New sulfur-oxygen mixed-donor ligand *N*,*N'*-dimethyl-piperazine-3-oxo-2-thione (Me₂pipto) and its Ni(II) and Fe(II) complexes†

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Structural and electronic features of the novel title sulfur-oxygen donor ligand Me$_2$pipto (1), are discussed in comparison with those of the corresponding dithione ligand Me$_2$pipdt. A tuning of the electronic and coordination properties of the ligand, relatable to the soft/hard power of the donor atoms, is achieved. Coordination properties have been checked towards Ni(II) and Fe(III) cations obtaining [Ni(Me$_2$pipto)$_3$](BF$_4$)$_2$ (2) and [Fe(Me$_2$pipto)$_3$](BF$_4$)$_2$ (4) complexes, which show significant differences when compared with the corresponding reaction products when using Me$_2$pipdt.

Due to the softness of the donor atoms and of the chelating properties of two vicinal sulfur atoms in the thioamidic groups, the ligand *N*,*N'*-dialkyl-piperazine-2-,3-dithione (R$_2$pipdt) has been shown to possess remarkable coordinative properties towards nd^8 transition metal ions. This capability has been employed to favour the dissolution of the crude metals, including the noble ones Pd and Pt, by using mild oxidation agents such as diiodine or triiodide.[1] The reaction products are salts, iodides-triiodides, of $[M(R_2pipdt)_2]^{2+}$ dications consisting of square-planar complexes. These dications, which can also be obtained by reacting a salt of the metal ion with R$_2$pipdt, show four reversible reduction processes and are the first example of positively charged metal-dithiolenes obtained by chemical methods.[2] These compounds have been employed as precursors to prepare mixed-ligand dithiolenes, and some of them show second-order nonlinear optical (NLO) properties at the molecular level[3] of interest for optoelectronic applications.[4] Optical properties are relatable to the electrodonating/withdrawing properties of the two ligands as well as the π-delocalization involving the dithiolene core (π-localised with a dithione-dithiolate description or π-delocalized dithiolene description for the two ligands).[5] Potential as a second-order NLO chromophore has been also observed in (Me$_2$pipdt)Mo(CO)$_4$.[6] A possible dithiolate or dithione behaviour of dithio-oxamide ligands in (R$_4$N$_2$C$_2$S$_2$)Mo(CO)$_2$(PR$_3$)$_2$[7] or in (R$_4$N$_2$C$_2$S$_2$)Mo(CO)$_4$[6,8] respectively, has been discussed on the basis of metrical parameters and theoretical calculations.

With the aim to tune the electronic structure, it seemed interesting to us to investigate the influence of varying the donor atom (O *vs.* S) on coordination and electrodonating/withdrawing properties of R$_2$pipdt. Here we report the synthesis and characterization of *N*,*N'*-dimethyl-piperazine-3-oxo-2-thione (Me$_2$pipto, **1**)† where one O atom substitutes one sulfur in Me$_2$pipdt. The X-ray structure‡ of Me$_2$pipto is reported in Fig. 1a. The short C–S (1.642(4) Å) and C–O (1.218(5) Å) bond distances are consistent with a double bond character. On the other hand, the trigonal planar geometry of the nitrogen atoms, the C(1)–C(2) long distance (1.538(6)), and the relatively short C–N distances (1.348(5) and 1.361(5) Å for C(1)–N(2) and C(2)–N(1), respectively) suggest a certain degree of delocalization of the double bonds over the nitrogen atoms. This type of structure exhibits similar features to analogous sulfur or oxygen donor ligands previously reported.[9,10] The cyclic voltammetry measurements§ performed on Me$_2$pipdt ligand in CH$_3$CN solution, show an irreversible oxidation process at +0.94 V and a *quasi*-reversible reduction one at −1.42 V. EPR spectroelectrochemical studies performed on this ligand, show that the unpaired electron of the reduced species is highly delocalized on the π-LUMO orbital.[11] In the case of Me$_2$pipto, both oxidation (+0.94 V) and reduction processes are irreversible, and the reduction wave falls at very negative potential (−1.92 V). Electronic structure DFT-calculations on Me$_2$pipto and Me$_2$pipdt

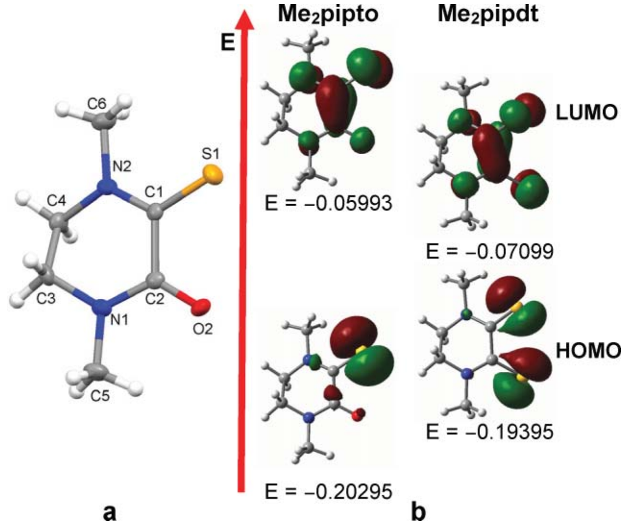

Fig. 1 (a) Molecular drawing of Me$_2$pipto with thermal ellipsoids at the 30% probability level. (b) Diagram of the relative energy levels and a drawing of the HOMO and LUMO for Me$_2$pito and Me2pidt. Energies in hartrees and isosurface contour value of 0.04 au are reported.

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† Electronic supplementary information (ESI) available: Synthesis and characterizations of **1**, **2** and **4**, Fig. S1–S2, Scheme S1 and RX data and selected bond lengths and angles (Tables S3-S6), calculated relative energies and selected bond distances (Table S1) and Mulliken spin densities (Table S2). CCDC reference numbers 771140–771142. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00803f

for comparison¶ have been performed. The obtained frontier orbitals (FO), which are energetically well separated from the lower and higher lying orbitals, are reported in Fig. 1b and Fig. S1†. As shown, the composition and energy of the FO in the two ligands are different, and relatable to the low contribution of the oxygen orbitals in Me$_2$pipto. Accordingly, differences in the electrochemical properties can be explained. In particular, the higher π-delocalization and lower energy of the LUMO in the Me$_2$pipdt compared to the corresponding orbital in Me$_2$pipto, are in agreement with observed reduction processes: *quasi*-reversible wave and lower potential for the former and irreversible for the latter. Moreover, a different behaviour in the coordination with metal-ions is predictable. In fact, by reacting Me$_2$pipto with a nickel salt, the pseudo-octahedral complex [Ni(Me$_2$pipto)$_3$](BF$_4$)$_2$ (**2**) has been obtained in spite of the square-planar complex [Ni(Me$_2$pipdt)$_2$](BF$_4$)$_2$[9a,b] obtained working at the same experimental conditions with Me$_2$pipdt. The molecular structure of the cation in **2** is shown in Fig. 2.‡ The metal exhibits an octahedral geometry achieved by three bidentate SO donor ligands. The disposition of the sulfur and oxygen atoms is such that the complex is in the *fac* configuration. The C–S and C–O bond distances are in the range 1.669(2)–1.676(2) Å and 1.241(2)–1.246(2) Å, respectively, suggesting a double bond character for these moieties. Nevertheless, the planar nature of the thioamide-like or amide-like functions within each ligand and the short C–N bonds of these groups (range 1.308(2)–1.321(2) Å) point to a certain amount of electron delocalization over the NCS or NCO atoms. As a consequence of the coordination, a decrease (increase) of CO and CS (CN) double bond character is observed with respect to the free ligand (see Scheme S1†). This is reflected by the shift of the ν(CO) and ν(CN) stretching vibrations to lower (1642 cm^{-1}) and higher (1559 cm^{-1}) frequencies, respectively, with respect to the free ligand (1669 and 1527 cm^{-1})‖. The smaller stabilization energy of the SO ligand compared to the dithione one, due to the reduced π-acceptor capability of the former, explains the different stoichiometries of the Ni complexes. In particular, in these cases, the π-back-donation from the metal *d*-orbitals to the sulfur's empty *d*-orbitals seems to play a crucial role. This is in agreement with the *fac* configuration of the complex, in fact, each sulfur is located *trans* to an oxygen atom, which can not compete for the metal's electrons. Further work to investigate the magnetic properties of this compound, as well as its potential to work as a precursor for mixed-ligand oxo-thione-dithiolate complexes, is foreseen.

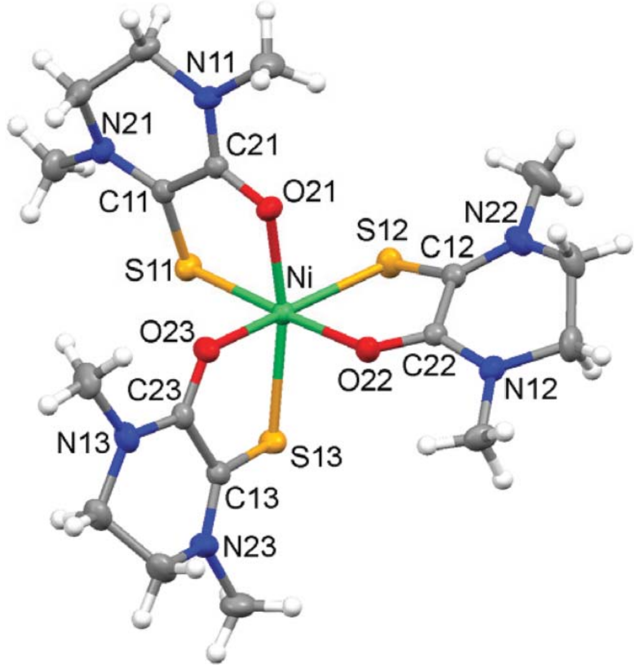

Fig. 2 Molecular drawing of **2** with thermal ellipsoids at the 30% probability level; the BF$_4^-$ counter-ions have been removed for clarity.

In addition, to further investigate the potential of this ligand in tuning the properties of selected metal complexes due to the soft/hard character of the donor atoms we have allowed Me$_2$pipto and Me$_2$pipdt to react with FeCl$_3$ in CH$_3$CN solution, under the same experimental conditions. The obtained products are: [Fe(Me$_2$pipto)$_2$Cl$_2$](BF$_4$) and [Fe(Me$_2$pipdt)$_3$](BF$_4$)$_2$ (**3**).[12] Using the sulfate-salt as the source of Fe(III) to avoid the presence of the more coordinating Cl$^-$ anion, the [Fe(Me$_2$pipto)$_3$](BF$_4$)$_2$ (**4**) complex was obtained. The crystal structure of **4** is shown in Fig. 3.‡ Three bidentate SO donor ligands define the octahedral geometry of the metal. The complex lies on a binary axis so that one ligand is found disordered in two equivalent positions. For both of the images, the disposition of the sulfur and oxygen atoms is such that the complex exhibits a *mer* configuration. The considerations of the ligand in the nickel complex (*e.g.* bond distances reflected by related vibrational markers) also apply in the iron case.

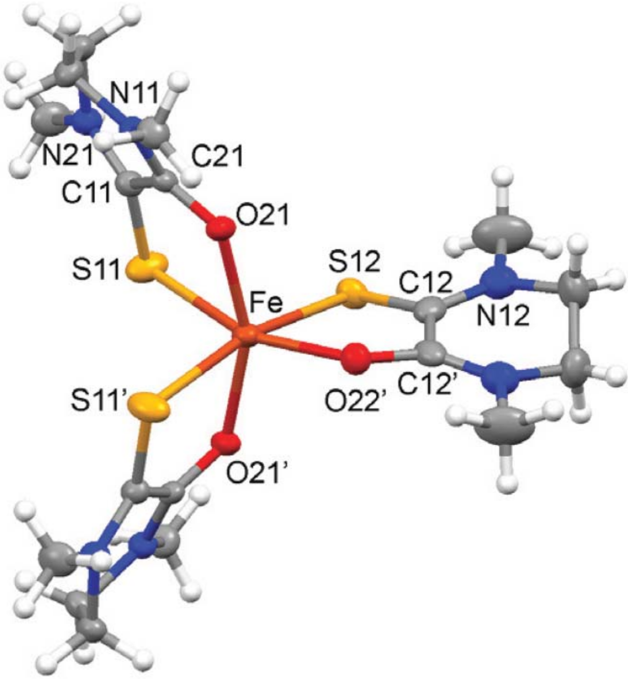

Fig. 3 Molecular drawing of **4** with thermal ellipsoids at the 30% probability level; the BF$_4^-$ anions have been removed for clarity. Selected bond lengths (Å): Fe–S(11) 2.465(2), Fe–O(21) 2.072(3), C(11)–S(11) 1.654(4), C(21)–O(21) 1.222(4), C(11)–C(21) 1.493(5), C(11)–N(21) 1.288(5). Symmetry code ' = 1 − x, y, $\frac{1}{2}$ − z.

Interestingly, the iron ion is reduced to the 2+ oxidation state and preliminary magnetic measurements on these complexes show that, in the 400–5 K range, Fe(II) exhibits a high spin state in **4**, but low-spin magnetic behaviour in $[Fe(Me_2pipdt)_3](BF_4)_2$ (**3**). The different magnetic behaviour can be explained by the difference in the π-acceptor capability of the ligands. In fact, in the case of the dithione the π-back-donation, which stabilizes the t_{2g} orbitals of the metal ion, is stronger than for the SO ligand, increasing the 10Dq separation energy between the *d*-orbitals and consequently stabilizing the low-spin state. To support this, a DFT study on complexes **3** and **4** was performed. In addition to the hybrid B3LYP functional, the pure OLYP functional was used due to its good performances in predicting the ground states of a number of iron complexes.[13,14] Accordingly, the geometries were optimized with the OLYP functional for the singlet (S = 0) and quintet (S = 2) states (see ESI†). From a comparison of the experimental and calculated bond distances, the preferred ground states for complexes **4** and **3** are the S = 2 and S = 0, respectively. With the OLYP functional, $[Fe(Me_2pipto)_3]^{2+}$ exhibits an energy preference for the S = 2 state over the S = 0 one of 60.14 kJ mol^{-1}, whereas $[Fe(Me_2pipdt)_3]^{2+}$ favours the S = 0 state over the S = 2 one by 31.88 kJ mol^{-1}. The spin density of **3** in the quintet state is located primarily on the iron atom and to a minor extent over the sulfur and oxygen atoms, Fig. 4. A different scenario is encountered when using the B3LYP functional, since it decisively favours the S = 2 state for both compounds. This is nevertheless in line with the property of this density functional, which tends to overstabilize high spin states. In order to obtain compounds that exhibit spin transition, experiments to prepare mixed iron complexes of these ligands in the 2 : 1 and 1 : 2 molar ratio are in progress. It can be anticipated that $[Fe(Me_2pipto)_2Cl_2](BF_4)$ will show high/low spin transition at low temperature.

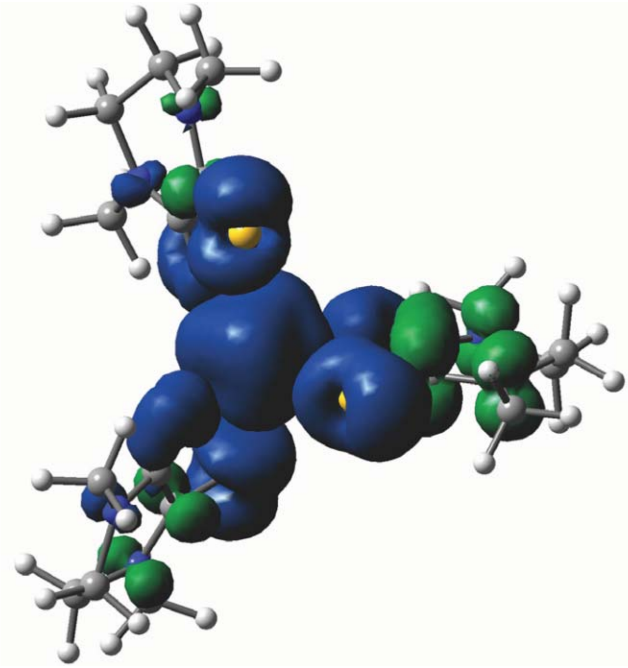

Fig. 4 Spin density contour plot for $[Fe(Me_2pipto)_3]^{2+}$ in the quintet spin state (S = 2). The isodensity value is 0.0008 a.u. (OLYP/6-311G(d)).

In conclusion, a novel sulfur-oxygen mixed donor ligand has been prepared and characterized. The results and theoretical calculations highlight the differences in the electronic structures of Me_2pipto and Me_2pipdt ligands and in their coordination properties towards metal ions, as shown in the cases reported here: high spin *vs.* low spin in the iron(II) case, and octahedral *vs.* square planar coordination in the nickel case.

Moreover the variation of the donor atom (O *vs.* S) will allow evaluation of the influence of charge-separated character by comparing the NLO-properties of mixed-ligand complexes of the Nickel-triad[15] based on dithiolate/R_2pipdt or R_2pipto ligands.

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Notes and references

‡ Crystal data for **1**: $C_6H_{10}N_2OS$, $M = 158.22$, orthorhombic, space group $Pna2_1$, $a = 9.758(4)$, $b = 6.731(3)$, $c = 11.686(6)$ Å, $V = 767.5(6)$ Å^3, $T = 293(2)$ K, $Z = 4$, 1067 measured reflections, 962 unique ($R_{int} = 0.0320$). $R_1 = 0.0431$ ($I > 2\sigma(I)$), $wR_2 = 0.0857$(all data); CCDC 771140. Crystal data for **2**: $C_{18}H_{30}B_2F_8N_6NiO_3S_3$, $M = 706.99$, monoclinic, space group $P2_1/n$, $a = 12.541(1)$, $b = 12.255(1)$, $c = 19.659(1)$ Å, $\beta = 101.198(3)°$, $V = 2963.9(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, 49228 measured reflections, 9916 unique ($R_{int} = 0.0355$). $R_1 = 0.0397(I > 2\sigma(I))$, $wR_2 = 0.1226$(all data); CCDC 771141. Crystal data for **4**: $C_{18}H_{30}B_2F_8FeN_6O_3S_3$, $M = 704.13$, monoclinic, space group $C2/c$, $a = 20.40(1)$, $b = 10.992(8)$, $c = 16.20(1)$ Å, $\beta = 129.60(2)°$, $V = 2799(3)$ Å^3, $T = 293(2)$ K, $Z = 4$, 13694 measured reflections, 2731 unique ($R_{int} = 0.0396$). $R_1 = 0.0547(I > 2\sigma(I))$, $wR_2 = 0.1702$(all data); CCDC 771142.

§ The cyclic voltammetry measurements were performed in CH_3CN solution, with Ag/AgCl 3 M as the reference electrode and ferrocene/ferrocenium couple (0.43 V in these conditions) as an internal standard.

¶ The results on Me_2pipdt are in agreement with those reported in ref. 6.

‖ Because of the presence of a strong broad peak centered near 1050 cm^{-1} for the BF_4^- anion, the peak of the ν(CS) stretching vibration can not be observed.

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