

Supplementary Material

New Sulphur-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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Experimental section

All the reagents and solvents were purchased from Aldrich and used without further purification.

Preparation

Me₂pipto (1). *Synthesis:* 3.00 g (21.1 mmol) of *N,N'*-dialkyl-piperazine-2-,3-dione and 5.12 g (12.6 mmol) of Lawesson's reagent (molar ratio 1:0.6) were placed at reflux in 300 ml of toluene until the color of the solution turned from pale yellow to light brown. The solvent was evaporated and the crude product washed several times with petroleum ether 40/60 and dissolved with hot ethanol. A crystalline yellow precipitate appeared and the precipitation was completed on cooling (-18 °C for three hours) by addition of diethyl ether. The product was collected by filtration and washed with cold EtOH (three times) and with diethyl ether (three times) (yield 1.98 g, 12.5 mmol; 59.3%). Analytical results are in accordance with the formula Me₂pipto. *Elemental Analysis:* calculated for C₆H₁₀N₂OS (158.22): C 45.55, H 6.37, N 17.71, S 20.27; found: C 45.32, H 6.77, N 17.73, S 20.55. *UV-vis* (in CH₃CN solution): λ/nm ($\epsilon/\text{mol}\cdot\text{cm}^{-1}\cdot\text{dm}^{-3}$) 310 ($7.35\cdot 10^3$); 265 ($4.65\cdot 10^3$). *FT-IR* (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2970(w); 2954(w); 2920(mw); 2878(w); 2859(w); 1669(vs); 1527(vs); 1487(s); 1453(s); 1453(s); 1429(ms); 1395(s); 1348(vs); 1260(s); 1199(s); 1151(m); 1046(mw); 1019(w); 955(s); 894(ms); 837(w); 762(s); 687(ms); 582(ms); 549(mw); 494(m); 420(ms).

[Ni(Me₂pipto)₃](BF₄)₂ (2). *Synthesis:* 80.0 mg (0.51 mmol) of **1** in 25 ml of CH₂Cl₂, yellow solution, was added drop-wise to a solution of NiCl₂·6H₂O (58.3 mg, 0.25 mmol) in EtOH (50 ml). After 1 hour of warming (60°C) and stirring, the solvent was evaporated and the obtained crude product dissolved with ethanol (30 ml) and filtered, then 55.0 mg of NaBF₄ in 50 ml of EtOH were added to the solution, and after 1 hour under stirring, 80 ml of diethyl ether were added. A crystalline green-yellow solid appeared 14 hours after, the precipitate was collected by filtration and washed with a cold H₂O/EtOH (1:1) mixture (once), acetone/diethyl ether (1:1, two times) and diethyl ether (three times) (yield 34.2 mg, $4.8\cdot 10^{-2}$ mmol; 38.7%). Analytical results are in accordance with the formula [Ni(Me₂pipto)₃](BF₄)₂. *Elemental Analysis:* calculated for C₁₈H₃₀N₆O₃S₃NiB₂F₈ (706.95): C 30.58, H 4.28, N 11.89, S 13.60; found: C 30.21, H 4.38, N 11.43, S 13.34. *UV-vis* (in CH₃CN solution): λ/nm ($\epsilon/\text{mol}\cdot\text{cm}^{-1}\cdot\text{dm}^{-3}$) 370 (sh); 310 ($2.10\cdot 10^4$); 275 ($1.90\cdot 10^4$). *FT-IR* (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2978(w); 2925(w); 1642(vs); 1559(vs); 1494(ms); 1443(mw); 1408(ms); 1368(s); 1263(ms); 1209(ms); 1159(ms); 1106(s); 1028(s); 963(m); 898(m); 830(w); 754(m); 696(m); 583(m); 562(m); 533(m); 521(m); 494(m); 448(m).

[Fe(Me₂pipto)₃](BF₄)₂ (3). *Synthesis:* 316.0 mg (2.0 mmol) of **1** in 40 ml of CH₃CN, yellow solution, was added drop-wise to a suspension of Fe₂(SO₄)₃.xH₂O (133.0 mg, 0.34 mmol) in the same solvent (50 ml); after adding few drops of H₂SO₄ 96% the solution turned orange. After the addition of 240 mg of NaBF₄ (2,2 mmol) the solution turned red-violet during the stirring at reflux (3 h). The solvent was evaporated and the crude product dissolved with CH₃CN (60 ml). This solution was filtered to separate a white solid, and Na₂SO₄ was added to remove water. The addition of THF caused the formation of a white precipitate that was removed before a drop-wise addition of diethyl ether; the formed lacquer, became slowly a crystalline solid that was recrystallized from acetone/Et₂O; the precipitate was collected by filtration and washed with diethyl ether (three times) (yield 55.4 mg, 0.078 mmol; 23.4%). Analytical results are in accordance with the formula [Fe(Me₂pipto)₃](BF₄)₂. *Elemental Analysis:* calculated for C₁₈H₃₀N₆O₃S₃FeB₂F₈ (704.11): C 30.70, H 4.29, N 11.94, S 13.66; found: C 31.00, H 3.91, N 11.94, S 13.30. *UV-vis* (in CH₃CN solution): λ/nm (ε/mol·cm⁻¹·dm⁻³) 530 (400); 430 (500); 310 (1.73·10⁴); 270 (1.63·10⁴). *FT-IR* (KBr): ν_{max}/cm⁻¹ 2930(w); 2859(vw); 1639(vs); 1558(vs); 1507(w); 1489(w); 1439(w); 1404(mw); 1369(m); 1262(w); 1208(mw); 1160(w); 1083(ms); 1054(s); 961(w); 896(w); 830(vw); 755(w); 695(w); 668(vw); 584(mw); 521(w); 501(vw); 418(m).

Measurements

Elemental analyses were performed by means of a Carlo Erba CHNS Elemental Analyzer Model EA1108. Electronic spectra (900–200 nm) were recorded on a Cary 5 spectrophotometer in CH₃CN solutions. I.R. spectrum (4000–400 cm⁻¹) was recorded with a Bruker IFS55 FT-IR Spectrometer on KBr pellets. Cyclic voltammograms were carried out with a *Princeton Applied Research* potentiostat-galvanostat model Versastat 3, by using a conventional three-electrode cell consisting of a platinum wire working electrode, a platinum wire as counter-electrode and Ag/AgCl in 3 M KCl solution, as reference electrode. The experiments were performed at room temperature (25°C), with the analyte in the concentration of 5·10⁻³ M, in dry and argon-degassed CH₃CN containing 0.1 mol dm⁻³ Bu₄NPF₆ as supporting electrolyte, at 100 mV s⁻¹ scan rate. Half-wave potential for ferrocene/ferrocenium couple (internal standard) is 0.43 V under the above conditions.

DFT calculations.

DFT calculations were carried out using the Gaussian 03 program suite.¹ Geometry optimization were performed for the Me₂pipto and Me₂pipdt ligands starting from X-ray geometries. The calculation were performed with the gradient-corrected hybrid density functional B3LYP^{2,3} and with the 6-31G(d) basis set.^{4,5} Molecular orbital diagrams were generated with the GaussView program.⁶ The geometry optimizations of [Fe(Me₂pipto)₃]²⁺ and [Fe(Me₂pipdt)₃]²⁺ were performed starting from the X-ray geometries for both the singlet (S=0) and quintet (S=2) states, using the pure density functional OLYP⁷ and the 6-31G(d) basis set. Vibrational frequencies were calculated at the same level of theory to ensure that the stationary points were true minima. Single point calculations were performed with the OLYP and B3LYP density functionals and with the 6-311G(d) basis set.

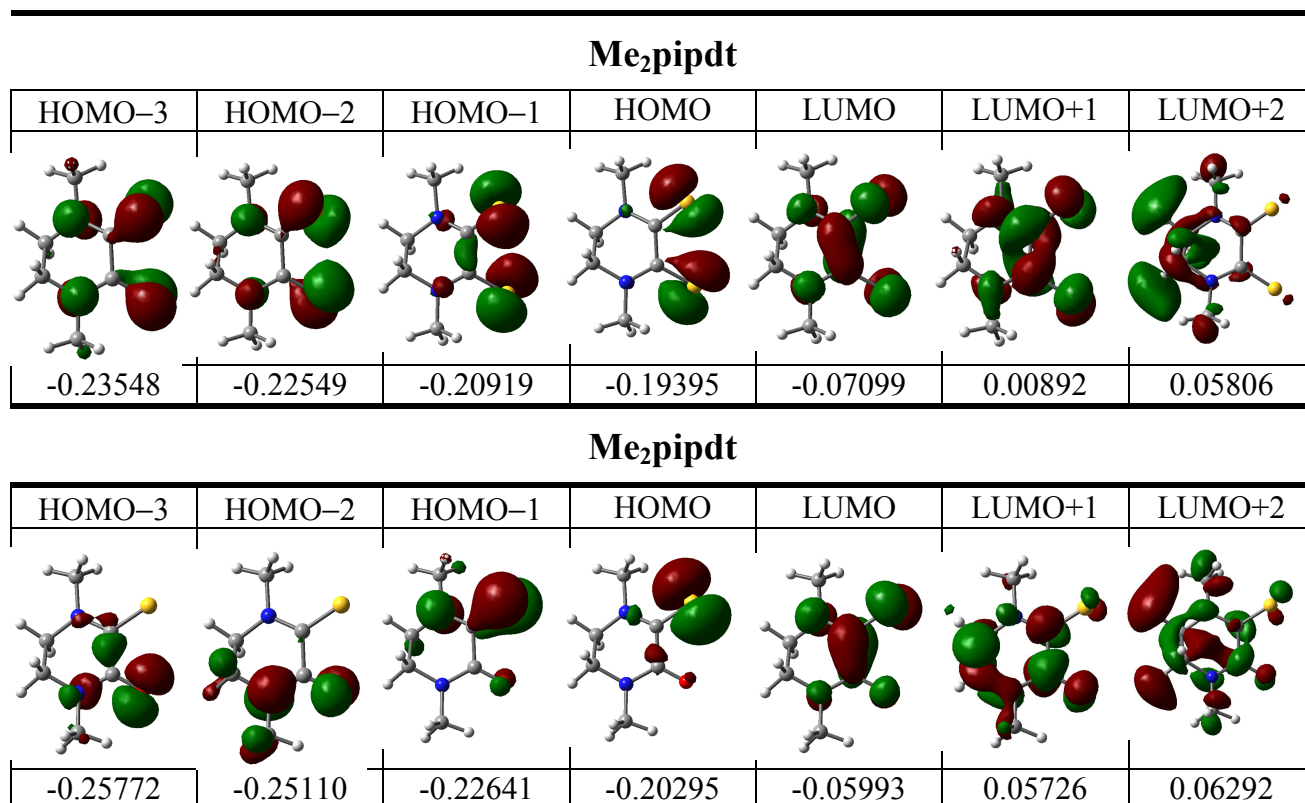


Fig. S1. Molecular orbital diagrams of Me₂pipto and Me₂pipdt with the isosurface plot at 0.04 a.u.. The MO energies are reported in hartrees. The larger HOMO-LUMO gap for the Me₂pipto is in agreement with the increased *hard* character of this ligand if compared to Me₂pipdt.⁸

Table S1. Relative energies (kJ/mol) and selected bond distances (Å) of [Fe(Me₂pipto)₃]²⁺ and [Fe(Me₂pipdt)₃]²⁺ in singlet and quintet spin states.

	X-ray	OLYP		B3LYP	
		S = 0	S = 2	S = 0	S = 2
Relative Energy					
[Fe(Me ₂ pipto) ₃] ²⁺		60.14	0	96.56	0
[Fe(Me ₂ pipdt) ₃] ²⁺		0	31.88	41.48	0
Bond distances					
[Fe(Me ₂ pipto) ₃] ²⁺					
Fe-O	2.041(6) ^a	1.932	2.126	-	-
	2.072(3)	1.973	2.105		
		1.935	2.056		
Fe-S	2.465(2) ^a	2.291	2.518	-	-
	2.511(3)	2.290	2.566		
		2.243	2.538		
[Fe(Me ₂ pipdt) ₃] ²⁺					
Fe-S	2.278(2) ^a	2.273	2.471	-	-
	2.291(2)	2.272	2.471		
	2.315(1)	2.270	2.513		
		2.276	2.543		
		2.275	2.543		
		2.272	2.512		

a: crystallographic symmetry elements reduce the number of independent parameters.

Table S2. Mulliken spin densities and $\langle S^2 \rangle$ expectation value of [Fe(Me₂pipto)₃]²⁺ and [Fe(Me₂pipdt)₃]²⁺ in the quintet spin state (S=2), basis set 6-311G(d).

		OLYP					B3LYP			
		Fe	O	S	$\langle S^2 \rangle$		Fe	O	S	$\langle S^2 \rangle$
[Fe(Me ₂ pipto) ₃] ²⁺	3.780	0.040	0.066	6.171	3.758	0.026	0.025	6.020		
		0.061	0.100	(6.001) ^a		0.030	0.061	(6.000) ^a		
		0.034	0.074			0.017	0.047			
[Fe(Me ₂ pipdt) ₃] ²⁺	3.666	-	0.112	6.242	3.722	-	0.011	6.021		
			0.081	(6.002) ^a			0.021	(6.000) ^a		
			0.068				0.037			
			0.112				0.011			
			0.068				0.021			
			0.081				0.037			

a: after annihilation of the first spin contaminant

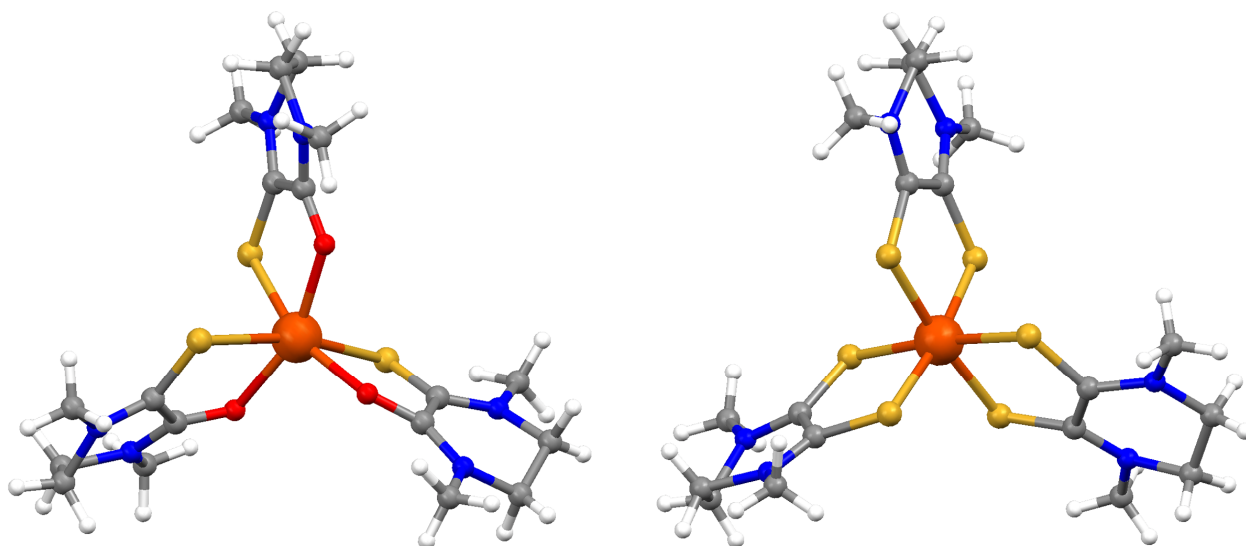
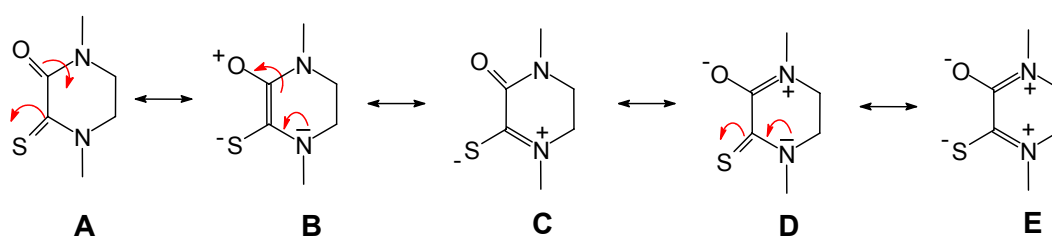


Fig. S2. Ball and stick drawing of the X-ray molecular structures of [Fe(Me₂pipto)₃]²⁺ (left) and [Fe(Me₂pipdt)₃]²⁺ (right) that were used for the DFT geometry optimizations.



Scheme S1. Resonance structures of R₂pipto ligand. When the ligand coordinates the structures C, D and E contribute more than in the free ligand.

X-ray crystallography

A summary of data collection and structure refinement for Me₂pipto (**1**), [Ni(Me₂pipto)₃](BF₄)₂ (**2**), and [Fe(Me₂pipto)₃](BF₄)₂ (**4**) are reported in Tables S1. Single crystal data were collected with a *Philips PW 1100* (**1**), with a *Bruker Smart APEXII* area detector diffractometer (**2**) and with a *Bruker AXS Smart 1000* (**4**). All data collection were performed with the Mo K α radiation ($\lambda = 0.71073$ Å). Cell constants of Me₂pipto were obtained by a least-square refinement of the setting angles of 24 randomly distributed and carefully centered reflections, whereas the unit cell parameters of [Ni(Me₂pipto)₃](BF₄)₂ and [Fe(Me₂pipto)₃](BF₄)₂ were obtained using 60 ω -frames of 0.5° width and scanned from three different zone of reciprocal lattice. The intensity data of **2** and **4** were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space.⁹ Absorption corrections were applied using the program NEWABS92 (Me₂pipto, min. and max. transmission factors: 0.905-1.000),¹⁰ and the program SADABS¹¹ (**2** and **4** with min. and max. transmission factors of 0.850-1.000 and 0.651-1.000, respectively). The structures were solved by direct methods (SIR97¹²) and refined on F^2 with full-matrix least squares (SHELXL-97¹³), using the Wingx software package.¹⁴ In the [Ni(Me₂pipto)₃](BF₄)₂ complex the BF₄⁻ counterions were both disordered in two positions and were refined with site occupancy factors of 0.68/0.32 and 0.55/0.45. The complex [Fe(Me₂pipto)₃](BF₄)₂ lie on a binary axis and one of the ligands is disordered in two equivalent positions in which the O and S atoms are exchanged. Non hydrogen atoms were refined anisotropically for all compounds, and the hydrogen atoms were placed at their calculated positions. Graphical material was prepared with the ORTEP3 for Windows¹⁵ and Mercury 2.0¹⁶ programs. CCDC 771140-771142 contain the supplementary crystallographic data for this paper.

Table S3. Summary of X-ray crystallographic data for **1**, **2** and **4**.

	Me ₂ pipto (1)	[Ni(Me ₂ pipto) ₃](BF ₄) ₂ (2)	[Fe(Me ₂ pipto) ₃](BF ₄) ₂ (4)
Empirical formula	C ₆ H ₁₀ N ₂ OS	C ₁₈ H ₃₀ B ₂ F ₈ NiN ₆ O ₃ S ₃	C ₁₈ H ₃₀ B ₂ F ₈ FeN ₆ O ₃ S ₃
Formula weight	158.22	706.99	704.13
Colour, habit	Yellow, block	Brown, block	Brown, prism
Crystal size, mm	0.43x0.40x0.30	0.47 x 0.31 x 0.16	0.55x0.45x0.30
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	9.758(4)	12.541(1)	20.40(1)
<i>b</i> , Å	6.731(3)	12.255(1)	10.992(8)
<i>c</i> , Å	11.686(6)	19.659(1)	16.20(1)
α, deg.	90	90	90
β, deg.	90	101.198(3)	129.60(2)
γ, deg.	90	90	90
<i>V</i> , Å ³	767.5(6)	2963.9(4)	2799(3)
<i>Z</i>	4	4	4
<i>T</i> , K	293(2)	293(2)	293(2)
ρ (calc), Mg/m ³	1.369	1.584	1.671
μ, mm ⁻¹	0.354	0.949	0.851
θ range, deg.	3.49 to 26.99	1.78 to 31.85	2.25 to 26.00
Rflcn collected	1067	49228 / 9916	13694 / 2731
Indep Rflcn (<i>R</i> _{int})	962 (0.0320)	9916(0.0355)	2731 (0.0396)
Abs. struct. Param.	-0.09(15)	-	-
GooF	1.005	1.004	1.075
<i>R</i> 1 [<i>I</i> >2σ(<i>I</i>)]	0.0431	0.0397	0.0547
<i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0738	0.1079	0.1429

$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR2 = \frac{[\sum (w(F_o^2 - F_c^2)^2)]}{\sum [w(F_o^2)^2]}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

Table S4. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for Me₂pipto (**1**).

S1	C1	1.642(4)	C1	N2	C4	122.4(4)	N1	C2	O2	122.3(4)
N2	C1	1.348(5)	C1	N2	C6	121.4(4)	N1	C2	C1	116.5(4)
N2	C4	1.469(6)	C4	N2	C6	115.9(4)	O2	C2	C1	121.3(4)
N2	C6	1.480(6)	C3	N1	C2	121.9(4)				
N1	C3	1.461(5)	C3	N1	C5	117.4(4)				
N1	C2	1.361(5)	C2	N1	C5	119.8(4)				
N1	C5	1.465(5)	S1	C1	N2	124.4(4)				
O2	C2	1.218(5)	S1	C1	C2	118.7(3)				
C1	C2	1.538(6)	N2	C1	C2	116.9(4)				
C4	C3	1.502(6)	N2	C4	C3	108.6(4)				
			N1	C3	C4	109.9(4)				

Table S5. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for [Ni(Me₂pipto)₃](BF₄)₂ (**2**).

Ni	S12	2.4174(6)	S12	Ni	S13	103.59(2)	C22	N12	C32	120.9(2)
Ni	S13	2.4150(7)	S12	Ni	S11	96.07(2)	C22	N12	C52	121.0(2)
Ni	S11	2.3839(5)	S12	Ni	O23	167.91(4)	C32	N12	C52	117.9(2)
Ni	O23	2.032(1)	S12	Ni	O21	88.69(4)	O22	C22	N12	123.0(2)
Ni	O21	2.051(1)	S12	Ni	O22	82.14(4)	O22	C22	C12	119.6(2)
Ni	O22	2.074(1)	S13	Ni	S11	93.46(2)	N12	C22	C12	117.4(2)
S12	C12	1.669(2)	S13	Ni	O23	82.76(4)	S12	C12	N22	125.9(2)
S13	C13	1.676(2)	S13	Ni	O21	167.55(4)	S12	C12	C22	116.8(1)
S11	C11	1.675(2)	S13	Ni	O22	88.03(4)	N22	C12	C22	117.3(2)
O23	C23	1.241(2)	S11	Ni	O23	93.77(4)	N11	C21	O21	122.1(2)
N11	C21	1.317(3)	S11	Ni	O21	83.01(4)	N11	C21	C11	117.8(2)
N11	C31	1.458(3)	S11	Ni	O22	177.90(4)	O21	C21	C11	119.8(2)
N11	C51	1.458(3)	O23	Ni	O21	85.55(5)	S11	C11	N21	123.8(1)
O21	C21	1.246(2)	O23	Ni	O22	87.88(5)	S11	C11	C21	117.6(1)
N22	C12	1.313(3)	O21	Ni	O22	95.84(5)	N21	C11	C21	118.5(2)
N22	C42	1.467(3)	Ni	S12	C12	96.31(7)	N11	C31	C41	111.3(2)
N22	C62	1.463(3)	Ni	S13	C13	96.53(7)	C23	N13	C33	121.3(2)
O22	C22	1.241(2)	Ni	S11	C11	96.73(6)	C23	N13	C53	119.3(2)
N21	C11	1.308(2)	Ni	O23	C23	122.1(1)	C33	N13	C53	119.0(2)
N21	C41	1.476(3)	C21	N11	C31	123.0(2)	S13	C13	C23	117.9(1)
N21	C61	1.456(3)	C21	N11	C51	119.6(2)	S13	C13	N23	124.6(2)
C23	N13	1.318(2)	C31	N11	C51	117.1(2)	C23	C13	N23	117.5(2)
C23	C13	1.520(3)	Ni	O21	C21	120.4(1)	N13	C33	C43	109.6(2)
N23	C13	1.316(3)	C12	N22	C42	120.0(2)	N21	C41	C31	111.0(2)
N23	C43	1.475(3)	C12	N22	C62	121.9(2)	N22	C42	C32	110.0(2)
N23	C63	1.466(3)	C42	N22	C62	117.9(2)	N12	C32	C42	109.6(2)
N12	C22	1.321(2)	Ni	O22	C22	120.1(1)	N23	C43	C33	110.4(2)
N12	C32	1.462(3)	C11	N21	C41	119.3(2)				
N12	C52	1.461(3)	C11	N21	C61	121.0(2)				
C22	C12	1.511(2)	C41	N21	C61	119.4(2)				
C21	C11	1.515(2)	O23	C23	N13	122.1(2)				
C31	C41	1.486(3)	O23	C23	C13	119.1(2)				
N13	C33	1.463(3)	N13	C23	C13	118.8(2)				
N13	C53	1.455(3)	C13	N23	C43	120.4(2)				
C33	C43	1.491(3)	C13	N23	C63	121.3(2)				
C42	C32	1.493(4)	C43	N23	C63	117.9(2)				

Table S6. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for [Fe(Me₂pipto)₃](BF₄)₂ (**4**).

C(11)	N(21)	1.288(5)	N(21)	C(11)	C(21)	117.0(3)	O(22)#1	Fe	O(21)#1	103.2(2)
C(11)	C(21)	1.493(5)	N(21)	C(11)	S(11)	124.9(3)	O(22)	Fe	O(21)#1	95.0(2)
C(11)	S(11)	1.654(4)	C(21)	C(11)	S(11)	118.1(3)	O(21)	Fe	O(21)#1	158.9(2)
C(12)	O(22)	1.243(7)	O(22)	C(12)	N(12)	138.3(5)	O(22)#1	Fe	S(11)	159.2(2)
C(12)	N(12)	1.278(6)	O(22)	C(12)	C(12)#1	103.7(4)	O(22)	Fe	S(11)	100.4(2)
C(12)	C(12)#1	1.483(9)	N(12)	C(12)	C(12)#1	117.8(3)	O(21)	Fe	S(11)	79.01(9)
C(12)	S(12)	1.672(5)	N(12)	C(12)	S(12)	112.0(4)	O(21)#1	Fe	S(11)	87.32(9)
C(31)	N(11)	1.445(5)	C(12)#1	C(12)	S(12)	130.2(2)	O(22)#1	Fe	S(11)#1	100.4(2)
C(31)	C(41)	1.467(6)	N(11)	C(31)	C(41)	109.7(3)	O(22)	Fe	S(11)#1	159.2(2)
C(32)	N(12)	1.421(7)	N(12)	C(32)	C(32)#1	110.4(4)	O(21)	Fe	S(11)#1	87.32(9)
C(32)	C(32)#1	1.46(1)	N(21)	C(41)	C(31)	109.4(3)	O(21)#1	Fe	S(11)#1	79.01(9)
C(41)	N(21)	1.450(5)	O(21)	C(21)	N(11)	123.3(3)	S(11)	Fe	S(11)#1	99.22(9)
C(51)	N(11)	1.432(5)	O(21)	C(21)	C(11)	118.2(3)	O(22)#1	Fe	S(12)#1	16.6(2)
C(52)	N(12)	1.431(7)	N(11)	C(21)	C(11)	118.5(3)	O(22)	Fe	S(12)#1	77.6(2)
C(61)	N(21)	1.439(5)	C(21)	N(11)	C(51)	121.6(3)	O(21)	Fe	S(12)#1	89.0(1)
C(21)	O(21)	1.222(4)	C(21)	N(11)	C(31)	121.2(3)	O(21)#1	Fe	S(12)#1	105.4(1)
C(21)	N(11)	1.297(5)	C(51)	N(11)	C(31)	116.8(3)	S(11)	Fe	S(12)#1	167.19(6)
O(21)	Fe	2.072(3)	C(12)	N(12)	C(32)	122.1(4)	S(11)#1	Fe	S(12)#1	84.69(9)
F(1)	B	1.361(7)	C(12)	N(12)	C(52)	120.9(6)	O(22)#1	Fe	S(12)	77.6(2)
F(2)	B	1.351(7)	C(32)	N(12)	C(52)	116.7(6)	O(22)	Fe	S(12)	16.6(2)
F(3)	B	1.340(7)	C(11)	N(21)	C(61)	120.5(3)	O(21)	Fe	S(12)	105.4(1)
F(4)	B	1.328(7)	C(11)	N(21)	C(41)	121.0(3)	O(21)#1	Fe	S(12)	89.0(1)
S(11)	Fe	2.465(2)	C(61)	N(21)	C(41)	118.2(3)	S(11)	Fe	S(12)	84.69(9)
S(12)	Fe	2.511(3)	C(21)	O(21)	Fe	124.0(2)	S(11)#1	Fe	S(12)	167.19(6)
O(22)	Fe	2.041(6)	C(11)	S(11)	Fe	97.99(14)	S(12)#1	Fe	S(12)	94.2(1)
Fe	O(22)#1	2.041(6)	C(12)	S(12)	Fe	91.5(2)				
Fe	O(21)#1	2.072(3)	C(12)	O(22)	Fe	135.4(5)				
Fe	S(11)#1	2.465(2)	O(22)#1	Fe	O(22)	61.2(4)				
Fe	S(12)#1	2.511(3)	O(22)#1	Fe	O(21)	95.0(2)				
			O(22)	Fe	O(21)	103.2(2)				

#1 = 1-x, y, 1/2-z.

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