Electronic Supplementary Information

A new system for cyclohexane functionalization employing iron(III) catalysts and trichloroisocianuric acid

C. A. Gomes,[a] Leonardo M. Lube,[b] Christiane Fernandes,[a] Roberto W. A. Franco,[c] Jackson A. L. C. Resende,[d] Adolfo Horn Jr.[a]*

Experimental:

Catalytic studies: The catalytic assays were carried out in a system containing a solution of the catalyst (**1** or **2**) ($7.0x10^{-4}$ mol dm^{-3}) in CH_3CN (4.62 cm^3), cyclohexane (0.38 cm^3) and TCCA in a ratio 1:1000:333 or 1:1000:33. The reactions were conducted during 24 h at 25ºC or 50ºC. A sample (0.4 cm^3) was taken and 0.02 cm^3 of 1-chloropropanol (internal standard) was added. Quantitative analyses of the products were executed in a Varian GC-430-FID equipped with a 30 m×0.25 mm (0.25 μm i.d.) CP-WAX 58 column. Product identification was performed by injecting a real sample of chlorocyclohexane purchased for Sigma-Aldrich. Furthermore, similar reactions in the absence of iron(III) catalysts and in the presence of $FeCl_3$ were conducted as blank reaction.

EPR Spectroscopy: Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker E500 spectrometer with a high sensitive cylindrical cavity, operating in the X-band (9 GHz), at 100 K (-173ºC), with a 10.0 mW microwave power, a 100 kHz modulation frequency and a 5 G modulation amplitude. Spectra were measured from samples containing only the catalysts and the catalyst in the presence of TCCA at ratios of 1:10 and 1:100.

X-ray diffraction : The single crystal X-ray diffraction data of compound was collected at room temperature on a Bruker D8 Venture diffractometer. The structure was solved by direct methods using Intrinsic Phasing and the model was refined applying the full-matrix least-squares method using SHELXL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms are placed at calculated positions and refined using a riding model.

ESI-(+)-MS: Full scan mass spectra (MS mode) were obtained on a MicroTOF LC Bruker Daltonics spectrometer equipped with an electrospray source operating in positive ion mode. Samples were dissolved in CH_3CN and were injected in the apparatus by direct infusion.

Table ESI 1. Crystal data and structure refinement for iron complex [Fe(HBPClNOL)$(Cl)_2$, **2**.

Empirical formula	$C_{18}H_{22}Cl_3FeN_3O_{2.5}$
Formula weight	482.58
Temperature/K	297.79
Crystal system	orthorhombic
Space group	Pnma
a/Å	20.7516(16)
b/Å	28.169(2)
c/Å	7.3729(6)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4309.8(6)
Z	4
$\rho_{calc}g/cm^3$	1.488
μ/mm^{-1}	1.092
F(000)	1984.0
Crystal size/mm^3	0.377 × 0.142 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.876 to 50.886
Index ranges	$-23 \leq h \leq 25$, $-33 \leq k \leq 33$, $-8 \leq l \leq 8$
Reflections collected	37930
Independent reflections	4039 [R_{int} = 0.0870, R_{sigma} = 0.0442]
Data/restraints/parameters	4039/0/258
Goodness-of-fit on F^2	1.199
Final R indexes [I>=2σ (I)]	R_1 = 0.1218, wR_2 = 0.2875
Final R indexes [all data]	R_1 = 0.1442, wR_2 = 0.2980
Largest diff. peak/hole / e $Å^{-3}$	1.75/-0.68

Table ESI2. Main bond Lengths(Å) for [Fe(HBPClNOL)$(Cl)_2$, **2**.

Fe1- Cl1	2.310(4)
Fe1- Cl2	2.299(3)
Fe1- O1	1.865(8)
Fe1- O2	2.175(8)
Fe1- N1	2.218(9)
Fe1- N2	2.190(9)

Table ESI3. Main bond angles(°) for [Fe(HBPClNOL)$(Cl)_2$, **2**.

Cl2-Fe1-Cl1	100.52(14)
O1-Fe1-Cl1	98.1(3)
O1-Fe-Cl2	99.8(3)
O1-Fe-O2	90.2(4)
O1-Fe-N1	88.5(3)
O1-Fe-N2	163.7(3)
O2-Fe-Cl1	167.0(2)
O2-Fe-Cl2	87.8(2)
O2-Fe-N1	75.5(3)
O2-Fe-N2	81.6(3)
N1-Fe-Cl1	94.6(3)
N1-Fe-Cl2	161.5(3)
N2-Fe-Cl1	87.8(3)
N2-Fe-Cl2	93.9(3)
N2-Fe-N1	75.9(3)

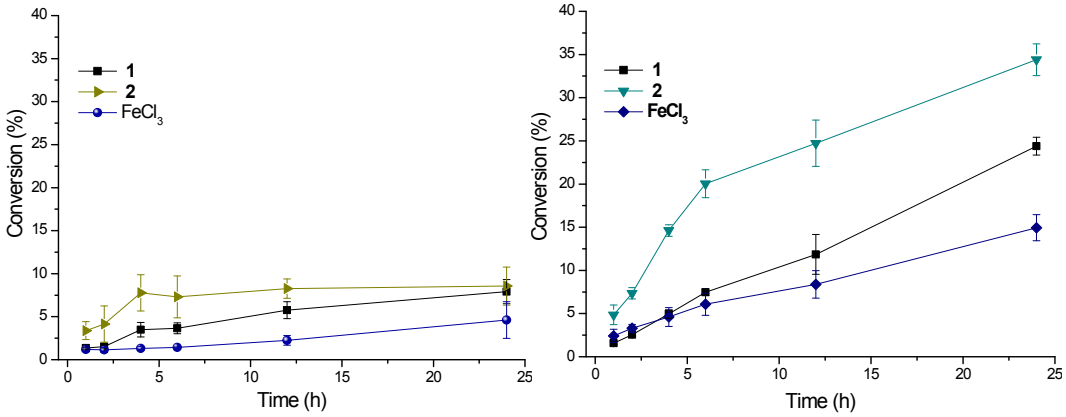

Figure ESI 1. Time course of cyclohexane chlorination catalyzed by **1**, **2** and FeCl3 in acetonitrile at 25 (left) and 50ºC (right).

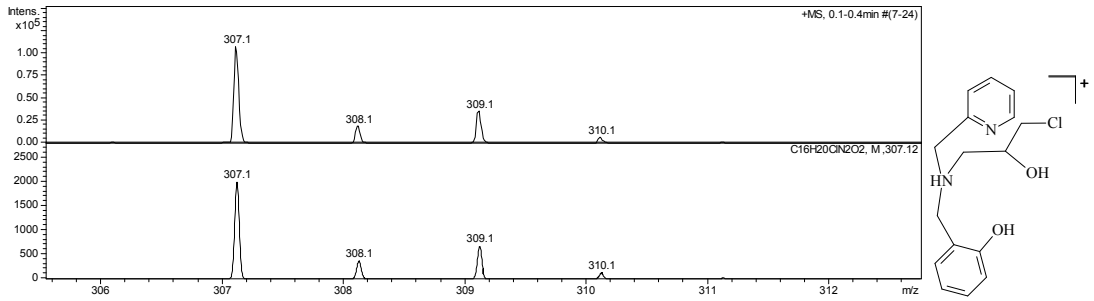

Figure ESI 2. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 307observed in the ESI-(+)-MS spectrum of **2** and a proposal of structure for the cation with chemical composition $C_{16}H_{20}ClN_2O_2$.

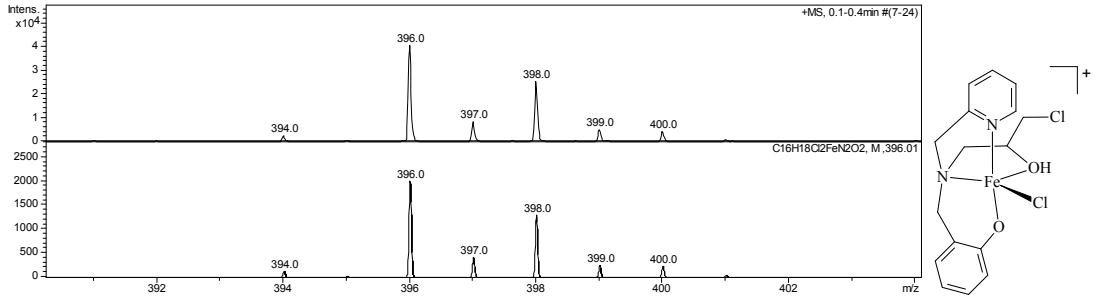

Figure ESI 3. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 396 observed in the ESI-(+)-MS spectrum of **2** and a proposal of structure for the cation with chemical composition $C_{16}H_{18}Cl_2FeN_2O_2$.

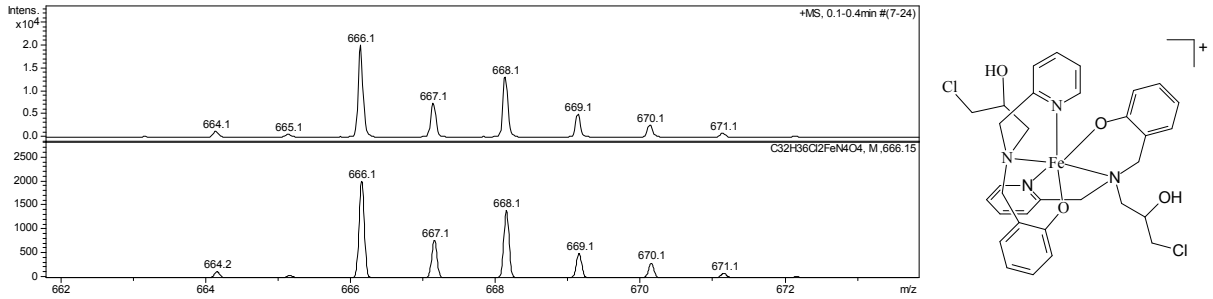

Figure ESI 4. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 666 observed in the ESI-(+)-MS spectrum of **2** and a proposal of structure for the cation with chemical composition $C_{32}H_{36}Cl_2FeN_4O_4$.

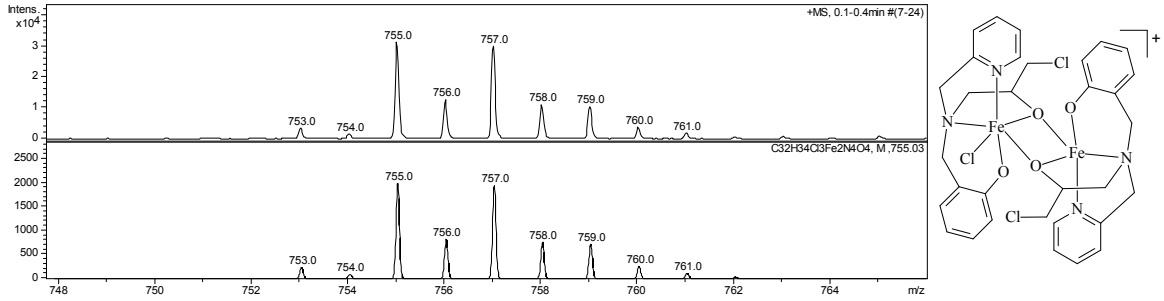

Figure ESI 5. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 755 observed in the ESI-(+)-MS spectrum of **2** and a proposal of structure for the cation with chemical composition $C_{32}H_{34}Cl_3Fe_2N_4O_4$.

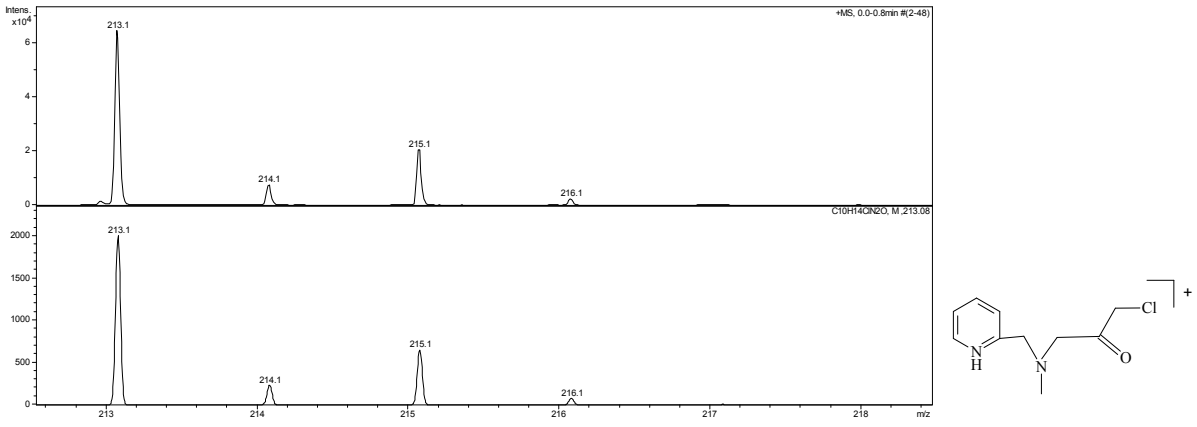

Figure ESI 6. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 213 observed in the ESI-(+)-MS spectrum of **2+TCCA** and a proposal of structure for the cation with chemical composition $C_{10}H_{14}ClN_2O$.

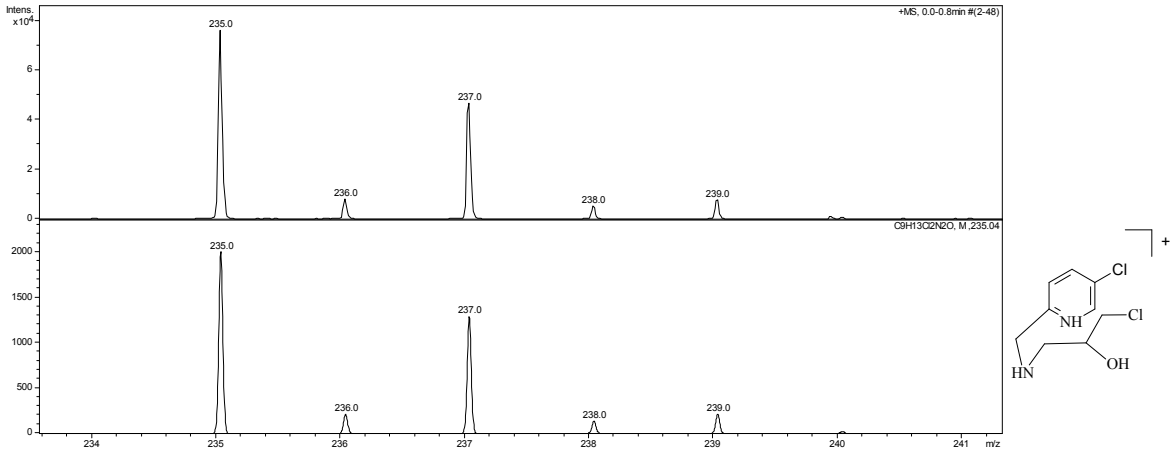

Figure ESI 7. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 235 observed in the ESI-(+)-MS spectrum of **2+TCCA** and a proposal of structure for the cation with chemical composition $C_9H_{13}Cl_2N_2O$.

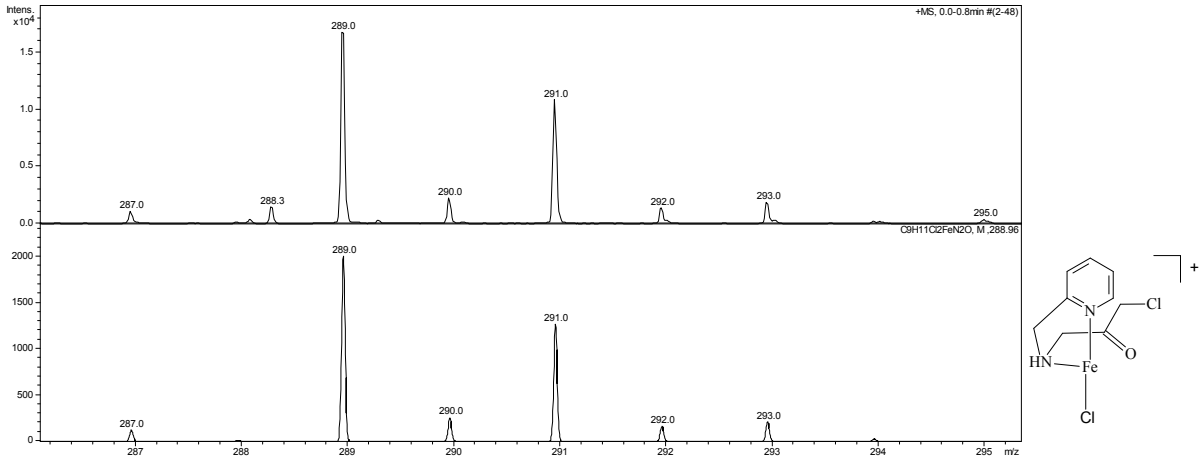

Figure ESI 8. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 289 observed in the ESI-(+)-MS spectrum of **2+TCCA** and a proposal of structure for the cation with chemical composition $C_9H_{11}Cl_2FeN_2O$.

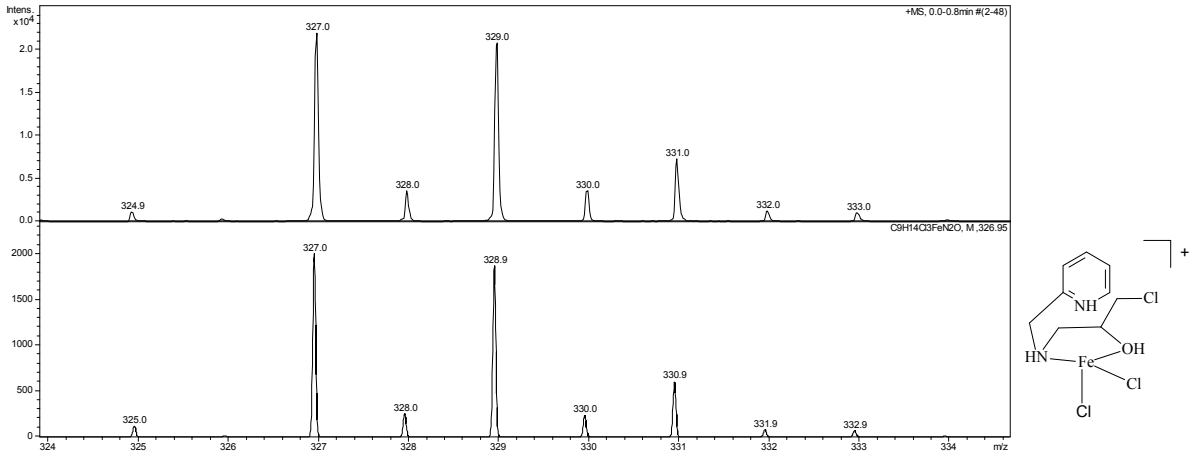

Figure ESI 9. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 289 observed in the ESI-(+)-MS spectrum of **2+TCCA** and a proposal of structure for the cation with chemical composition $C_9H_{14}Cl_3FeN_2O$.

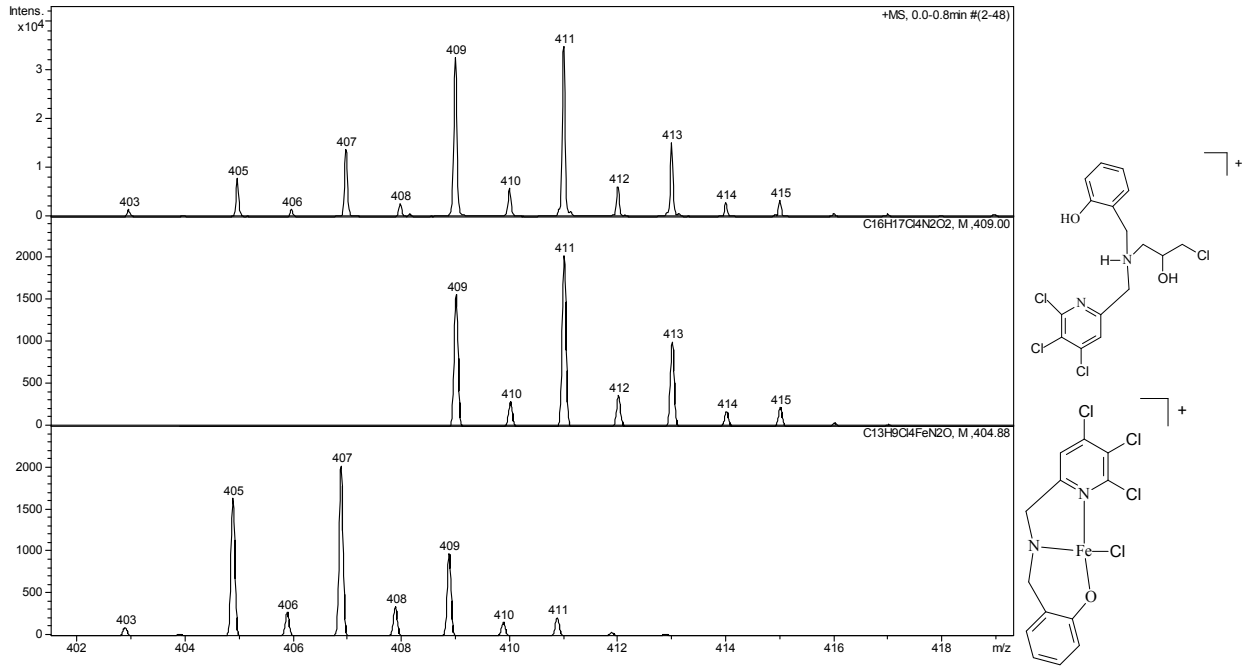

Figure ESI 10. Experimental (top) and simulated (middle and bottom) isotopic patterns for the ions with m/z 403 and 409 observed in the ESI-(+)-MS spectrum of **2+TCCA** and proposal of structures for the cations with chemical composition $C_{13}H_9Cl_4FeN_2O$ (403) and $C_{16}H_{17}Cl_4N_2O_2$ (409).

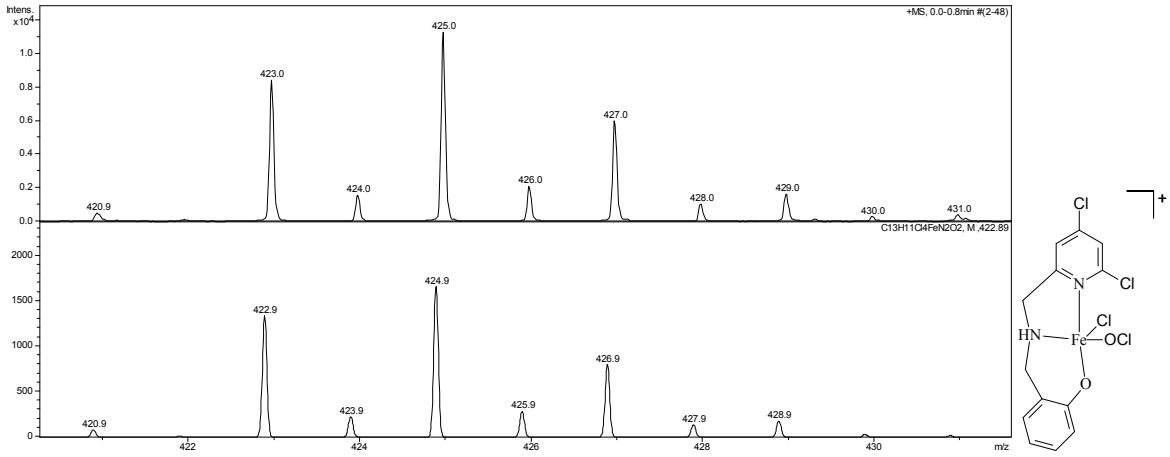

Figure ESI 11. Experimental (top) and simulated (bottom) isotopic patterns for the ion with m/z 423 observed in the ESI-(+)-MS spectrum of **2+TCCA** and a proposal of structure for the cation with chemical composition $C_{13}H_{11}Cl_4FeN_2O_2$.