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Thio-azo proligands based on 5,6-derivatives-1,10-phenanthroline and their use for iron(II) complexes: Synthesis, characterization and crystal structures

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ABSTRACT

The preparation and characterization of 5,6-substituted-1,10-phenanthrolines, phdtos = 5,6-bistosyl-1,10-phenanthroline (**1**) and phdbt = 5,6-dibenzyltiol-1,10-phenanthroline (**2**) are described. The synthesis of (**1**) was achieved in good yield via the corresponding dihydroxide and **2** was obtained by cross-coupling reaction of 5,6-dibromo-1,10-phenanthroline and benzylthiol mediated by a palladium catalytic system in refluxing toluene (120 °C). These phenanthroline derivatives were used as ligands to afford $[Fe^{II}(phdtos)_3](PF_6)_2$ (**5**) and $[Fe^{II}(phdbt)_3](PF_6)_2$ (**6**) complexes.

1. Introduction

The 1,10-phenanthrolines have experienced an increasingly important role in the field of supramolecular chemistry, as ligands in different transition metal complexes, which has stimulated the preparation of many 1,10-phenanthroline derivatives either 2,9-, 3,8-, 4,7- or 5,6-disubstituted. The 5,6-disubstituted phenanthrolines, particularly with *S*-derivatives, are however a lot less explored in spite of being very attractive dithio-diazo ligands due to the presence of two different coordinating functionalities in the same molecule, the diimine function and the dithiolate function, and also due to its extensive electronic delocalization which may help the connection between the different coordinated species.

In this paper, we describe the synthesis of two 5,6-substituted-1,10-phenanthrolines, namely phdtos = 5,6-bistosyl-1,10-phenanthroline (**1**) and phdbt = 5,6-dibenzyltiol-1,10-phenanthroline (**2**) the last one being a direct precursor of a dithio-diazo ligand similar to the ones we have recently described [1] (Scheme 1).

The diimine function coordination ability of the new 5,6-disubstituted-1,10-phenanthrolines **1** and **2** is explored by the synthesis of Fe(II) tris phenanthroline complexes $[Fe^{II}(phdtos)_3](PF_6)_2$ (**5**) and $[Fe^{II}(phdbt)_3](PF_6)_2$ (**6**).

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2. Experimental

2.1. Materials and methods

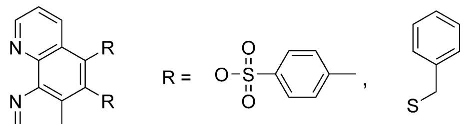
Whenever required, the solvents were dried according to the standard literature procedures [2], freshly distilled, and saturated with nitrogen prior to use. All the reagents used on the synthesis were purchased from commercial sources and used without further purification or synthesized from published methods. The 5,6-dihydroxy-1,10-phenanthroline [3] (**3**) was synthesized according to the literature reports by refluxing 5,6-dione-1,10-phenanthroline [4] in ethanol with dithioxamide. The synthesis of the 5,6-dibromo-1,10-phenanthroline (**4**) was performed according to a procedure reported by Feng et al. [5].

^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^1H and ^{13}C chemical shifts are given in ppm and were referenced with the residual solvent resonances relative to $SiMe_4$. Elemental analyses were performed on an EA 110 CE Instruments automatic analyser.

2.2. Synthesis

2.2.1. 5,6-Bistosyl-1,10-phenanthroline (*1*)

To a suspension of 5,6-dihydroxy-1,10-phenanthroline [3] (2 g; 9.4 mmol) in dry pyridine (250 ml), at 0 °C, 3 equiv. of *p*-toluenesulfonyl chloride (5.4 g; 28.2 mmol) were added, in small portions, under nitrogen. During five days the reaction mixture was allowed to stir at room temperature, under a nitrogen atmosphere and then



(1) **(2)**

Scheme 1. 5,6-Substituted-1,10-phenanthrolines.

poured into ice (1 dm^3). A white solid formed immediately. The suspension was stirred to room temperature. After filtration the obtained solid was washed with MeOH and recrystallized from EtOH. The product is recovered as a crystalline white precipitate. Yield: 3.9 g, 7.5 mmol (80%); m.p. 227–230 °C. *Anal.* Calc. for $C_{26}H_{20}N_2O_6S_2$: C, 59.99; H, 3.87; N, 5.38; S, 12.32. Found: C, 58.65; H, 3.87; N, 5.36; S, 12.13%. ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm: 9.23 (dd, *J* = 1.5, 4, 2H, 2H), 8.44 (dd, *J* = 1.5, 8.1, 2H, H3), 7.66 (t, *J* = 4.2, 2H, H4), 7.62 (dd, *J* = 7.2, 4H, phenyl); 7.29 (dd, *J* = 9.3, 4H, phenyl), 2.48 (s, 6H, CH_3). ^{13}C NMR, (75.373 MHz, $CDCl_3$): δ 21.819, 123.430, 124.329, 128.744, 129.807, 132.035, 132.205, 135.819, 145.208, 146.143, 151.263.

*2.2.2. 5,6-Dibenzylthiol-1,10-phenanthroline (**2**)*

5,6-Dibromo-1,10-phenanthroline [5] (5.92 mmol; 2 g), $Pd_2(dba)_3$ (3 mol%; 0.184 g), bis-[2-(diphenylphosphino)phenyl]ether (PDEphos) (6 mol%; 0.191 g), *t*-BuOK (2.2 equiv., 13.01 mmol, 1.46 g), and 80 ml of dry and degassed toluene were mixed in a Schlenk tube under inert atmosphere. The solution was stirred for 1 h at room temperature. The benzylthiol (2.2 equiv., 13.01 mmol, 1.42 ml) was added by syringe. A condenser was adapted to the Schlenk tube and under argon atmosphere the reaction mixture was heated to 120 °C. After 48 h, the reaction mixture was allowed to reach room temperature, then filtered and concentrated under vacuum leading to an orange oil. This oil was chromatographed (Silica gel; AcOEt:MeOH:NH_3; (20:1:0.5)) and the product was recovered as a crystalline yellow precipitate. Yield: 1.78 g, 4.2 mmol (71%); m.p. 170–171 °C. *Anal.* Calc. for $C_{26}H_{20}N_2S_2$: C, 73.55; H, 4.75; N, 6.60; S, 15.10. Found: C, 73.53; H, 4.85; N, 5.76; S, 12.46%. ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm: 9.15 (dd, *J* = 1.8, 4.2, 2H, H2), 8.97 (dd, *J* = 1.8, 8.4, 2H, H4), 7.57 (dd, *J* = 4.2, 8.4, 2H, H3), 7.06 (m, 10H, phenyl), 4.06 (s, 4H, CH_2). ^{13}H NMR (75.373 MHz, $CDCl_3$): δ 42.172, 123.287, 130.293, 136.334, 137.116, 139.626, 146.202, 150.681.

*2.2.3. [Fe(phdtos)$_3$](PF$_6$)$_2$ (**5**)*

To a suspension of 5,6-bistosyl-1,10-phenanthroline (**1**) (3 equiv., 24.5 mg; 0.471 mmol) in 20 ml of a MeOH/H_2O (60/40) solution was added a MeOH/H_2O (50/50) solution of $FeCl_3 \cdot 6H_2O$ (1 equiv., 42.4 mg; 0.157 mmol). The reaction mixture was allowed to reflux with stir overnight, gradually turning to red. The hot mixture was filtered and a MeOH/H_2O (50/50) solution of $NaPF_6$ (3 equiv., 79.1 mg; 0.471 mmol) was added. The above reaction mixture was left in the refrigerated for several hours. A red precipitated was collected by vacuum filtration, washed with cold water and dried under vacuum. Yield: 101.8 mg, 0.0534 mmol (34%); m.p. 234–236 °C. *Anal.* Calc. for $C_{78}H_{60}F_{12}FeN_6O_{18}P_2S_6$: C, 49.11; H, 3.17; N, 4.41; S, 10.09. Found: C, 48.58; H, 3.26; N, 4.36; S, 9.22%.

*2.2.4. [Fe(phdbt)$_3$](PF$_6$)$_2$ (**6**)*

Following the previous procedure and using the 5,6-dibenzylthiol-1,10-phenanthroline (**2**) (3 equiv., 0.2 g; 0.471 mmol) instead of **1** a red precipitate was obtained. Yield: 104.7 mg, 0.0646 mmol (41%); m.p. 167–170 °C. *Anal.* Calc. for $C_{78}H_{60}F_{12}FeN_6P_2S_6$: C, 57.85; H, 3.73; N, 5.19; S, 11.88. Found: C, 57.76; H, 4.09; N, 5.18; S, 11.85%.

2.3. X-ray crystallographic study

Single crystals of **1** and **2** suitable for X-ray crystallographic analysis were obtained by slow evaporation in MeOH/CH_2Cl_2 solution and by slow diffusion of hexane into a CH_2Cl_2 saturated solution, respectively. Single crystals of the iron complexes (**5** and **6**) suitable for an X-ray structure determination were obtained by slow diffusion in an H shape cell. A saturated $NaPF_6$ solution in MeOH/H_2O (50:50) was placed in one compartment of a H cell and $Fe(L)_3$ (*L* = **5** and **6**) in a MeOH/H_2O (60:40) solution in the other compartment. Both solutions were layered with EtOH. Red crystals were obtained after a week.

The data collections of the single crystals suitable for single X-ray were obtained using graphite monochromated Mo Kα radiation

Table 1
Crystallographic data and refinement parameters for ligands the 5,6-bistosyl-1,10-phenanthroline (**1**) 5,6-dibenzylthiol-1,10-phenanthroline (**2**) and for the complexes [Fe^{II}(phendtos)$_3$] (PF$_6$)$_2$ (**5**) and [Fe^{II}(phendbt)$_3$] (PF$_6$)$_2$ (**6**)

Compound	**1**	**2**	**5**	**6**
Formula	$C_{26}H_{20}N_2O_6S_2$	$C_{26}H_{20}N_2S_2$	$C_{78}H_{60}F_{12}FeN_6O_{18}P_2S_6$	$C_{78}H_{60}F_{12}FeN_6P_2S_6$
Formula weight (g mol^{-1})	520.56	424.56	1907.47	1619.53
Crystal system, space group	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1/c$	orthorhombic, *Pbcn*	monoclinic, $P21/n$
a (Å)	9.5073(15)	15.9858(7)	10.5444(7)	19.7632(7)
b (Å)	13.4731(19)	8.2106(3)	31.955(2)	32.8181(14)
c (Å)	18.112(2)	16.2844(8)	24.2972(16)	22.7482(9)
β (°)	90	107.749(2)	90	108.128(2)
V (Å^3); *Z*	2320.0(6); 4	2035.64(15); 4	8186.9(9); 4	14021.9(10); 4
ρ_{calc} (Mg/m^3); μ (mm^{-1})	1.490; 0.278	1.385; 0.278	1.548; 0.477	1.534; 0.523
F(000)	1080	888	3896	6640
Crystal size (mm)	0.4 × 0.3 × 0.08	0.35 × 0.30 × 0.10	0.28 × 0.20 × 0.16	0.20 × 0.08 × 0.04
θ Range (°	1.88–25.99	2.63–25.35	2.56–25.35	1.65–25.46
Collected *hkl*	$-11 \leqslant h \leqslant 1$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 22$	$-18 \leqslant h \leqslant 18$, $-9 \leqslant k \leqslant 4$, $-15 \leqslant l \leqslant 18$	$-11 \leqslant h \leqslant 12$, $-38 \leqslant k \leqslant 38$, $-29 \leqslant l \leqslant 26$	$-23 \leqslant h \leqslant 23$, $-39 \leqslant k \leqslant 39$, $27 \leqslant l \leqslant 27$
Reflections collected	2888	6984	65 100	141 228
Independent reflections [R_{int}]	2850 [0.0136]	3443 [0.0292]	7482 [0.0831]	25 790 [0.2857]
Completeness to θ (%)	25.99, 99.7	25.35, 92.7	25.35, 99.7	25.46, 99.2
Maximum and minimum transmission	0.9992 and 0.9831	0.9727 and 0.9090	0.9276 and 0.8781	0.9794 and 0.9026
Data/restraints/parameters	2850/0/325	3443/0/271	7482/13/559	25 790/0/1891
Goodness-of-fit on F^2	1.037	1.027	1.100	0.855
Final *R* indices [$I > 2\sigma I$)]	R_1 = 0.0382, wR_2 = 0.0793	R_1 = 0.0423, wR_2 = 0.0992	R_1 = 0.0697, wR_2 = 0.1865	R_1 = 0.0838, wR_2 = 0.1514
R indices (all data)	R_1 = 0.0584, wR_2 =0.0851	R_1 = 0.0670, wR_2 = 0.1075	R_1 = 0.1160, wR_2 = 0.2070	R_1 = 0.2602, wR_2 = 0.1924
Largest difference in peak and hole (e Å^{-3})	0.192 and −0.226	0.510 and −0.336	0.702 and −0.799	0.844 and −0.781

($\lambda = 0.71073$ Å). Crystallographic data of **1** were collected at 294 K on Enraf-Nonius CAD4 diffractometer in the $\omega - 2\theta$ scan mode. Empirical absorption correction (ψ-scans) and data reduction were performed with WINGX suite of programs [6].

Crystallographic data for compounds **2**, **5**, **6** were collected on a Bruker AXS APEX CCD area detector diffractometer equipped with an Oxford Cryosystems low-temperature device at 130 K (**2**) and 150 K (**5** and **6**) in the ω and ϕ scans mode. A semi empirical absorption correction was carried out using SADABS [7]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [8].

The structures were solved by direct methods using SIR 97 [9] and refined by full matrix least-squares methods with the SHELXL 97 [10] program using the WINGX software package.

For **6** the crystals obtained were of poor diffraction quality, which results in a low percentage (35%) of observed data [$I > 2\sigma(I)$], even those, the number of reflections was enough for a satisfying structure refinement and unambiguously determination of the geometry of the complex, which is of interest for the present discussion.

In **5** one of the phenyl groups is disordered and in **6** one of the PF_6 anion is also disordered, we tried without success to applied disorder models but it was not possible to achieve a good structure solution refinement. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP3 [11] and MERCURY 1.4.2 [12]. A summary of the crystal data, structure solution and refinement are given in Table 1.

3. Results and discussion

3.1. Synthesis

Different synthetic strategies can be envisaged for the preparation of 5,6-dithiosubstituted-1,10-phenanthroline dithio-diazo ligands. As possible starting materials for these preparations both 5,6-dione-1,10-phenanthroline [4] and 5,6-dibromo-1,10-phenanthroline [5] (**4**) were considered as candidates.

However several of these approaches proved ineffective in our hands:

(1) Starting with the 5,6-dione-1,10-phenanthroline the thionation with P_4S_{10} or Lawesson's reagent [13,14] in the appropriated refluxing solvent proved to be ineffective, even after addition of a nickel chloride solution possibly leading directly to the bisdithiolene complex.

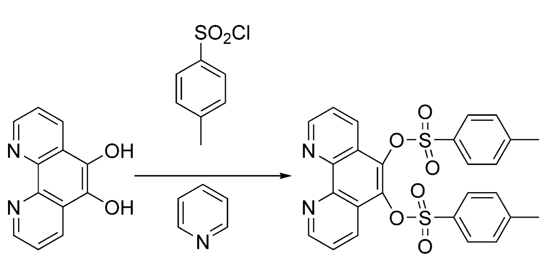
(2) As an alternative, also starting from the 5,6-dione-1,10-phenanthroline, it was envisaged the preparation of the 1,10-phenanthroline-5,6-bistosyl (**1**) via the corresponding dihydroxide [3] (**3**) compound treated with toluenesulfonyl chloride (Scheme 2). The preparation of (**1**) was achieved in good yield as demonstrated by single crystal X-ray structure analyses as well as by ^{1}H and ^{13}H NMR and elemental analyses.The tosyl groups on **1** could be good leaving groups for future nucleophilic aromatic substitution reactions. In spite of the successful preparation of **1** this compound proved to be ineffective for subsequent nucleophilic substitution reactions either with dithiooxamide for the obtention of the corresponding dithiol, or with potassium trithiocarbonate or sodium trithiocarbonate for the obtention of the corresponding 1,3-dithiole-2-thione. We also tried with **1**, without success, two further nucleophilic substitutions with either isopropyl mercaptan, or with benzyl mercaptan aiming at the obtention of the corresponding 5,6-dithiosubstituted 1,10 phenanthrolines.

(3) Starting from 5,6-dibromo-1,10-phenanthroline [5] (**4**) procedures based on the creation of the aryl-sulfur bond including nucleophilic aromatic substitutions, either with isopropyl mercaptan, or with benzyl mercaptan and also treatment of aryl lithium with sulfurated electrophiles, were first tried however all proved unsuccessful. The 5 and 6, 1,10-phenanthroline positions seem to be inactivated for the direct nucleophilic substitution as well as for the treatment of aryllithium with sulfurated electrophiles.

A successful synthesis to obtain the 5,6-dithiosubstituted phenanthroline was the synthesis of 5,6-dibenzylthiol-1,10-phenanthroline (**2**), achieved in good yield starting from **4** by a palladium cross-coupling catalyzed reaction with benzylthiol in the presence of a base and using as catalyst the $Pd_2(dba)_3$/DPEphos system (PDE = bis-[2-(diphenylphosphino)phenyl]ether) (Scheme 3). The compound **2** was unambiguously identified and characterized by single crystal X-ray diffraction, ^{1}H and ^{13}H NMR and elemental analysis.

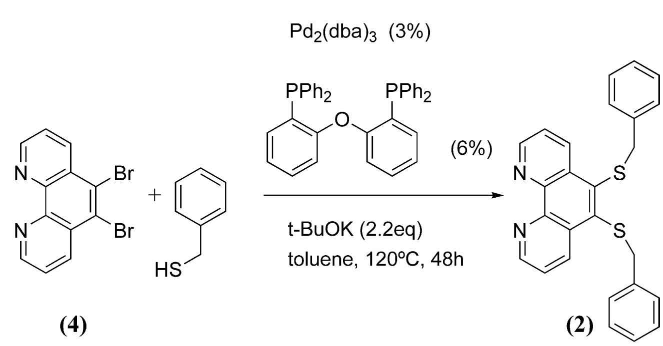
This Pd-catalyzed cross coupling reaction is related to the one introduced by Migita in 1980 between aryl bromides and thiols [15] for which since then various efficient catalytic systems using bidentate phosphines have been described [16]. Our protocol for preparing **2** involves the deprotonation of the benzylthiol with *t*-BuOK, followed by heating, in refluxing toluene, the resulting potassium benzylthiolate with **4** in the presence of $Pd_2(dba)_3$/DPEphos. Compound **2** can be used as precursor to prepare the corresponding thio-azo ligand. Preliminary experiments aimed at deprotecting the thiolate function have shown that the Pyridine/Na treatment[17] is efficient to generate the 1,2-dithiolate function and the thereof transition metal complexes can be obtain. However, this requires an effective control of the coordination ability to different poles, as it will be published subsequently.

In this work, the diimine function coordination ability of these substituted phenanthroline ligands was explored by the synthesis of the iron(II) complexes **5** and **6** using standard conditions for the



(3) **(1)**

Scheme 2. Synthesis of 5,6-bistosyl-1,10-phenanthroline (**1**).



(4) **(2)**

Scheme 3. Synthesis of 5,6-dibenzylthiol-1,10-phenanthroline (**2**).

preparation of Fe(II) phenanthroline complexes. The elemental analyses of the two complexes are consistent with a 1:2 anion:cation stoichiometry, as confirmed by the X-ray crystal structure determination, indicating Fe(II) in spite of starting from $FeCl_3$.

3.2. Crystal structure

Compounds **1**, **2**, **5** and **6** have been characterized by single crystal X-ray diffraction technique. The ORTEP views of these compounds are shown in Figs. 1–4. Crystallographic data, selected bond angles and distances are given in Tables 1–3.

The compound **1** crystallizes in the orthorhombic system, $P2_12_12_1$ space group. Its asymmetric unit consists of one molecule shown in Fig. 1. The 1,10-phenanthroline core of the molecule and the two oxygen in the 5,6-substituted positions are almost planar (Rms deviation of fitted atoms = 0.0341 Å). The two tosyl groups are tilted 45.76(7)° and 26.30(8)° in opposite directions with respect to the 1,10-phenanthroline core plane, and the other bond distances and angles assume standard values (see Table 2).

The compound **2** crystallizes in the monoclinic system, $P2_1/c$ space group and the asymmetric unit contains one molecule (Fig. 2). Also in this compound the 1,10-phenanthroline core of

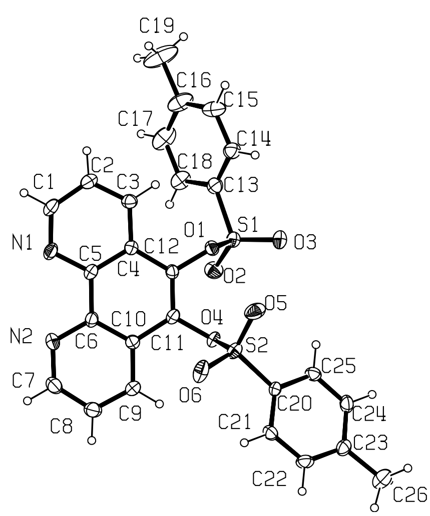


Fig. 1. ORTEP diagram of **1** drawn at a 40% probability level.

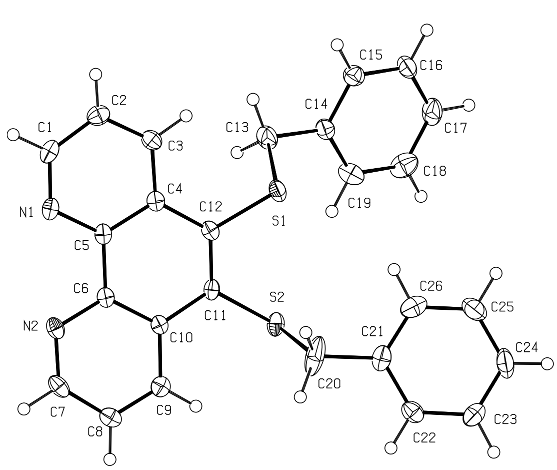


Fig. 2. ORTEP diagram of **2** drawn at a 40% probability level.

the molecule and the two sulfur atoms in the 5,6 positions are almost planar (Rms deviation of fitted atoms = 0.1027 Å). The two benzyl groups are tilted 14.56(9)° and 17.98(10)° with respect to the 1,10-phenanthroline core plane. Bond lengths and angles assume standard values (see Table 2).

The compound **5** crystallizes in the orthorhombic system, *Pbcn* space group, with the iron atom lying on a twofold axis. The asymmetric unit has one half of the $[Fe^{II}(phdtos)_3]^{2+}$ cation and two PF_6^- anions (see ORTEP view Fig. 3). One of the 1,10-phenanthroline

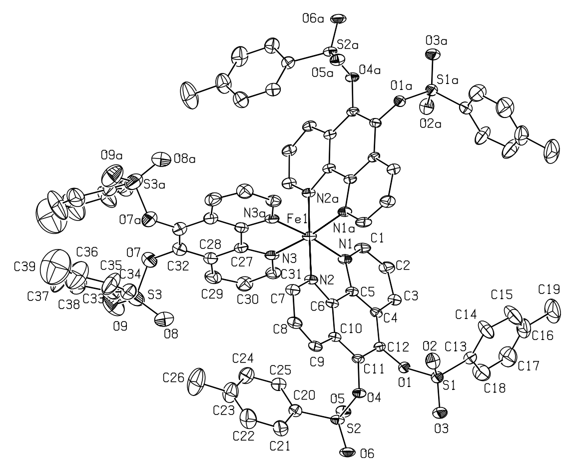


Fig. 3. ORTEP diagram of $[Fe(phdtos)_3]^{2+}$ cation in **5** drawn at a 30% probability level. *Symmetry code*: #*a*: $-x + 2, y, -z + 3/2$.

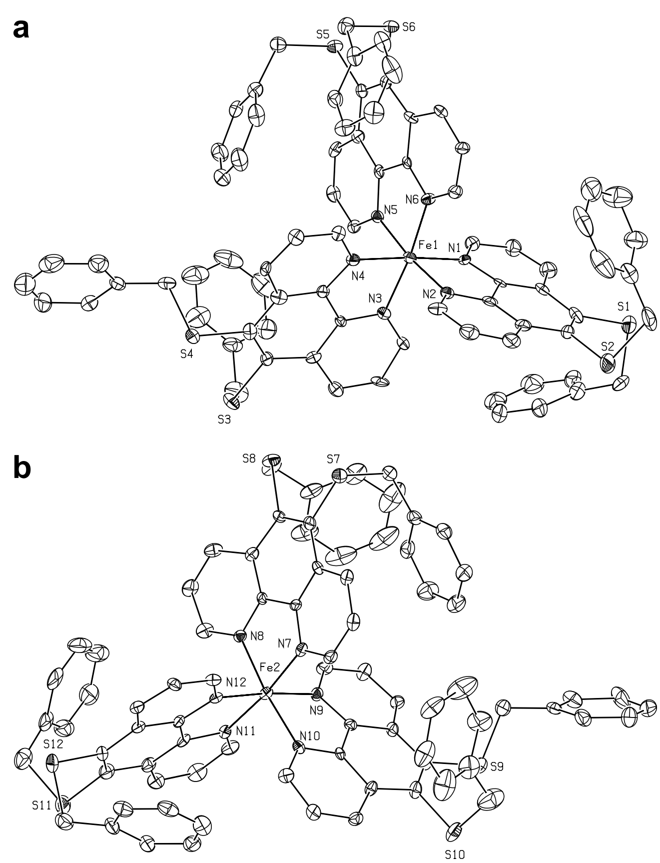


Fig. 4. ORTEP diagram of the two $[Fe(phdbt)_3]^{2+}$cations in the asymmetric unit of **6** drawn at a 40% probability level.

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

Bond lengths	Compound **1**	Compound **2**	Torsion angles	Compound **1**	Compound **2**
N(1)–C(1)	1.327(5)	1.323(3)	C10–C11–C12–C4	4.18(53)	−5.41(34)
N(1)–C(5)	1.367(4)	1.379(3)	O4–C11–C12–O1	1.27(50)	
N(2)–C(7)	1.321(5)	1.326(3)	S2–C11–C12–S1		−13.49(28)
N(2)–C(6)	1.353(5)	1.345(3)	C4–C12–O1–S1	−96.13(32)	
C(5)–C(6)	1.436(5)	1.451(3)	C10–C11–O4–S2	−91.96(32)	
C(12)–O(1)	1.398(4)		C13–S1–C12–C4		−70.05(21)
C(11)–O(4)	1.405(4)		C20–S2–C11–C10		−87.39(21)
S(1)–C(12)		1.763(2)			
S(2)–C(11)		1.800(2)			
Bond angles			Bond angles		
C1–N1–C5	116.47(29)	118.82(20)	C6–N2–C7	117.62(32)	115.83(20)
N1–C5–C6	117.98(29)	119.48(20)	N2–C6–C5	118.71(32)	116.49(20)

core units is almost planar (Rms deviation of fitted atoms = 0.0167 Å), the two other phenanthroline cores present a slight deviation from planarity (Rms deviation of fitted atoms = 0.0561 Å). As the uncoordinated ligand, the two tosyl groups are tilted, in opposite directions, with respect to the phenanthroline core plane 28.59(24)° in the ligand containing N3 and 28.16(16)° and 53.77(14)° on the two other ligands containing N1 and N2. The dihedral angles between the phenanthroline cores are 85.32(5)° and 88.07(5)°. The bond distances and angles of the coordinated ligands in complex **5** do not assume relevant deviation from the compound **1** values, except in the fact that the tosyl groups have different tilted directions and the associated torsion angles are necessarily different.

The compound **6** crystallizes in the monoclinic system, in the $P2_1/n$ space group. The asymmetric unit contains two independent cations $[Fe(phdbt)_3]^{2+}$ and four anions PF_6^- (see ORTEP view Fig. 4). In the Fe1 cation, one of the coordinated phenanthroline cores is almost planar (Rms deviation of fitted atoms 0.023 Å, for the ligand containing N1 and N2) and the two others present small deviation from planarity (Rms deviation of fitted atoms 0.104 and 0.061 Å, for the ligands containing N3–4 and N5–6, respectively). The Fe2 cation presents a similar planarity (Rms deviation of fitted atoms 0.121, 0.090 and 0.023 Å, for the ligands containing N7–8, N9–10, N11–12).

In each cation of **6** only one of the coordinating ligands has the 5,6-disubstituted groups tilted towards opposite sides of the core mean plane. In the Fe1 cation, two of the ligands have the benzyl groups tilted towards the same side of the core mean plane 61.3(2)°, 22.8(2)° and 30.7(2)°, 35.8(2)°. The other ligand has the two benzyl groups tilted towards opposite sides of the core mean plane, with angles of 36.8(2)° and 43.0(3)°. In Fe2 cation, the correspondent angles are 54.5(2)°, 35.8(2)° and 34.2(2)°, 63.3(2)° for the groups tilted towards the same side and 40.0(2)°, 31.6(2)° for the groups tilted towards opposite sides. Similarly to complex **5**, for **6** bond distances and angles of the ligands do not assume relevant deviations from the corresponding values in compound **2**. Also the benzyl groups have different tilted directions and the associated torsion angles are necessarily different.

A common characteristic of the crystal structures of **5** and **6** is the occurrence of parallel cation chains. However they have different packing patterns of anionic and cationic units (Figs. 5 and 6). Whereas in **6**, sheets of cationic layers alternate with anionic ones, in **5** there is not a so clear segregation of cations and anions. In all cases, due to the bulky substituted ligands the iron–iron distances are very large and the shortest Fe–Fe distance in both compounds is 10.5 Å.

The infinite chains of $[Fe(L)_3]^{2+}$ (L = **1** and **2**) complexes in **5** and **6** are shown in Figs. 7 and 8. These chains in **6** are composed of two crystallographic distinct complexes while those of **5** are made of only one complex. The shortest Fe–Fe distance within a chain is 12.2 Å for compound **5** and 10.5 Å for compound **6**.

Within the chains is possible to observe several short contacts but none of them correspond to π–π interactions. In compound **5**, hydrogen bonds between oxygen atoms of the tosyl groups and hydrogen atoms in the phenanthroline rings, O3···H30#*f* 2.327(4) Å, hydrogen bonds between oxygen atoms of the tosyl groups and hydrogen atoms of other tosyl group, O5···H25#*f* 2.601(3) Å, O8···H18#*f* 2.649(5) Å, and also a O···C short contact between a oxygen atom of a tosyl group and a phenanthroline carbon O3···C30#*f* 3.080(7)Å, #*f* = $2 - x, -y, 1 - z$ (see supplementary material SM1).

The short intrachain contacts in **6** are between sulfur and phenanthroline carbon atoms S3···C130#*b* 3.492(8) Å, #*b* = $-1 + x, y, z$; S5···C82#*a*, 3.487(22) Å, S5···C139#*a* 3.487(21) Å, S7···C1#*a* 3.483(18) Å, S8···C1#*a* 3.404(20) Å, S7···C58#*a* 3.434(16) Å, $a = x, y, z$. Between phenanthroline carbon atoms and benzyl carbon atoms C49···C132#*b* 3.393(11) Å. Hydrogen bonds between sulfur and phenanthroline rings S3···H130#*b* 2.7391(21) Å, S6···H139#*a* 2.836(19) Å, S8···H1#*a* 2.697(24) Å, S10··· H10#*c* 2.7785(22) Å, $c\# = 1 + x, y, z$. Hydrogen mediated short contacts between benzyl groups C50···H151#*b* 2.897(13) Å and C51···H151#*b* 3.822(16) Å (see supplementary material SM2).

Although the mean Fe–N distances and the N–Fe–N angles are in the range usually found in other iron-phenanthroline derivatives [18] there are deviations from a regular octahedron more clearly denoted by other structural parameters. Shortest and longest Fe–N distances are 1.967(4) and 1.989(3) Å in compound **5** and 1.953(5) and 1.983(5) Å in compound **6**. This distortion is not merely an elongation and compression along an axis, as the angles between the phenanthroline moieties differ also from orthogonality, attaining values as low as 82.1(2)° both in **5** and **6**.

The comparison of the N–C bonds lengths in the free ligands and in these coordinating the Fe atom does not reveal any significant change within experimental uncertainty.

Magnetic susceptibility measurements[1] of the **5** and **6** compounds in the 4–300 K range indicate a diamagnetic behavior, indicative of the low spin $S = 0$ state as expected for Fe(II) complexes in an octahedral coordinating geometry.

These results show that the coordination distortion observed is not significant in order to allow an intermediate $S = 1$ spin state, as

[1] Magnetic susceptibility measurements were performed using a longitudinal Faraday system (Oxford Instruments) with a magnetic field of 5 T and gradient field of 1 T/m in a polycrystalline sample (~20 mg) placed inside a previous calibrated thin wall Teflon bucket. The force was measured with a microbalance (Sartorius S3D-V). Magnetization data were corrected for contributions due to the sample holder and core diamagnetism, estimated from tabulated Pascal constants as -11.8×10^{-4} and -9.5×10^{-4} emu/mol for **5** and **6**, respectively.

Table 3
Bond lengths d (Å) and angles ω (°) in the coordination polyhedron of the Fe atom

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
*Compound **5***					
Fe(1)–N(1)	1.970(4)	Fe(1)–N(3)	1.967(4)		
Fe(1)–N(2)	1.989(3)				
N(1)–C(1)	1.338(6);	N(1)–C(5)	1.357(5);		
N(2)–C(7)	1.346(6);	N(2)–C(6)	1.356(5);		
N(3)–C(31)	1.333(6)	N(3)–C(27)	1.342(6)		
Angle	**ω (°)**	**Angle**	**ω (°)**	**Angle**	**ω (°)**
N(3)#a–Fe(1)–N(3)	83.5(2)	N(1)#a–Fe(1)–N(1)	90.3(2)	N(3)#a–Fe(1)–N(2)	91.52(15)
N(3)#a–Fe(1)–N(1)#a	93.44(16)	N(3)#a–Fe(1)–N(2)#a	89.34(15)	N(3)–Fe(1)–N(2)	89.34(15)
N(3)–Fe(1)–N(1)#a	172.96(14)	N(3)–Fe(1)–N(2)#a	91.52(15)	N(1)#a–Fe(1)–N(2)	97.08(14)
N(3)#a–Fe(1)–N(1)	172.96(14)	N(1)#a–Fe(1)–N(2)#a	82.10(14)	N(1)–Fe(1)–N(2)	82.10(14)
N(3)–Fe(1)–N(1)	93.44(16)	N(1)–Fe(1)–N(2)#a	97.08(14)	N(2)#a–Fe(1)–N(2)	178.8(2)
C(1)–N(1)–C(5)	116.7(4);	C(7)–N(2)–C(6)	116.2(4);	C(31)–N(3)–C(27)	118.7(4)
#a −x + 2, y, −z + 3/2					
Bond	**d (Å)**	**Bond**	**d (Å)**	**Bond**	**d (Å)**
*Compound **6***					
Fe(1)–N(2)	1.953(5)	Fe(1)–N(4)	1.981(5)	Fe(2)–N(7)	1.970(5)
Fe(1)–N(1)	1.968(5)	Fe(1)–N(5)	1.981(5)	Fe(2)–N(10)	1.973(5)
Fe(1)–N(3)	1.971(5)	Fe(2)–N(11)	1.967(5)	Fe(2)–N(8)	1.980(5)
Fe(1)–N(6)	1.981(5)	Fe(2)–N(12)	1.968(5)	Fe(2)–N(9)	1.983(5)
N(1)–C(1)	1.319(8)	N(2)–C(10)	1.339(8)	N(3)–C(27)	1.334(8)
N(1)–C(5)	1.370(8)	N(2)–C(6)	1.371(8)	N(3)–C(31)	1.350(8)
N(4)–C(36)	1.338(8)	N(5)–C(53)	1.332(7)	N(6)–C(62)	1.312(8)
N(4)–C(32)	1.375(7)	N(5)–C(57)	1.376(7)	N(6)–C(58)	1.365(7)
N(7)–C(77)	1.339(8)	N(8)–C(86)	1.325(8)	N(9)–C(103)	1.354(8)
N(7)–C(81)	1.374(7)	N(8)–C(82)	1.348(7)	N(9)–C(107)	1.368(7)
N(10)–C(112)	1.314(8)	N(11)–C(130)	1.315(7)	N(12)–C(139)	1.339(7)
N(10)–C(108)	1.367(8)	N(11)–C(134)	1.378(8)	N(12)–C(135)	1.375(8)
Angle	**ω (°)**	**Angle**	**ω (°)**	**Angle**	**ω (°)**
N(2)–Fe(1)–N(1)	82.7(2)	N(2)–Fe(1)–N(5)	173.5(2)	N(7)–Fe(2)–N(10)	93.7(2)
N(2)–Fe(1)–N(3)	91.5(2)	N(1)–Fe(1)–N(5)	93.2(2)	N(11)–Fe(2)–N(8)	92.6(2)
N(1)–Fe(1)–N(3)	93.5(2)	N(3)–Fe(1)–N(5)	93.9(2)	N(12)–Fe(2)–N(8)	91.0(2)
N(2)–Fe(1)–N(6)	92.6(2)	N(6)–Fe(1)–N(5)	82.3(2)	N(7)–Fe(2)–N(8)	82.2(2)
N(1)–Fe(1)–N(6)	92.0(2)	N(4)–Fe(1)–N(5)	87.5(2)	N(10)–Fe(2)–N(8)	173.8(2)
N(3)–Fe(1)–N(6)	173.5(2)	N(11)–Fe(2)–N(12)	82.3(2)	N(11)–Fe(2)–N(9)	95.3(2)
N(2)–Fe(1)–N(4)	96.9(2)	N(11)–Fe(2)–N(7)	173.5(2)	N(12)–Fe(2)–N(9)	175.4(2)
N(1)–Fe(1)–N(4)	175.7(2)	N(12)–Fe(2)–N(7)	93.8(2)	N(7)–Fe(2)–N(9)	88.9(2)
N(3)–Fe(1)–N(4)	82.2(2)	N(11)–Fe(2)–N(10)	91.8(2)	N(10)–Fe(2)–N(9)	82.1(2)
N(6)–Fe(1)–N(4)	92.3(2)	N(12)–Fe(2)–N(10)	94.0(2)	N(8)–Fe(2)–N(9)	93.1(2)
C(1)–N(1)–C(5)	115.5(6)	C(27)–N(3)–C(31)	116.8(5)	C(53)–N(5)–C(57)	117.0(6)
C(10)–N(2)–C(6)	116.2(6)	C(36)–N(4)–C(32)	117.0(6)	C(62)–N(6)–C(58)	118.0(6)
C(77)–N(7)–C(81)	116.3(6)	C(86)–N(8)–C(82)	117.6(5)	C(103)–N(9)–C(107)	116.7(6)
C(112)–N(10)–C(108)	118.5(6)	C(130)–N(11)–C(134)	116.6(6)	C(139)–N(12)–C(135)	117.6(6)

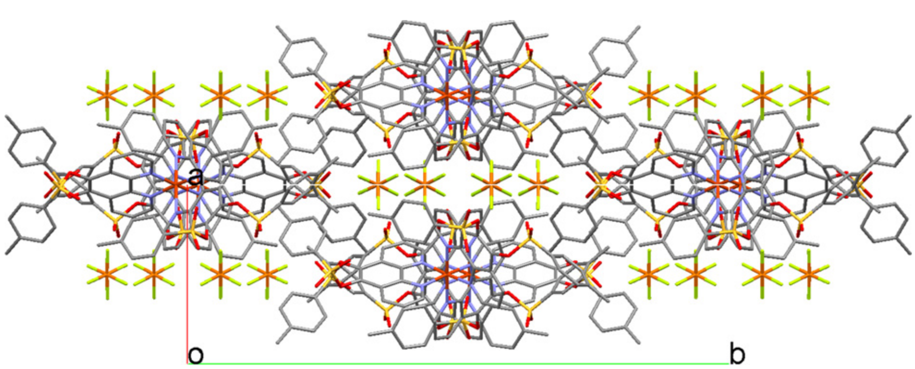


Fig. 5. Crystal structure of **5**, viewed along the *c*-axis.

it has been shown to occur in cases of more severely distorted hexacoordinated complexes. Several examples of iron (II) complexes with substituted phenanthrolines are known with this intermediate spin state [19], usually in square planar or heavily distorted hexacoordinated complexes. Examples of iron(II) complexes, where the metal atom is coordinated to six nitrogen atoms of bipyridine ligands, exhibiting magnetic moments varying with temperature and whose interpretation was based in a two-step transition involving also a $S = 1$ state, are also known [18c]. However the present complexes apparently are not so significantly, distorted from the ideal octahedral geometry to allow such intermediate spin state.

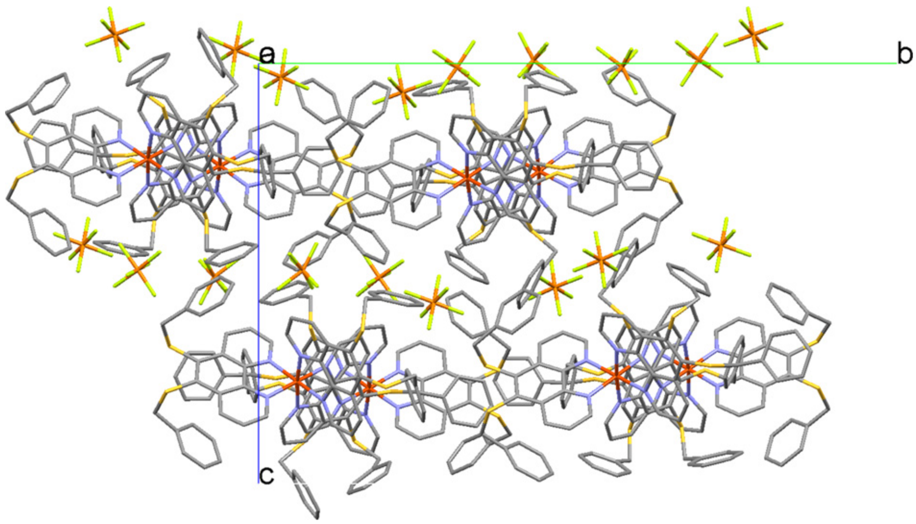


Fig. 6. Crystal structure of **6**, viewed along the *a*-axis.

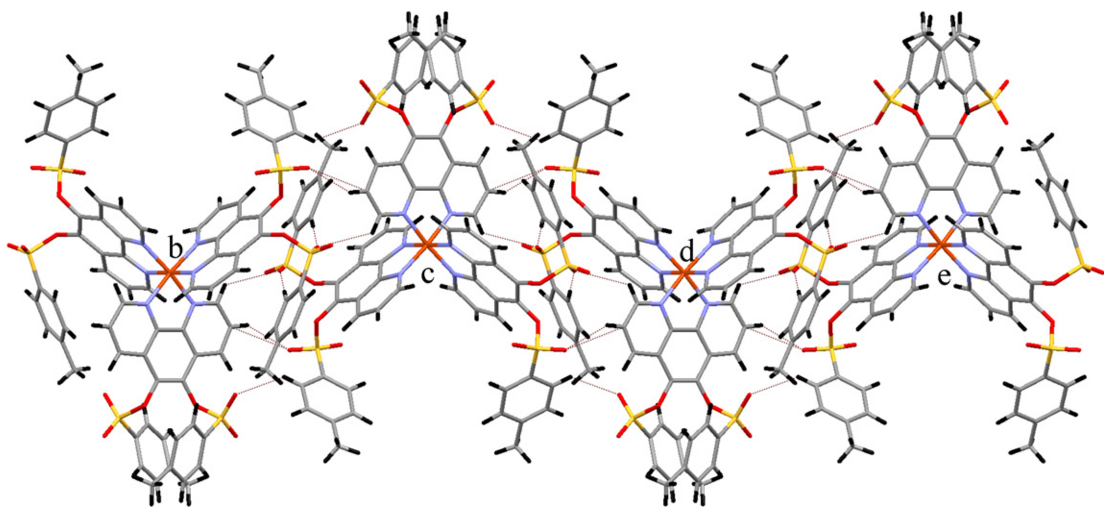


Fig. 7. Infinite chain of $[Fe(phdtos)_3]^{2+}$ complexes in compound **5**. View perpendicular to *a*-axis. [*Symmetry codes*: (b) $1-x$, $-y$, $1-z$; (c) $-1+x$, y, z; (d) $1-x$, $-y$, $2-z$; (e) $-1+x$, y, $1+z$].

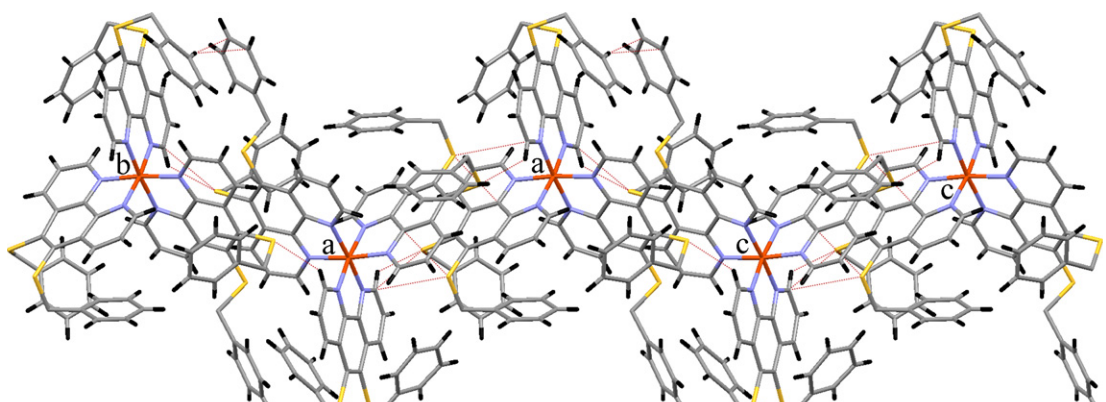


Fig. 8. Infinite chain of $[Fe(phdbt)_3]^{2+}$ complexes in compound **6**. View perpendicular to the *c*-axis. [*Symmetry codes*: (a) x, y, z; (b) $-1+x$, y, z; (c) $1+x$, y, z].

4. Conclusion

In summary, we achieved the synthesis of two new 5,6-substituted-1,10-phenanthrolines. Particularly, we have developed a convenient method for preparing sample quantities of the 5,6-dibenzylthiol-1,10-phenanthroline in two steps from commercially available phenanthroline. This is the first example of a cross-coupling reaction with a 5,6-dihalo-1,10-phenanthroline, achieving a new thio-azo ligand precursor, which can be explored in subsequent work for the preparation of thio-azo ligands. Preliminary experiments have shown that is possible to generate the 1,2 dithiolate function and the thereof transition metal complexes can be obtained. However, this requires an effective control of the coordination ability to different poles. In this report, we have used the diimine function coordination ability of the 5,6-disubstituted-1,10-phenanthroline ligands, and these two new phenanthroline ligands allowed for the preparation of $[Fe(phdtos)_3](PF_6)_2$ and $[Fe(phdbt)_3](PF_6)_2$ complexes.

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Appendix A. Supplementary data

CCDC 601085, 601086, 656658 and 656659 contain the supplementary crystallographic data for **1**, **2**, **5** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.03.016.

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