphere (d).

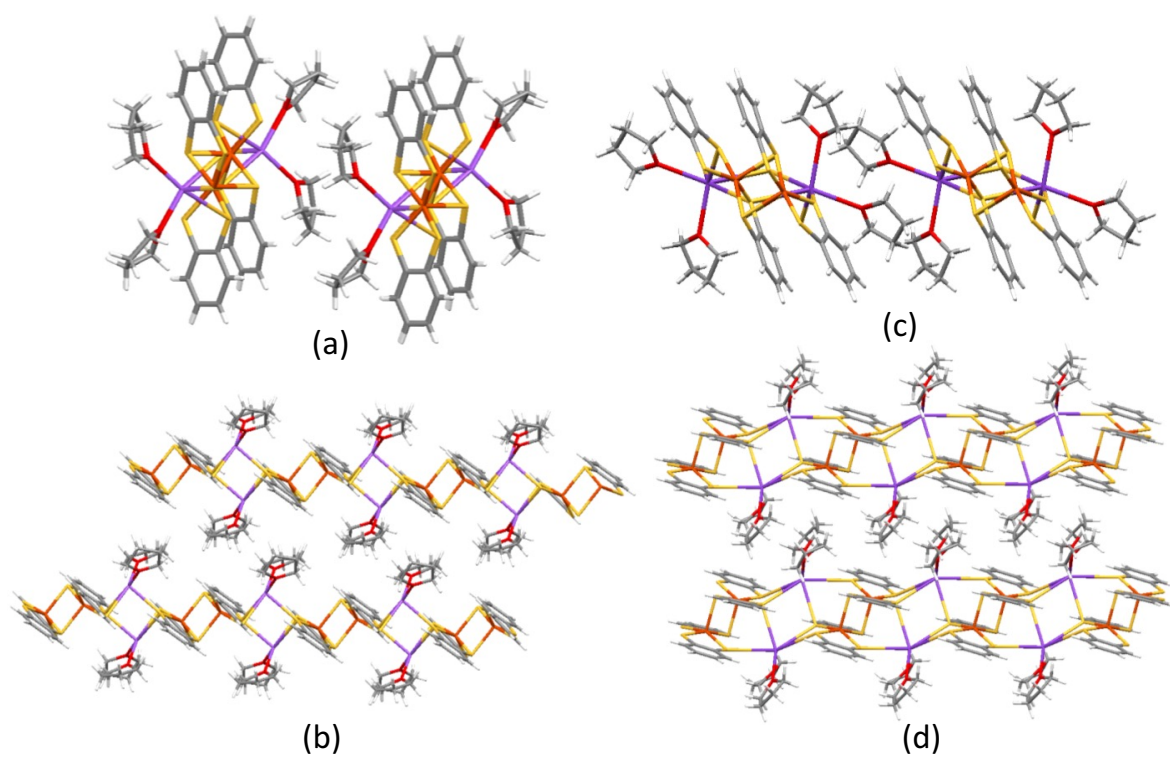


Figure 6. Frontal and lateral views of two adjacent chains in compounds **4** (a, b) and **5** (c, d).

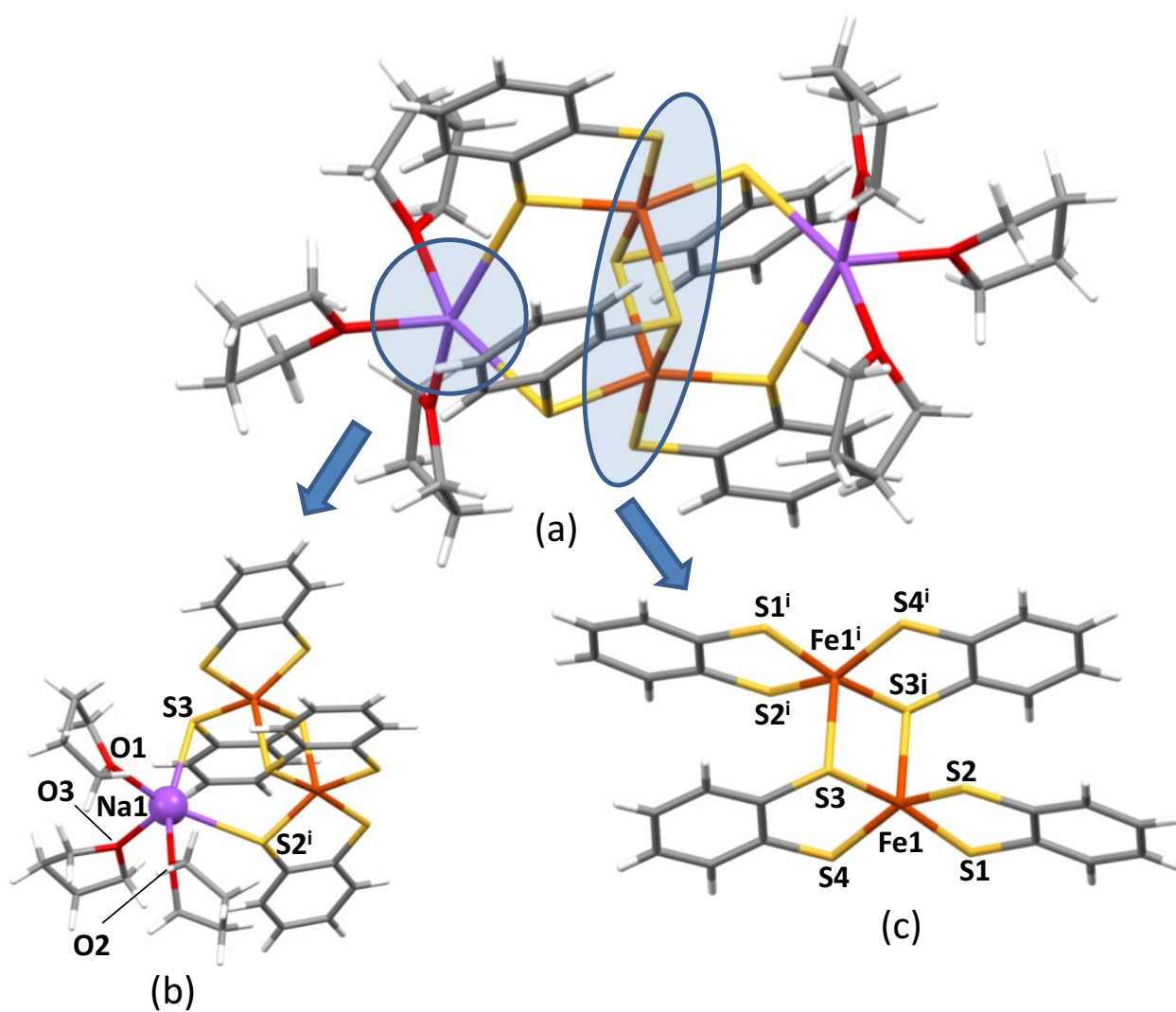


Figure 7. Tetrametallic $[(\text{thf})_3\text{Na}][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4][\text{Na}(\text{thf})_3]$ discrete entities (a) emphasizing the sodium (b) and iron (c) coordination environments found in compound **6a**.

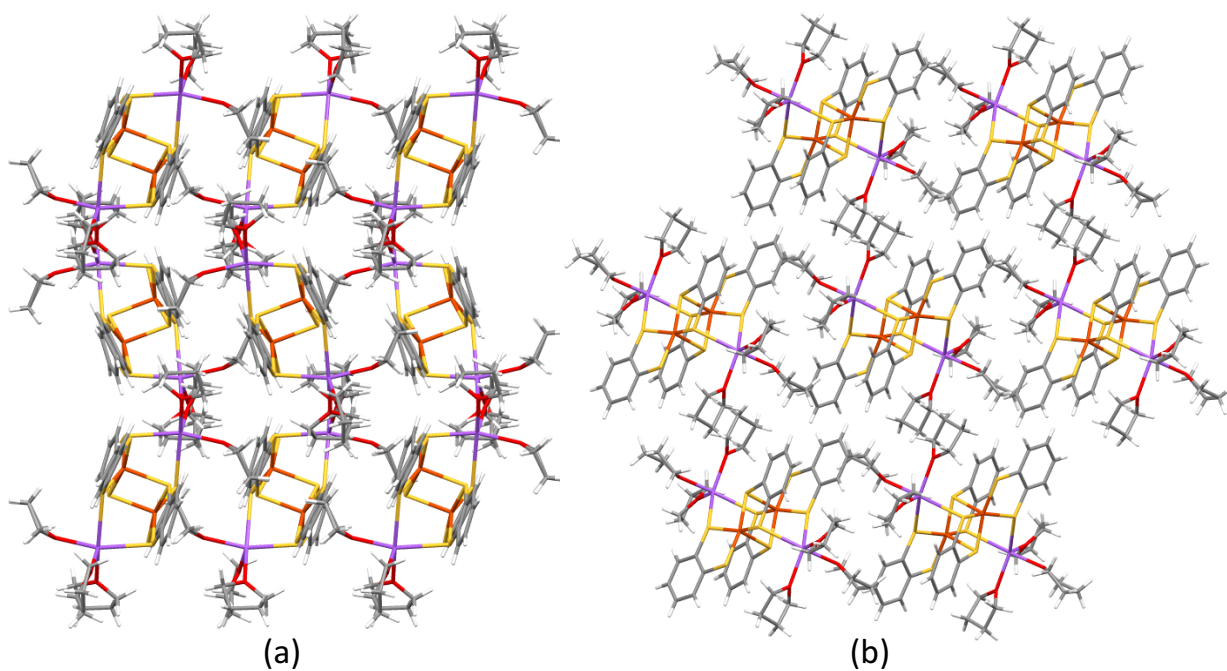


Figure 8. Different crystal packing of the $[(\text{thf})_3\text{Na}][\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4][\text{Na}(\text{thf})_3]$ entities in the polymorphs **6a** (a) and **6b** (a).

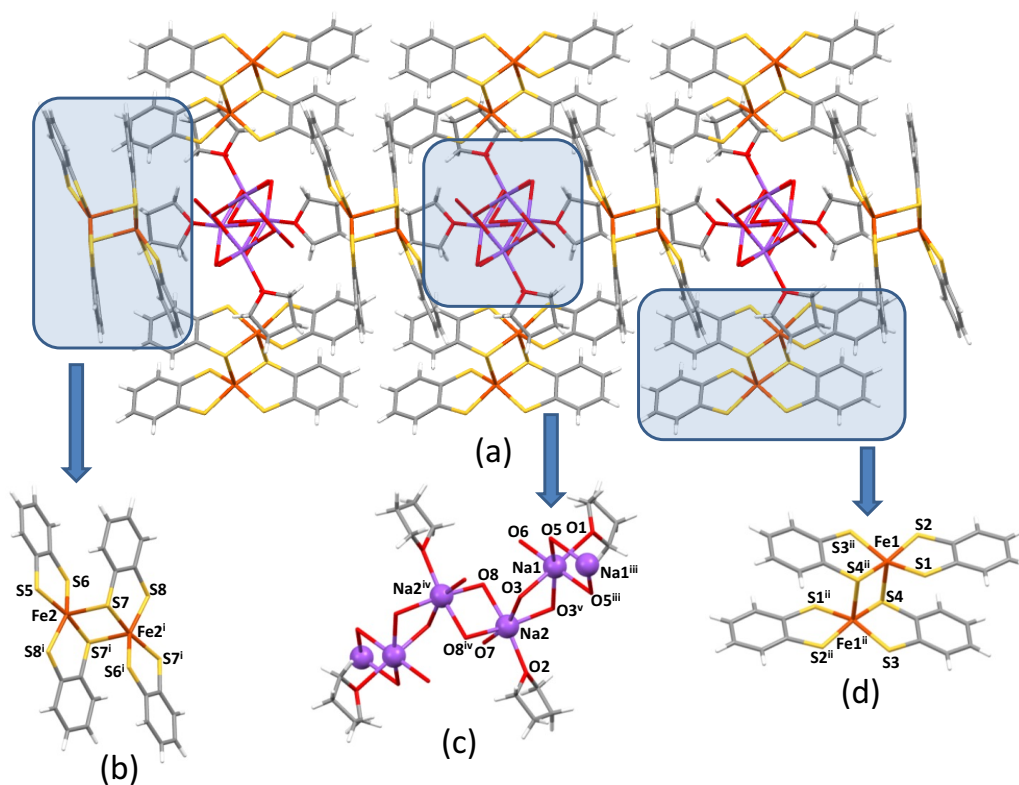


Figure 9. Crystal packing (a) of compound **7** showing the $[\text{Na}_2(\mu\text{-H}_2\text{O})_4(\text{H}_2\text{O})_2(\text{thf})_2]^{n+}$ cationic chain (c) and the dinuclear $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{S})_4]^{2-}$ anionic entities (b and d).

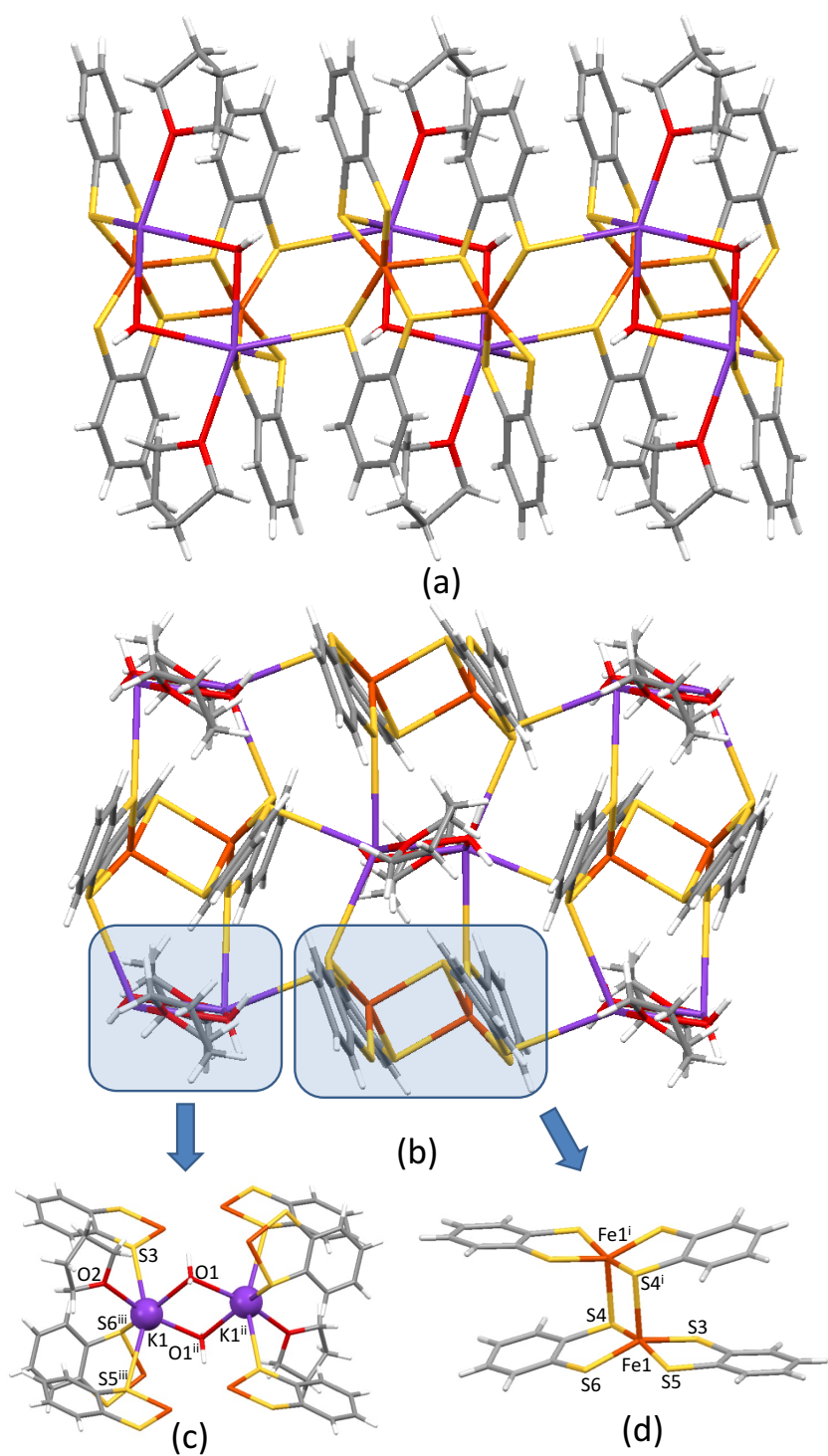


Figure 10. Lateral (a) and perpendicular (b) view of a $\{[K_2(thf)_2(\mu-H_2O)_2][Fe_2(SC_6H_4S)_4]\}_n$ **8** sheet showing the potassium (c) and iron (d) coordination environments.

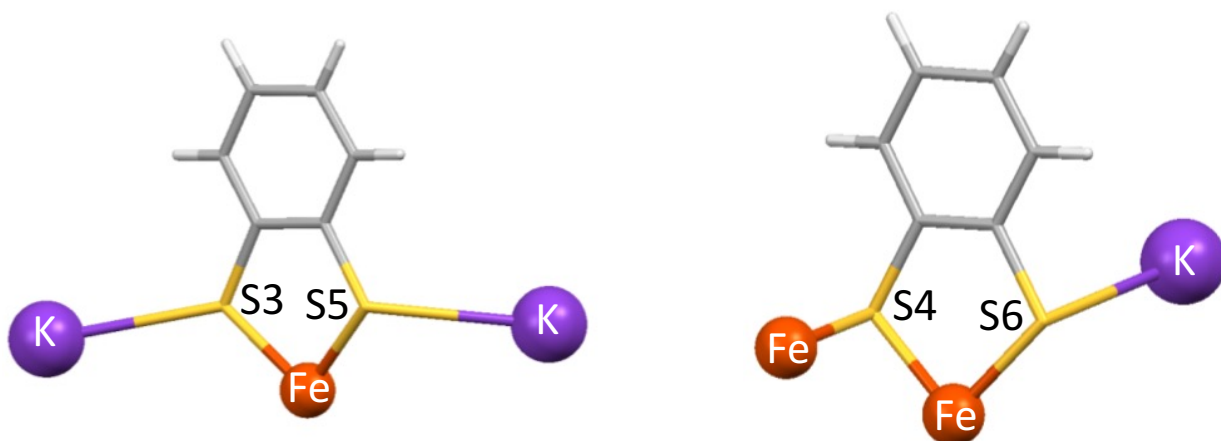
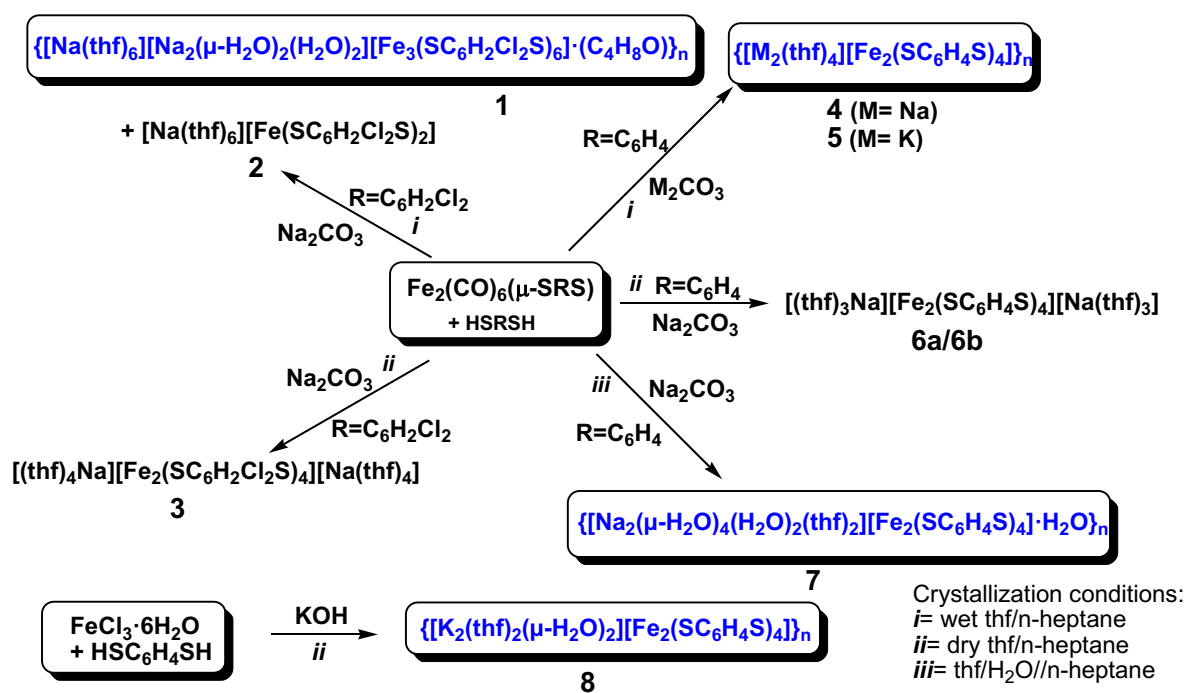
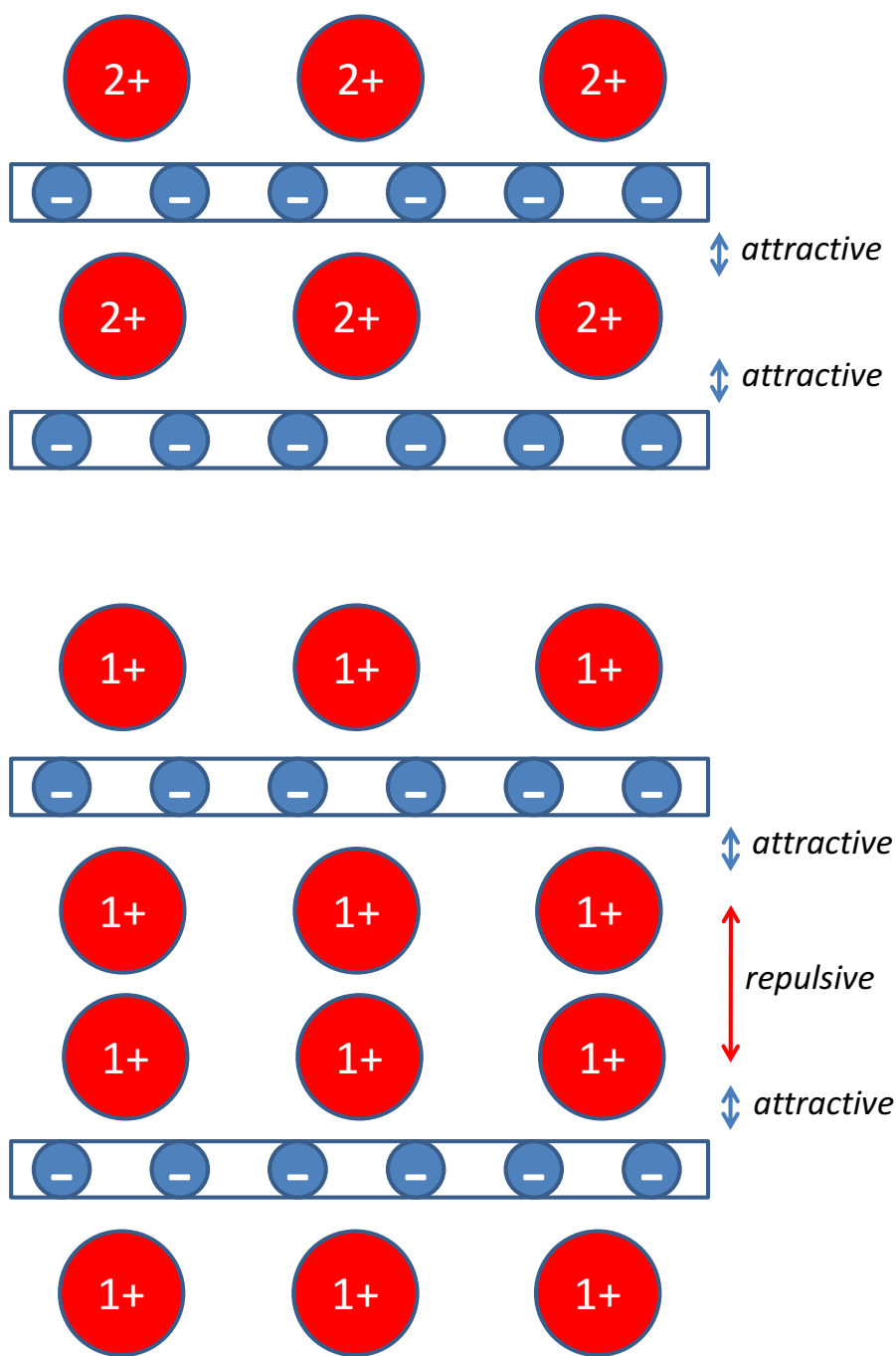


Figure 11. Coordination modes of dithiolene ligands in compound **8**.



Scheme 1. Summary of the reactions.



Scheme 2. Electrostatic interactions taking place between an anionic 1D polymeric chain and monovalent and divalent cationic entities to counterbalance the charge.

Table 1. Crystallographic data and structure refinement details of compounds **1-8**.

	1	2	3	4	5	6a	6b	7	8
Empirical formula	C ₆₄ H ₆₈ Cl ₁₂ Fe ₃ Na ₃ O ₁₁ S ₁₂	C ₃₆ H ₅₂ Cl ₄ FeNaO ₆ S ₄	C ₂₈ H ₃₆ Cl ₄ FeNaO ₄ S ₄	C ₂₀ H ₂₄ FeNaO ₂ S ₄	C ₂₀ H ₂₄ FeKO ₂ S ₄	C ₄₈ H ₆₄ Fe ₂ Na ₂ O ₆ S ₈	C ₄₈ H ₆₄ Fe ₂ Na ₂ O ₆ S ₈	C ₃₂ H ₄₆ Fe ₂ Na ₂ O ₉ S ₈	C ₁₆ H ₁₈ FeKO ₂ S ₄
Formula weight	2059.82	929.65	785.45	503.47	519.58	1151.15	1151.15	988.85	465.49
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>Pbca</i>
<i>a</i> (Å)	9.3220(6)	21.931(6)	11.1529(6)	9.2141(5)	11.6050(5)	15.1252(4)	11.8936(6)	10.9902(5)	9.181(5)
<i>b</i> (Å)	13.0083(10)	12.647(4)	12.8623(6)	10.0805(6)	22.2412(9)	17.3330(4)	9.8630(6)	13.5451(6)	13.593(6)
<i>c</i> (Å)	18.3477(13)	16.399(5)	13.2607(6)	13.6928(7)	8.9899(3)	20.2348(5)	22.6427(14)	14.4191(6)	29.281(9)
α (°)	75.226(4)	—	67.319(2)	109.046(3)	—	—	—	88.739(2)	—
β (°)	83.517(4)	108.17(2)	74.607(2)	97.741(3)	96.808(2)	—	100.353(2)	77.110(2)	—
γ (°)	73.140(3)	—	87.413(2)	104.436(3)	—	—	—	88.337(2)	—
<i>V</i> (Å ³)	2057.0(3)	4322(2)	1688.70(14)	1131.35(11)	2304.01(16)	5304.9(2)	2612.9(3)	2091.24(16)	3654(3)
<i>Z</i>	1	4	2	2	4	4	2	2	8
ρ_{calcd} (gcm ⁻³)	1.663	1.429	1.545	1.478	1.498	1.441	1.463	1.570	1.692
μ (mm ⁻¹)	1.287	0.841	1.056	1.068	1.211	0.924	0.938	1.163	1.517
Temperature (K)	100(2)	200(2)	100(2)	200(2)	200(2)	100(2)	110(2)	110(2)	200(2)
Reflections measured	7519	3906	31808	36970	55531	85526	76911	60559	55019
Unique data/parameters	7519/477	3906/232	6146/379	4130/253	4204/253	5433/298	4776/298	7654/520	3458/217
Reflections with $I \geq 2\sigma(I)$	6184	1721	5515	3408	3502	4018	4429	6363	1744
<i>R</i> _{int}	0.0427	0.1253	0.0319	0.0442	0.0495	0.0721	0.0298	0.0504	0.2253
GOF ^a	1.069	0.925	1.022	1.032	1.021	1.011	1.046	1.015	1.023
Final R indices									
[<i>I</i> > 2σ(<i>I</i>)] <i>R</i> 1 ^b / <i>wR</i> 2 ^c	0.0377/0.0916	0.0699/0.1276	0.0322/0.0794	0.0307/0.0725	0.0254/0.0591	0.0312/0.0629	0.0192/0.0478	0.0278/0.0586	0.0804/0.1349
All data <i>R</i> 1 ^b / <i>wR</i> 2 ^c	0.0498/0.0984	0.1904/0.1575	0.0372/0.0824	0.0424/0.0792	0.0357/0.0633	0.0576/0.0718	0.0219/0.0496	0.0389/0.0628	0.168/0.162

^[a] $S = [\sum w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$; ^[b] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^[c] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2, 0) + 2Fc^2)/3$ with $a = 0.0407$ (**1**), 0.0385 (**2**), 0.0333 (**3**), 0.0590 (**4**), 0.0283 (**5**), 0.0255 (**6a**), 0.0204 (**6b**), 0.0259 (**7**), and 0.0390 (**8**); and $b = 4.3914$ (**1**), 2.0889 (**3**), 0.8652 (**4**), 1.2498 (**5**), 5.2815 (**6a**), 1.6607 (**6b**), and 1.3337 (**7**).

Table 2. Selected distances in compounds **1-8**.

	M	Fe-S _{equatorial}	Fe-S _{apical}	M-O _{water}	M-O _{thf}	M-S	M-Cl
1	Na	2.198- 2.227	2.547- 2.603	2.236 ^t 2.328- 2.432 ^b	2.357/2.406	3.010	3.118
2	Na	2.170- 2.184	-	-	2.322/2.441	-	-
3	Na	2.217- 2.235	2.497	-	2.277/2.373	2.997	-
4	Na	2.221- 2.231	2.442	-	2.267/2.277	2.826- 2.980	-
5	K	2.219- 2.231	2.479	-	2.663/2.692	3.223- 3.407	-
6a	Na	2.216- 2.239	2.496	-	2.278/2.315	2.819- 3.044	-
6b	Na	2.220- 2.238	2.476	-	2.280/2.339	2.837- 2.934	-
7	Na	2.215/2.249	2.445- 2.463	2.335/2.433 ^t 2.406/2.463 ^b	2.370/2.462	-	-
8	K	2.196/2.215	2.468	2.722/2.758 ^b	2.713	3.294- 3.384	-

t= terminal, b= bridging

ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

***Corresponding Author.** esther.delgado@uam.es (E.D.)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENTS. Financial support from Spain's MICINN (MAT2013-46753-C2-1-P and MAT2013-46502-C2-1-P) and Factoría de Cristalización (CONSOLIDER-INGENIO 2010), and Eusko Jaurlaritza (IT477-10) is gratefully acknowledged.

REFERENCES

1. Robertson, N.; Cronin, L. *Coord. Chem. Rev.* **2002**, 227, 93-127.
2. *Dithiolene Chemistry: Synthesis, Properties and Applications*; John Wiley & Sons, Inc.: New York, 2004; Vol. 52.
3. Muller-Westerhoff, U. T.; Vance, B. *Comprehensive coordination chemistry*; Pergamon Press: Oxford, U. K., 1987; Vol. 2.
4. Clemenson, P. I. *Coord. Chem. Rev.* **1990**, 106, 171-203.
5. Belo, D.; Almeida, M. *Coord. Chem. Rev.* **2010**, 254, 1479-1492.
6. Ezzaher, S.; Gogoll, A.; Bruhn, C.; Ott, S. *Chem. Commun.* **2010**, 46, 5775-5777.
7. Alcácer, L.; Novais, H. In *Extended Linear Chain Compounds.*; Miller, J. S., Ed.; Springer US: New York, 1983; Cap. 6, 319-351.
8. Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, 110, 115-160.
9. Sproules, S.; Wiegardt, K. *Coord. Chem. Rev.* **2010**, 254, 1358-1382.
10. Garreau de Bonneval, B.; Moineau-Chane Ching, K. I.; Alary, F.; Bui, T. T.; Valade, L. *Coord. Chem. Rev.* **2010**, 254, 1457-1467.
11. Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, 107, 6253-6277.

12. Takaishi, S.; Hosoda, M.; Kajiware, T.; Miyasaka, H.; Yamashita, M.; Nakanishi, Y.; Kitagawa, Y.; Yamaguchi, K.; Kobayashi, A.; Kitagawa, H. *Inorg. Chem.* **2009**, *48*, 9048-9050.
13. Ribas, X.; Dias, J. C.; Morgado, J.; Wurst, K.; Molins, E.; Ruiz, E.; Almeida, M.; Veciana, J.; Rovira, C. *Chem. Eur. J.* **2004**, *10*, 1691-1704.
14. Llusar, R.; Uriel, S.; Vicent, C.; Clemente-Juan, J.; Coronado, E.; Gómez-García, C. J.; Braïda, B.; Canadell, E. *J. Am. Chem. Soc.* **2004**, *126*, 12076-12083.
15. Llusar, R.; Triguero, S.; Polo, V.; Vicent, C.; Gómez-García, C. J.; Jeannin, O.; Fourmigué, M. *Inorg. Chem.* **2008**, *47*, 9400-9409.
16. Gushchin, A. L.; Llusar, R.; Vicent, C.; Abramov, P. A.; Gómez-García, C. J. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2615-2622.
17. Dong, F. Y.; Dou, J. M.; Li, D. C.; Gao, X. K.; Wang, D. Q. *J. Mol. Struct.* **2005**, *738*, 79-84.
18. Gao, X. K.; Dou, J. M.; Li, D. C.; Dong, F. Y.; Wang, D. Q. *J. Mol. Struct.* **2005**, *738*, 181-186.
19. Gao, X. K.; Dou, J. M.; Li, D. C.; Dong, F. Y.; Wang, D. Q. *J. Incl. Phenom. Macrocycl. Chem.* **2005**, *53*, 111-119.
20. Dong, F. Y.; Dou, J. M.; Li, D. C.; Gao, X. K.; Wang, D. Q. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 231-237.
21. Bolligarla, R.; Das, S. K. *Cryst. Eng. Commun.* **2010**, *12*, 3409-3412.

22. Bolligarla, R.; Tripuramallu, B. K.; Sreenivasulu, V.; Das, S. K. *Indian J. Chem.* **2011**, *50A*, 1410-1417.
23. Amo-Ochoa, P.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martín, A.; Zamora, F. *Inorg. Chem.* **2013**, *52*, 5943-5950.
24. Benmansour, S.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martín, A.; Perles, J.; Zamora, F. *Inorg. Chem.* **2015**, *54*, 2243-2252.
25. Bruna, S.; Cuadrado, I.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Llusar, R.; Martín, A.; Menéndez, N.; Polo, V.; Zamora, F. *Dalton Trans.* **2014**, *43*, 13187-13195.
26. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, *26*, 343-350.
27. Sheldrick, G. SHELX-97, University of Göttingen, Germany, 1997.
28. Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837-838.
29. Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380-388.
30. Hahn, F. E.; Eiting, T.; Seidel, W. W.; Pape, T. *Eur. J. Inorg. Chem.* **2010**, *2010*, 2393-2399.
31. Bellamy, D.; Connelly, N. G.; Lewis, G. R.; Guy Orpen, A. *Cryst. Eng. Commun.* **2002**, *4*, 51-58.
32. Sellmann, D.; Lauderbach, F.; Heinemann, F. W. *Eur. J. Inorg. Chem.* **2005**, *2005*, 371-377.

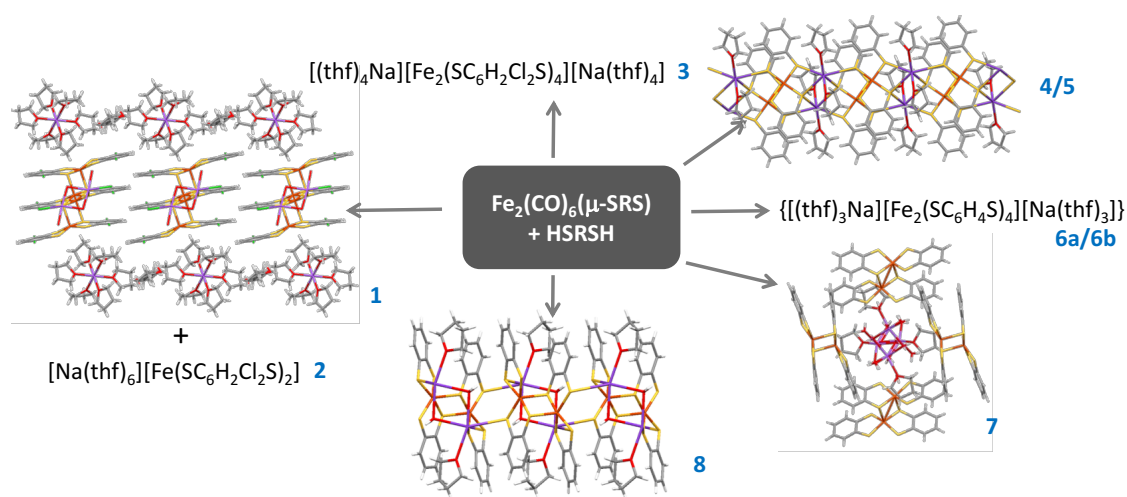
33. Tanaka, S.; Matsubayashi, G. E. *J. Chem. Soc., Dalton Trans.* **1992**, 2837-2843.
34. Zhou, B.; Ogura, S.; Kato, N.; Idobata, Y.; Kobayashi, A.; Kobayashi, H. *Chem. Lett.* **2013**, 42, 977-979.
35. Gupta, S.; Kirillova, M. V.; Guedes, S.; Pombeiro, A. J. L.; Kirillov, A. M. *Inorg. Chem.* **2013**, 52, 8601-8611.

For Table of Contents Use Only

Manuscript Title: Structural Diversity of Compounds Based on Iron-Dithiolene with Sodium or Potassium Complexes

Author List: Oscar Castillo, Esther Delgado,* Diego Hernández, Elisa Hernández, Avelino Martín, Ignacio Martín, Félix Zamora

TOC Graphic



Synopsis

A series of coordination compounds and 1D/2D coordination polymers containing two different iron-dithiolene entities, $[\text{Fe}(\text{SRS})]_n^{n-}$ ($\text{R}=\text{C}_6\text{H}_2\text{Cl}_2$, C_6H_4), and alkaline metal complexes, as counter-cations, have been prepared under different crystallization conditions and structurally characterized. The flexibility of the alkaline coordination environment seems to facilitate the structural diversity found for this family of dithiolene compounds.

