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Iron(II) complexes of hexaphenyl(1,2,5-thia/selenadiazolo)-porphyrazine: the direct replacement of Se by S in the 1,2,5-selenadiazole ring

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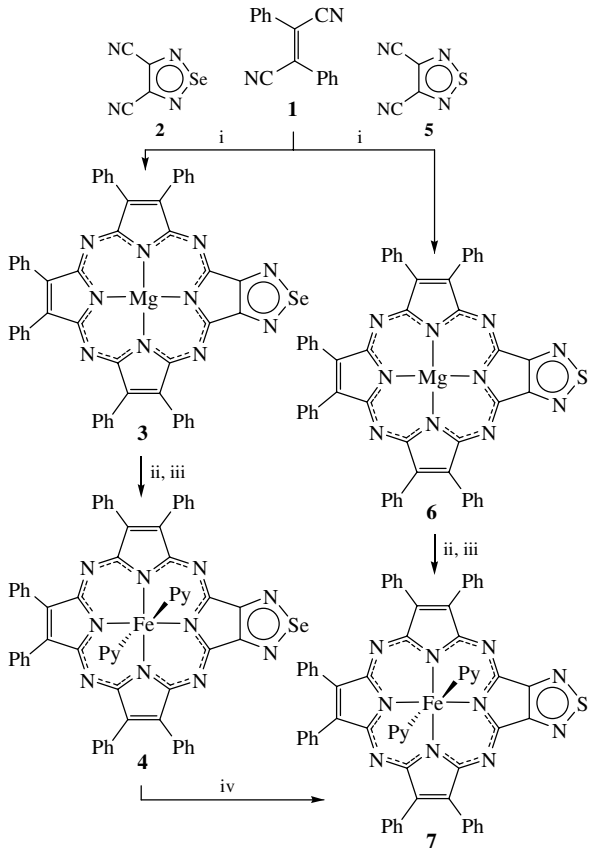
Iron(II) complexes of hexaphenyl(1,2,5-thia/selenadiazolo)porphyrazines have been prepared as bis(pyridine) adducts $[Py_2Fe(XN_2)PAPh_6]$ (X = S, Se) from the corresponding Mg^{II} complexes obtained by template co-cyclotetramerization of diphenylfumarodinitrile with 1,2,5-thia/selenadiazolo-3,4-dicarbonitriles, and the unusual direct replacement of Se by S in the reaction of $[Py_2Fe(SeN_2)PAPh_6]$ with H_2S has been observed.

The reductive opening of a 1,2,5-selenadiazole ring leads to vicinal diamino species,[1] and H_2S has been reported[2,3] as a convenient reducing agent. This reaction has been used[4–11] for the peripheral modification of porphyrazines with annulated 1,2,5-selenadiazole rings. In a common procedure, H_2S was bubbled through a pyridine solution of 1,2,5-selenadiazoloporphyrazines and, after a colour change, the reaction mixture was treated with aromatic aldehydes[9,10] or α-diketones[4,5,8] to give Schiff-base porphyrazines or pyrazinoporphyrazines, respectively. In the reaction with formic acid derivatives, acetylnitrite and thionyl chloride formation of imidazo-, triazolo- and 1,2,5-thiadiazoloporphyrazines was observed.[5] Since such a type of reactivity in condensation reactions is typical of aromatic *ortho*-diamines, the *in situ* formation of intermediate vicinal aminoporphyrazine species was postulated. However, attempts of their isolation and direct characterization were unsuccessful. In our study of porphyrazines with annulated 1,2,5-thia/selenadiazole rings, we prepared the Mg^{II} and Fe^{II} complexes of hexaphenyl(1,2,5-selenadiazolo)porphyrazine $[(H_2O)Mg(SeN_2)PAPh_6]$ **3** and $[Py_2Fe(SeN_2)PAPh_6]$ **4** and observed the unexpected replacement of the Se atom by S and the formation of the thiadiazole analogue $[Py_2Fe(SN_2)PAPh_6]$ **7** in the reaction with H_2S (Scheme 1).

Magnesium(II) complex **3** was prepared by the template co-cyclotetramerization of 1,2,5-selenadiazolo-3,4-dicarbonitrile **2** (1.6 mmol) with diphenylfumarodinitrile **1** (4.2 mmol) in the presence of Mg^{II} butoxide in Bu^nOH leading to a mixture of six Mg^{II} porphyrazines from which the target 1:3 product was isolated by column chromatography (Al_2O_3, second fraction eluted with CH_2Cl_2–EtOH, 100:1) as monoaqua complex $[(H_2O)Mg(SeN_2)PAPh_6]$ **3**.[†] The heating of this complex in DMF in the presence of a ten-fold excess of $FeSO_4{\cdot}5H_2O$ followed by precipitation with water and treatment of the residue with pyridine gave Fe^{II} bis(pyridinate), $[Py_2Fe(SeN_2)PAPh_6]$ **4**.[‡]



Scheme 1 *Reagents and conditions*: i, $Mg(OBu)_2$ in BuOH, reflux, 8 h; ii, $FeSO_4{\cdot}5H_2O$ in DMF, 140 °C, 2 h; iii, pyridine, 1 h; iv, H_2S in $CHCl_3$–pyridine (100:1).

[†] Mg^{II} complex **3**: yield 3.7%. MS (FAB), *m/z*: 899 (898 [M – H_2O]). UV-VIS (CH_2Cl_2, λ_{max}/nm): 373, 462, 565 (sh), 610, 676. IR (KBr, ν/cm^{-1}): 3060 (w), 1645 (m), 1600 (w), 1471 (m), 1446 (m), 1382 (m), 1367 (m), 1284 (m), 1243 (w), 1205 (w), 1145 (m), 1112 (m), 1074 (m), 1003 (m), 976 (vs), 914 (w), 885 (w), 874 (w), 806 (w), 770 (m), 746 (m), 694 (vs), 604 (m), 538 (m), 518 (w), 547 (w). ^{1}H NMR [$(CD_3)_2SO$, 373 K] δ: 8.2–8.3 (m 12H, *o*-Ph), 7.52–7.62 (m 12H, *m*-Ph), 7.67–7.75 (m, 6H, *p*-Ph).

[‡] Fe^{II} complex **4**: yield 82%. MS (Maldi-TOF), *m/z*: 930 (930 [M - 2Py]). UV-VIS [pyridine, λ_{max}/nm (lg ε)]: 353 (4.75), 460 (4.08), 502 (4.04), 547 (3.97), 597 (4.24). 655 (4.47). IR (KBr, ν/cm^{-1}): 3061 (w), 1699 (w), 1645 (m), 1603 (m), 1533 (w), 1484 (m), 1444 (m), 1385 (s), 1315 (w), 1277 (w), 1234 (w), 1157 (m), 1130 (m), 1003 (m), 986 (vs), 948 (m), 873 (w), 781 (w), 760 (m), 742 (m), 692 (vs), 655 (m), 607 (w), 592 (w), 460 (w). ^{1}H NMR ($CDCl_3$, 293 K) δ: 8.20–8.35 (m 12H, *o*-Ph), 7.35–7.50 (m, 12H, *m*-Ph), 7.50–7.60 (m, 6H, *p*-Ph), 6.13 (m, 2H, γ-Py), 5.29 (m, 4H, β-Py), 2.26 (m, 4H, α-Py). Found (%): C, 68.68; H, 3.87; N, 15.51. Calc. for $C_{62}H_{40}FeN_{12}Se$ (1087.88) (%): C, 68.45; H, 3.71; N, 15.45.

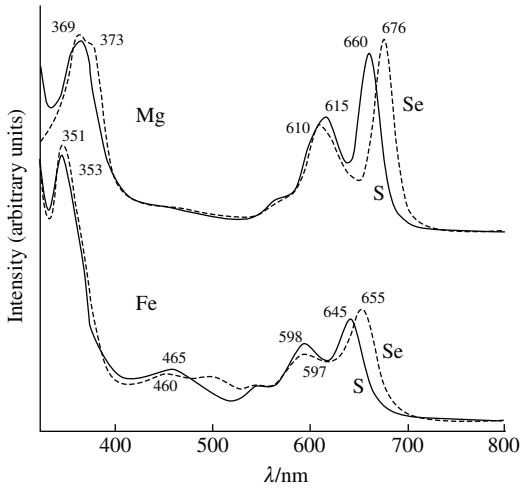


Figure 1 UV-VIS spectra of Mg^{II} complexes **3** and **6** and Fe^{II} complexes **4** and **7** in dichloromethane.

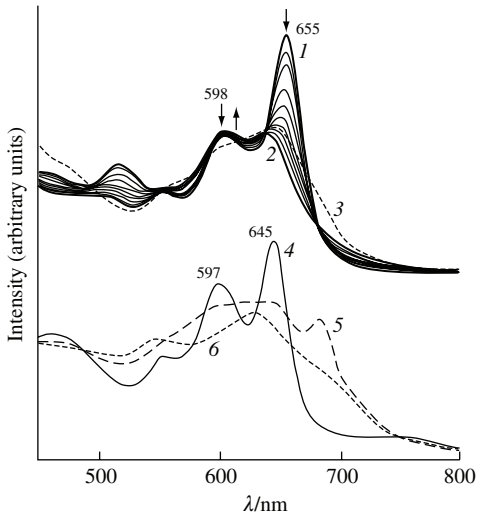


Figure 2 UV-VIS spectra of (*1*) $[Py_2Fe(SeN_2)PAPh_6]$ in $CHCl_3$ saturated with H_2S, (*1*→*2*) spectral changes observed 30 min after the addition of 1% pyridine, (*3*) after 12 h and (*4–6*) the spectra of fractions obtained in the course of chromatography.

In a similar way, using 1,2,5-thiadiazolo-3,4-dicarbonitrile **5** (2.2 mmol) instead of **2**, S-containing complexes $[(H_2O)Mg(SN_2)PAPh_6]$ **6**[§] and $[Py_2Fe(SN_2)PAPh_6]$ **7**[¶] were prepared.

In the mass spectra, the molecular ion peaks of the corresponding species without axial ligands are seen at *m*/*z* 851 and 899 for $[Mg(XN_2)PAPh_6]$ ($[M + H]^+$, X = S and Se) and *m*/*z* 882 and 930 for $[Fe(XN_2)PAPh_6]$ ($[M]^+$, X = S and Se). However, the presence of axially coordinated water and pyridine molecules is a common and characteristic feature of five-coordinated Mg^{II} and six-coordinated Fe^{II} porphyrazines, respectively, which are usually obtained under similar conditions.[4,7,12,13] The sharp lines observed in the ^1H NMR spectra of the Fe^{II} complexes indicate their diamagnetic low-spin state and the presence of two coordinated pyridine molecules is evidenced by their signals observed at ~2.3, 5.3 and 6.1 ppm for α-, β- and γ-pyridine protons, respectively. The slight down-field shift observed for the signal of *o*-Ph protons in the case of Fe^{II} complexes (8.3–8.4 ppm), as compared to Mg^{II} complexes (8.2–8.3 ppm), is due to the π-backbonding [$d_\pi(Fe) \rightarrow e_g^*(\pi)$] strengthening the macrocyclic π-ring current.

The UV-VIS spectra of complexes **3**, **4**, **6** and **7** (Figure 1) contain the split *Q*-band in the visible region, which is typical of porphyrazine complexes having C_{2v} symmetry of the π-chromophore. The maxima of the long-wave Q_1 component for Se-containing complexes **3**, **4** is shifted bathochromically, as compared to S-analogues **6**, **7**. This might indicate stronger π-acceptor properties of the thiadiazole rings due to stronger involvement in the π-conjugation of empty 3*d* orbitals of S than 4*d* orbitals of Se. The hypsochromic shift of the *Q* and Soret band maxima observed for Fe^{II} complexes **4** and **7**, as compared to Mg^{II} complexes **3** and **6**, is indicative of π backdonation [$d_\pi(Fe) \rightarrow e_g^*(\pi)$] leading to destabilization of the LUMO of the macrocycle. Additionally, characteristic charge-transfer bands are seen in the region 400–500 nm in the spectra of Fe^{II} complexes **4** and **7**.

The behaviour of Fe^{II} complexes **4** and **7** in the presence of H_2S was studied. The bubbling of H_2S in a solution of Fe^{II} complexes $[Py_2Fe(XN_2)PAPh_6]$ **4** and **7** in chloroform did not affect the UV-VIS spectra. However, addition of pyridine to the chloroform solution of the Se-containing complex **4** saturated with H_2S decreased the intensity and determined a hypsochromic shift of the Q_1 band to 636 nm and a bathochromic shift of the Q_2 band to 610 nm (Figure 2, curves *1*, *2*). Upon staying of the $CHCl_3$ solution, further spectral evolution was observed – the Q-band envelope was broadened and its maximum was shifted bathochromically to 645 nm (Figure 2, curve *3*).

The mass spectrum of the reaction product indicates the presence of several species, which give intense peaks at *m*/*z* 882 (100%) and 854 (40%) accompanied by lower intensity peaks at *m*/*z* 916, 930, 948, 965 and 996 (Figure 3). The peak at *m*/*z* 854 corresponds to the molecular ion of the expected diaminoporphyrazine $[FePAPh_6(NH_2)_2]$, while the main peak at *m*/*z* 882 indicates the replacement of the Se atom by S since it coincides with the molecular ion peak of the 1,2,5-thiadiazole derivative $[Fe(SN_2)PAPh_6]$. The minor peaks observed at higher *m*/*z* values correspond to the initial unreacted Se species $[Fe(SeN_2)PAPh_6]$ ($[M]^+$, *m*/*z* 930), its addition products $[M + H_2S]^+$ (964), $[M + H_2S_2]^+$ (996) and substitution products $[M - Se + H_2S_2]^+$ (916) and $[M - Se + H_2S_3]^+$ (948).

We attempted the chromatographic separation of the mixture (Al_2O_3, $CHCl_3$–MeOH) and obtained three fractions (Figure 2, curves *4–6*). The UV-VIS spectrum of the main first fraction (Figure 2, curve *4*) is identical to the spectrum of S-containing analogue **7** (Figure 1). The identity of the product in this fraction with **7** was further confirmed by the mass spectrum ($[M^+]$, *m*/*z* 882), IR spectra and elemental analysis. The second and third fractions contained small amounts of unstable products, which were characterised by UV-VIS spectra. Unlike the first fraction characterised by a well-resolved double *Q* band due to thiadiazole derivative **7**, for the second and third fractions, very broad absorption bands were observed at 550–700 nm (Figure 2, curves *5*, *6*). Such a kind of the *Q*-band broadening is characteristic of aminoporphyrazines for which two lowest π–π* transitions strongly overlap with the intense *n*–π* transitions of

[§] Mg^{II} complex **6**: yield 5.0%. MS (FAB), *m*/*z* (%): 851 (850 $[M - H_2O]$). UV-VIS (CH_2Cl_2, λ_{max}/nm): 369, 460, 561 (sh), 615, 660. IR (KBr, ν/cm^{-1}): 3060 (w), 1645 (m), 1600 (w), 1471 (m), 1446 (m), 1382 (m), 1367 (m), 1284 (m), 1243 (w), 1205 (w), 1145 (m), 1112 (m), 1074 (m), 1003 (m), 976 (vs), 914 (w), 885 (w), 874 (w), 806 (w), 770 (m), 746 (m), 694 (vs), 604 (m), 538 (m), 518 (w), 547 (w). ^1H NMR [$(CD_3)_2SO$, 373 K] δ: 8.18–8.26 (m, 12H, *o*-Ph), 7.66–7.77 (m, 12H, *m*-Ph), 7.50–7.62 (m, 6H, *p*-Ph).

[¶] Fe^{II} complex **7**: 85% yield from Mg^{II} complex **6**, 54% from Se precursor **4**. MS (Maldi-TOF), *m*/*z*: 882 (882 $[M - 2Py]$. UV-VIS [pyridine, λ_{max}/nm (lg ε)]: 351 (4.89), 465 (4.15), 551 (3.99), 598 (4.31), 645 (4.43). IR (KBr, ν/cm^{-1}): 3057 (w), 1699 (w), 1639 (m), 1601 (m), 1524 (m), 1487 (s), 1443 (s), 1385 (s), 1317 (w), 1244 (m), 1169 (m), 1132 (m), 1014 (m), 1003 (m), 986 (vs), 912 (m), 817 (m), 779 (w), 760 (m), 729 (w), 692 (vs), 657 (w), 626 (m), 569 (w), 534 (m), 482 (w). ^1H NMR ($CDCl_3$, 293 K) δ: 8.25–8.40 (m, 12H, *o*-Ph), 7.35–7.50 (m, 12H, *m*-Ph), 7.50–7.60 (m, 6H, *p*-Ph), 6.09 (m, 4H, α-Py), 5.27 (m, 4H, β-Py), 2.27 (m, 2H, γ-Py). Found (%): C, 71.78; H, 3.97; N, 16.09; S, 3.05. Calc. for $C_{62}H_{40}FeN_{12}S$ (1040.98) (%): C, 71.54; H, 3.87; N, 16.15; S, 3.08.

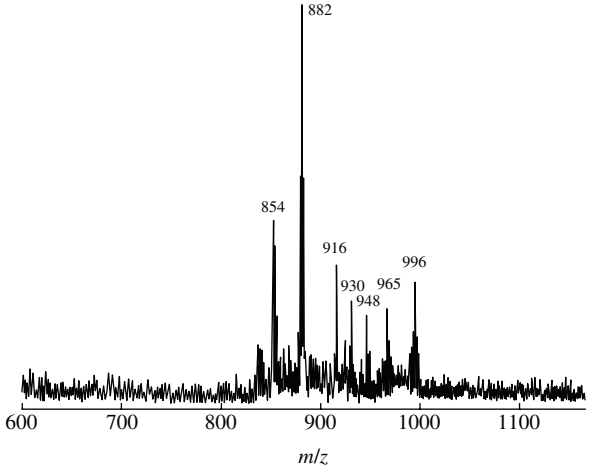


Figure 3 MALDI-TOF mass spectrum of the reaction mixture obtained in the reaction of $[Py_2Fe(SeN_2)PAPh_6]$ with H_2S in $CHCl_3$ containing 1% pyridine (corresponds to the UV-VIS spectrum *3* in Figure 2).

amino groups.[7,14] The spectrum of the third fraction is analogous to that reported[14] for the Zn^{II} complex of bis(dimethylamino)-hexapropylporphyrazine $[ZnPAPr_6(NMe_2)_2]$, in which n–π^* transitions of amino groups lead to a very similar broadening of the *Q* band. The spectrum of the second fraction is strikingly similar in the shape of the *Q* band to the spectrum observed in Zn^{II} hexapropylporphyrazine with annulated cyclic diamine $[ZnPAPr_6\{(NMeCHMe)_2CH_2\}]$,[7] in which less conformationally flexible amino groups incorporated in the cyclic fragment allow a better resolution of the *Q* band. Therefore, we suppose that the third fraction most likely contains porphyrazine $[Py_2FePAPh_6(NHY)_2]$ (Y = H, SH or SeH) with freely rotating amino groups, and the second contains the porphyrazine $[Py_2FePAPh_6\{(NH)_2X\}]$ with a cyclic six- or seven-membered fragment having two NH groups connected by a bridge (X) from S and Se atoms.

We can suggest that the replacement of the Se atom in the 1,2,5-selenadiazole ring of **4** by the S atom occurs through the nucleophilic addition of H_2S to the polar $^{\delta-}N{=}Se^{\delta'+}$ bonds leading first to mercapto derivative **8** and the following expansion of the five-membered ring in the tautomeric sulfide species **9** with the formation of six-membered S,Se-containing intermediate **10** (Scheme 2). This thiaselenadiazine derivative **10** can be stabilised by expulsion of H_2Se and aromatization to 1,2,5-thiadiazoloporphyrazine **7**. In the presence of excessive H_2S, further reduction with ring opening leads to diamino derivative **11**. Side reactions with the formation of cyclic six- and seven-membered species **12** (X = S, Se or absent) with two and even three S atoms are also very likely to occur.

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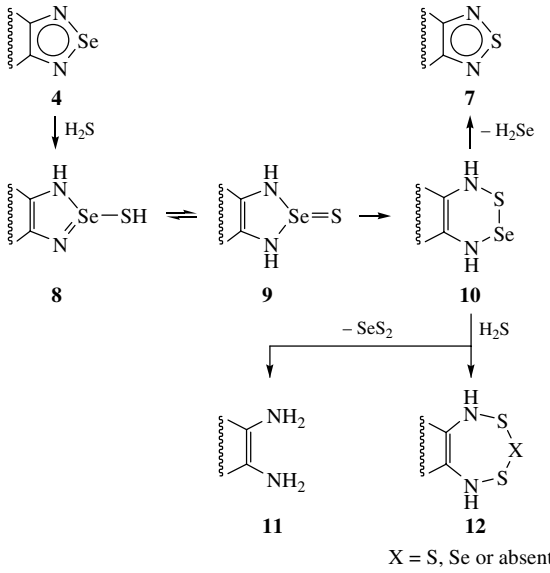

Scheme 2

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