The preparation and characterization of 5,6-substituted-1,10-phenanthrolines, phdtos = 5,6-bistosyl-1,10-phenanthroline (1) and phdbt = 5,6-dibenzylthiol-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)\((\text{phdtos})_3\)]\((\text{PF}_6)_2\) (5) and [Fe(II)\((\text{phdbt})_3\)]\((\text{PF}_6)_2\) (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-dibenzylthiol-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)(\text{phdtos})_3][\text{PF}_6]_2 (5) and [Fe(II)(\text{phdbt})_3][\text{PF}_6]_2 (6).

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 13C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; 1H and 13C chemical shifts are given in ppm and were referenced with the residual solvent resonances relative to SiMe₄. 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-toluene-sulfonyl 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
Scheme 1. 5,6-Substituted-1,10-phenanthrolines.

poured into ice (1 dm³). 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_{32}O_{4}N_{2}: C, 75.373 MHz, CDCl₃): δ 42.172, 123.287, 130.293, 136.334, 137.116, 139.626, 146.202, 150.681.

2.2. [Fe(phentos)] PF₆₂ (5)
To a suspension of 5,6-bis(benzyl-1,10-phenanthroline (1) (3 equiv., 24.5 mg; 0.471 mmol) in 20 ml of a MeOH/H₂O (60/40) solution was added a MeOH/H₂O (50/50) solution of FeCl₃–6H₂O (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/H₂O (50/50) solution of NaPF₆ (3 equiv., 79.1 mg; 0.471 mmol) was added. The above reaction mixture was left in the refrigerator for several hours. A red precipitate 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_{6}O_{18}P_{2}S_{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%.

2.2.4. [Fe(phenbt)] PF₆₂ (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_{28}H_{32}F_{2}FeN_{6}O_{18}P_{2}S_{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/CH₂Cl₂ solution and by slow diffusion of hexane into a CH₂Cl₂ 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 NaPF₆ solution in MeOH/H₂O (50:50) was placed in one compartment of a H cell and Fe(L)₃ (L = 5 and 6) in a MeOH/H₂O (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>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>6</th>
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<tr>
<td><strong>Formula</strong></td>
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<td>C_{26}H_{32}N_{2}S</td>
<td>C_{28}H_{32}F_{2}FeN_{6}O_{18}P_{2}S_{6}</td>
<td>C_{28}H_{32}F_{2}FeN_{6}O_{18}P_{2}S_{6}</td>
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<tr>
<td><strong>Formula weight (g mol⁻¹)</strong></td>
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<td>424.56</td>
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<td>orthorhombic, Pbcn</td>
<td>monoclinic, P21/n</td>
<td>monoclinic, P21/n</td>
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<td><strong>a (Å)</strong></td>
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<td>15.985(7)</td>
<td>10.544(7)</td>
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<tr>
<td><strong>b (Å)</strong></td>
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<td>8.2106(3)</td>
<td>31.935(2)</td>
<td>32.8181(14)</td>
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<tr>
<td><strong>c (Å)</strong></td>
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<td>16.284(4)</td>
<td>24.2972(16)</td>
<td>22.7482(9)</td>
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<tr>
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<td>1077.749(2)</td>
<td>108.128(2)</td>
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<td><strong>ρcalc (Mg/m³); μ (mm⁻¹)</strong></td>
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<td>1.385; 0.285</td>
<td>1.548; 0.477</td>
<td>1.534; 0.523</td>
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<td>**Crystal size (mm) 0.3–0.08</td>
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<td>0.35 ± 0.10</td>
<td>0.20 ± 0.02</td>
<td>0.20 ± 0.08</td>
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<tr>
<td>**Collect ed hkl ± 11 &lt; h &lt; 11</td>
<td>1.88–25.29</td>
<td>2.63–25.35</td>
<td>2.56–25.35</td>
<td>1.63–25.46</td>
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<td>7482 [0.0831]</td>
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<td>25.35, 99.7</td>
<td>25.46, 99.2</td>
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<td>**Maximum and minimum transmission 0.9992 and 0.9831</td>
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<td>0.9794 and 0.9026</td>
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<td>**Goodness-of-fit on F² 1.037</td>
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<td>1.100</td>
<td>1.100</td>
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<td>0.0838, wR₂ = 0.1514</td>
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<tr>
<td>**R indices (all data) 0.192 and –0.226</td>
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<td>0.702 and –0.799</td>
<td>0.844 and –0.781</td>
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(λ = 0.71073 Å). Crystallographic data of 1 were collected at 294 K on Enraf-Nonius CAD4 diffractometer in the ω – 2θ scan mode. Empirical absorption correction (v-scan) 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 > 2σ(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 PF6 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 ORTEP [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-diazole ligands. As possible starting materials for these preparations both 5,6-diene-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 P5S10 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-diene-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 1H and 13H 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 diithooxamide 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 phe- nanthrolines was the synthesis of 5,6-dibenzylthio-1,10-phenan- throline (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 Pd2(dba)3/DP Ephos system (PDE = bis-[2-(diphenylphosphino)phenyl]ether) (Scheme 3). The compound 2 was unambiguously identified and characterized by single crystal X-ray diffraction, 1H and 13H NMR and elemental analysis.

This Pd-catalyzed cross coupling reaction is related to the one introduced by Mignata 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 Pd2(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
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 FeCl₃.

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, P2₁2₁2₁ 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, P2₁/c space group and the asymmetric unit contains one molecule (Fig. 2). Also in this compound the 1,10-phenanthroline core of 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 45.76(7)° 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 PF₆⁻ anions (see ORTEP view Fig. 3). One of the 1,10-phenanthroline

![Fig. 1. ORTEP diagram of 1 drawn at a 40% probability level.](image1)

![Fig. 2. ORTEP diagram of 2 drawn at a 40% probability level.](image2)

![Fig. 3. ORTEP diagram of [Fe(II)(phdtos)₃]²⁺ cation in 5 drawn at a 30% probability level. Symmetry code: #a: -x + 2, y, -z + 3/2.](image3)

![Fig. 4. ORTEP diagram of the two [Fe(II)(phdtos)₃]²⁺ cations in the asymmetric unit of 6 drawn at a 40% probability level.](image4)
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 P2₁/n space group. The asymmetric unit contains two independent cations [Fe(phdbt)₃]²⁺ and four anions PF₆⁻ (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 other 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 0.023 Å, for the ligand containing N1 and N2) and the two others present small 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.

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⋯H30f 2.327(4) Å, hydrogen bonds between oxygen atoms of the tosyl groups and hydrogen atoms of other tosyl group, O5⋯H25f 2.601(3) Å, O6⋯H18f 2.649(3) Å, and also a O–C short contact between a oxygen atom of a tosyl group and a phenanthroline carbon O3⋯C30f 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⋯C130b 3.492(8) Å, #b = –1 + x, y, z; S5⋯C82a, 3.487(22) Å, S5⋯C139a 3.487(21) Å, S7⋯C1a 3.483(18) Å, S8⋯C1a 3.404(20) Å, S7⋯C58a 3.434(16) Å, a = x, y, z. Between phenanthroline carbon atoms and benzyl carbon atoms C49⋯C132b 3.393(11) Å. Hydrogen bonds between sulfur and phenanthroline rings S3⋯H100b 2.739(1) Å, S6⋯H139a 2.836(19) Å, S8⋯H1a 2.697(24) Å, S10⋯H10a 2.778(25) Å, c# = 1 + x, y, z. Hydrogen mediated short contacts between benzyl groups C50⋯H151b 2.897(13) Å and C51⋯H151b 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 in these coordinating the Fe atom does not reveal any significant change within experimental uncertainty.

The magnetic susceptibility measurements 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

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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 previously calibrated thin wall Teflon bucket. The force was measured with a microbalance (Sartorius S3V). Magnetization data were corrected for contributions due to the sample holder and core diamagnetism, estimated from tabulated Pascal constants as ~11.8 × 10⁻⁶ and ~9.5 × 10⁻⁶ emu/mol for 5 and 6, respectively.
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.

<table>
<thead>
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<th>$d$(Å)</th>
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<td>1.970(4)</td>
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<tr>
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<td>N(3)--C(31)</td>
<td>1.333(6)</td>
<td>N(3)--C(27)</td>
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Table 3
Bond lengths $d$(Å) and angles $\phi$(*) in the coordination polyhedron of the Fe atom

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<td>N(3)a--Fe(1)--N(3)</td>
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<td>N(1)a--Fe(1)--N(1)</td>
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<td>N(3)--Fe(1)--N(2)</td>
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<td>N(3)a--Fe(1)--N(1)</td>
<td>93.44(16)</td>
<td>N(2)a--Fe(1)--N(2)</td>
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</tr>
<tr>
<td>C(1)--N(1)--C(5)</td>
<td>116.7(4)</td>
<td>C(7)--N(2)--C(6)</td>
<td>116.2(4)</td>
</tr>
</tbody>
</table>

$\#a = x + 2, y, z + 3/2$

Fig. 5. Crystal structure of 5, viewed along the c-axis.
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 it is possible to generate the 1,2 dithio- 
lolate function and the thereof transition metal complexes can be 
obtained. However, this requires an effective control of the coordi-
nation 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 li-
gands allowed for the preparation of [Fe(phdtos)\textsubscript{3}][PF\textsubscript{6}]\textsubscript{2} and 
[Fe(phdbt)\textsubscript{3}][PF\textsubscript{6}]\textsubscript{2} complexes.

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Appendix A. Supplementary data

CCDC 601085, 601086, 656658 and 656659 contain the supple-
centary 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 Cen-
tre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-
033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data asso-
ciated with this article can be found, in the online version, at 

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