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Phenylthiolate as a σ- and π- donor ligand: synthesis of a 3-D organometallic coordination polymer $[K_2Fe(SPh)_4]_n$†

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The synthesis and crystal structure of the first mixed-metal organometallic polymer network containing phenylthiolato ligands, $[K_2Fe(SPh)_4]_n$, are investigated. The simple phenylthiolate acts as a σ- and π-donor ligand to give a 3-D potassium iron coordination polymer with both metal–carbon and metal–sulfur coordination interactions.

The design and the synthesis of organometallic networks *via* coordination is a rapidly growing area of interest for their specific topologies and potentially interesting properties.[1,2] For example, metal-directed self-assembly has been widely recognized as an efficient method for constructing well-defined discrete or infinite structures. However, at present the chemistry of organometallic polymeric compounds generated from multidenate organic ligands that can afford both heteroatoms and carbon atoms as coordination sites has received considerably less attention.[3] Most of the coordination polymers are organic/inorganic hybrid materials with only metal–heteroatom coordinations and synthesized by using soluble inorganic transition metal ions or unsaturated transition metal coordination complexes and organic bidentate or multifunctional ligands as precursors.[4,5] Families of organic ligands are found to assemble into large three-dimensional arrangements through metal-coordination.[6,7] Pyrazine,[8] bridged bidentate bipyridyl ligands[9] and nitrile-substituted pyridine[10] are the most commonly used donor groups in coordination polymers at present. An exciting yet little explored area of supramolecular chemistry is the synthesis of organometallic coordination polymers containing both metal–carbon and metal–heteroatom coordination interactions with chalcogenolato ligands, such as phenylthiolato ligands.

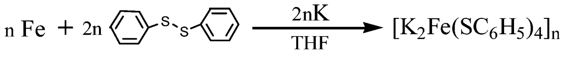
Here we report the synthesis of a new mixed-metal organometallic polymeric compound with both metal–carbon and metal–sulfur coordination interactions using phenylthiolato ligand. The result reported herein demonstrates that the use of phenylthiolate ligand as precursor to bind transition metal ions is in fact a new approach for the formation of novel organometallic molecular and supramolecular networks. In this paper a three-dimensional potassium iron assembly with phenylthiolato ligands *via* "molecular paneling" is synthesized and its crystal structure is characterized. The phenylthiolates, which act as σ- and π- donor ligands, are found to assemble into large three-dimensional arrangements through metal coordination. Although there are some reports on mono- and di-nuclear transition metal thiolates,[11] $[K_2Fe(SC_6H_5)_4]_n$ (**1**) is the first example of a mixed-metal polymeric network containing the phenylthiolates as both σ- and π- donor ligands with interactions between potassium and the carbon atoms of the phenyl rings.

It has been reported that the reaction of $FeCl_2$ with KSPh leads to a tetrahedral mononuclear complex of $[Ph_4P]_2[Fe(SPh)_4]$.[12] The 3-D polymer $[K_2Fe(SC_6H_5)_4]_n$ (**1**) is obtained directly from the reaction of Fe metal and Ph_2S_2 in the presence of K in THF solution (Scheme 1). X-ray crystal structure analysis of **1** shows a 3-D polymeric structure based on networks of coordinated Fe^{II} and K^{I} centers linked by phenyl thiolato ligands.‡ As indicated in Fig. 1, each unit contains one iron atom, two potassium atoms and four phenylthiolato ligands. The Fe^{II} atom is bonded to four μ_4-S atoms of phenylthiolato ligands in a distorted tetrahedral environment, while each K^{I} sphere consists of four μ_4-S atoms and two phenyl cycles which are η^6-coordinated to K. Each phenylthiolato ligand links three K atoms and one Fe center through the sulfur atom and the phenyl group. The sulfur atom is in μ_4-S mode and connected with two K atoms, one Fe atom and one C atom of the phenyl ring.

As a result, an extended neutral 3-D network is formed. Caves were generated between the puckered structure, and the channel sizes are *ca*. 10.339 Å × 10.339 Å along the *c*-axis and 10.339 Å × 12.095 Å along the *a*- or *b*-axes. The porosity in the framework is similar to that with phenyl rings omitted except the cavity size and can be better exhibited in Fig. 2. View along the *a* axis exhibits rhombic cavities formed by coordinating spheres resembling in the stack of two crowns with one upstanding and the other upside-down. View along the *b* axis is analogous to that along the *a* axis. As shown in view along the *c* axis, horizontal and erect rhombic cavities are alternately incorporated in the network.

The average Fe–S bond length is 2.3371(14) Å, in line with other iron complexes containing phenylthiolato ligands.[13] The respective K–S bond lengths are 3.385(2) and 3.540(2) Å. The average distance between the potassium atom and the centroids of the two phenyl rings is 3.1672 Å, which is among those found in analogous potassium η^5- and η^6-arene complexes.[14] The average C=C bond distance of the phenyl ring is 1.388 Å, similar to those in other complexes containing $M(\eta^6\text{-}C_6H_5)$ cations.[15] The distance between the adjacent iron atom and potassium atom is 3.9001(15) Å. The shortest K···K distance is 6.209 Å, far beyond the range for close metal–metal interactions.

The simple phenylthiolate acts as a σ- and π- donor ligand, coordinating with two different metals to form a mixed-metal three-



Scheme 1 Preparation of **1**.

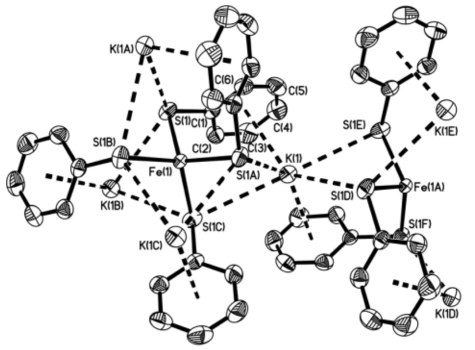


Fig. 1 The ORTEP drawing around the metal center with the hydrogen atoms omitted for clarity. Principal bond lengths (Å) and angles (°): Fe(1)–S(1) 2.3371(14), S(1)–K(1A) 3.540(2), S(1)–K(1B) 3.385(2), S(1)–C(1) 1.779(4), S(1A)–Fe(1)–S(1B) 104.07(3), S(1A)–Fe(1)–S(1) 104.07(3), S(1A)–Fe(1)–S(1C) 120.93(8), S(1B)–Fe(1)–S(1) 120.93(8), C(1)–S(1)–Fe(1) 102.88(14).

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† Electronic supplementary information (ESI) available: experimental procedures. See http://www.rsc.org/suppdata/cc/b4/b404443f/

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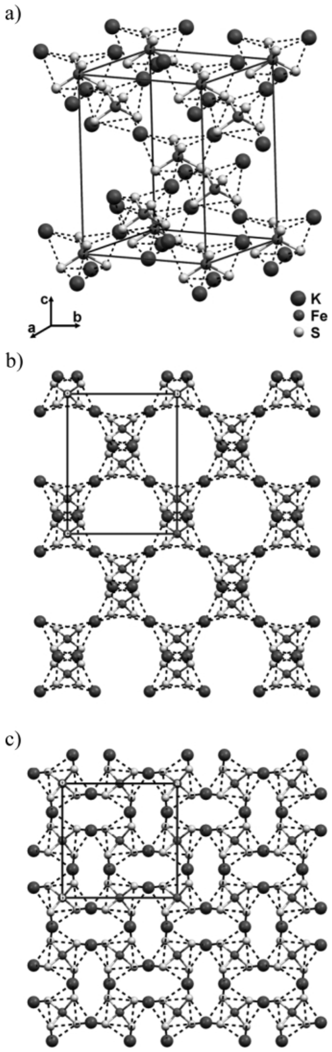

Fig. 2 View of the 3-D network of **1** with the phenyl rings are omitted for clarity: (a) cell overview; (b) view along *a* axis; (c) view along *c* axis.

dimensional organometallic polymer, in spite of some iron complexes having phenyl thiolate ligands.[12,13]

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Notes and references

‡ *Crystal data* for $[K_2Fe(SC_6H_5)_4]_n$ **1**: *n* $C_{24}H_{20}FeK_2S_4$, brown-yellow blocks, crystal dimensions 0.25 × 0.30 × 0.45 mm, M = 570.69, tetragonal, space group *I*-42*d*, a = 12.580(6), b = 12.580(6), c = 16.127(10) Å, V = 2552(2) Å^3, Z = 4, ρ_{calcd} = 1.485 Mg m^{-3}, μ = 1.255 mm^{-1}, $F(000)$ = 1168, Trans. min and max: 0.6021/0.7444, T = 293 K, MoKa, $-16 < h < 16$, $-16 < k < 9$, $-20 < l < 20$, 5983 reflections collected ($2.05 < \theta < 27.11°$) on the CCD-Bruker Smart APEX system, 1411 independent reflections (R_{int} = 0.0392),1319 ($I > 2\sigma(I)$) used in the structure refinement (71 parameters refined). R = 0.0445, R_w = 0.1235, GOF = 1.449. Largest peak 0.880 e Å^{-3}. CCDC 234591. See http://www.rsc.org/suppdata/cc/b4/b404443f/ for crystallographic data in .cif or other electronic format.

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