SUPPLEMENTARY MATERIAL

of

Metal complexes with N-(trifluoromethylbenzyl)iminodiacetate chelators (x3F ligands). Part I. Copper(II) chelates of p3F, m3F and o3F with or without imidazole coligands.

Journal of Coordination Chemistry

Corresponding author: Dr. Duane Choquesillo-Lazarte

Corresponding author Institution: Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Av. de las Palmeras 4, E-18100 Armilla, Granada, Spain. E-mail: duanec@ugr.es

Crystals of compound **4** ([Cu(m3F)(Him)(H₂O)])

CONTENTS

SM1. NMR SPECTRA OF CHELATING LIGANDS

SM2. FT-IR SPECTRA OF LIGANDS AND COPPER(II) COMPLEXES

SM2.1. FT-IR spectra of free ligands and HoTTG by-product.

SM2.2. FT-IR Spectra of the binary compounds **1** and **2**.

SM2.3. FT-IR Spectra of the ternary compounds having Him co-ligand **3-5**.

SM2.4. FT-IR Spectra of the ternary compounds having H5Meim co-ligand **6-8**.

SM3. ELECTRONIC (DIFFUSE REFLECTANCE) SPECTRA OF COPPER(II) COMPLEXES

SM4. COUPLED THERMOGRAVIMETRIC + FT-IR SPECTRA ANALYSIS,

SM4.1. FT-IR spectra of the evolved gases, for identification purposes.

SM4.2. Sheet with selected FT-IR spectra for both compounds.

SM4.3. Compound **2**: $[\text{Cu}(\text{m3F})(\text{H}_2\text{O})_2]$.

SM4.4. Compound **4**: $[\text{Cu}(\text{m3F})(\text{Him})(\text{H}_2\text{O})]$.

SM1. NMR SPECTRA OF CHELATING LIGANDS

NMR spectra have been recorded on a 300 MHz ^1H Varian Inova-TM spectrometer at room temperature. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak (deuterium oxide). Signals are designated as follows: s, singlet; d, doublet; m, multiplet.

a) $\text{H}_2\text{p3F}$ acid.

b) H₂m3F acid.

c) H₂O/3F acid.

The expected singlet of the methylene group in the o-trifluoromethyl-benzyl moiety is obviously overlapped with the solvent (HOD) signal at 4.79 ppm.!

d) HoTTG acid (amino diacid obtained as by-product in the synthesis of H₂O₃F).

SM2. FT-IR SPECTRA OF LIGANDS AND COPPER(II) COMPLEXES

SM2.1. FT-IR spectra of free ligands (H_2x3F) and HoTTG by-product.

a) H_2p3F acid.

b) H_2m3F acid.

c) H₂O₃F acid.

d) HoTTG acid (amino diacid obtained as by-product in the synthesis of H₂O₃F).

SM2.2. FT-IR Spectra of the binary compounds **1** and **2**

a) Compound **1**: $\{[\text{Cu}(\mu_2\text{-p3F})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$.

b) Compound **2**: $[\text{Cu}(\text{m3F})(\text{H}_2\text{O})_2]$.

SM2.3. FT-IR Spectra of the ternary compounds having Him coligand **3-5**.

a) Compound **3**: $[\text{Cu}(\text{p3F})(\text{Him})(\text{H}_2\text{O})]$.

b) Compound **4**: $[\text{Cu}(\text{m3F})(\text{Him})(\text{H}_2\text{O})]$.

c) Compound **5**: $[\text{Cu}(\text{o3F})(\text{Him})(\text{H}_2\text{O})]$.

SM2.4. FT-IR Spectra of the ternary compounds having H5Meim coligand **6-8**.

d) Compound **6**: $[\text{Cu}_2(\text{p3F})_2(\text{H5Meim})_2(\text{H}_2\text{O})_2]$.

e) Compound **7**: $[\text{Cu}(\text{m3F})(\text{H5Meim})(\text{H}_2\text{O})]$.

f) Compound **8**: $[\text{Cu}(\text{o3F})(\text{H5Meim})(\text{H}_2\text{O})]$.

SM3. ELECTRONIC (DIFFUSE REFLECTANCE) SPECTRA OF COPPER(II) COMPLEXES

Compound 1 $\{[\text{Cu}(\mu_2\text{-p3F})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$

Compound 2 $[\text{Cu}(\text{m3F})(\text{H}_2\text{O})_2]$

Compound 3 $[\text{Cu}(\text{p3F})(\text{Him})(\text{H}_2\text{O})]$
 $[\text{Cu}(\text{m3F})(\text{Him})(\text{H}_2\text{O})]$

Compound 4

Compound **5** $[\text{Cu}(\text{o}3\text{F})(\text{Him})(\text{H}_2\text{O})]$
 $[\text{Cu}_2(\text{p}3\text{F})_2(\text{H}5\text{Meim})_2(\text{H}_2\text{O})_2]$

Compound **6**

Compound **7** $[\text{Cu}(\text{m}3\text{F})(\text{H}5\text{Meim})(\text{H}_2\text{O})]$

Compound **8** $[\text{Cu}(\text{o}3\text{F})(\text{H}5\text{Meim})(\text{H}_2\text{O})]$

SM4. COUPLED THERMOGRAVIMETRIC + FT-IR SPECTRA ANALYSIS, EXEMPLIFIED FOR COMPOUNDS 2 AND 4.

SM4.1. FT-IR spectra of the evolved gases, for identification purposes.

SM4.2. Thermogravimetric results for compound **2**: $[\text{Cu}(\text{m3F})(\text{H}_2\text{O})_2]$

Sample C-798: 7.064 mg.

Air-dry flow: 100.0 mL/minute.

Increasing rate of temperature: 10 °C/minute.

a) The TG plot of compound **2** as a function of the time (bottom axis) and temperature (right axis). Weight sample is indicated at the left axis.

b) The TG-plot of compound **2** with weight loss as a function of the temperature (bottom axis)

c) Five sheets below show a time-spaced sequential series of thirty FT-IR spectra, recorded at increasing times (minutes) which enable the identification of the evolved gases.

Sheet 1:

Sheet 2:

Sheet 3:

Sheet 4:

Sheet 5:

d) Additional amplification of the FT-IR spectrum at 26.536 minutes (see sheet 2) during the step 2. The absorptions at 1331, 1178, 1146 and 1078 cm^{-1} revealed the production of trifluorotoluene.

e) Summary the TG-data and interpretation of results.

	Temperature	Time	Weight		
Step or residue	°C	Min.	Experimental %	Calculated %	Gases or residue
1	50-155	2-13	8.727	9.268	2H ₂ O, CO ₂ (t)
2	155-330	13-32.5	63.569	-	H ₂ O, CO ₂ , CO, TFT, TMA
3	330-595	32.5-54	7.320	-	H ₂ O, CO ₂ , CO, TFT, N ₂ O, NO
Residue	595	-	20.377	20.460	CuO

t = trace or low amounts, TFT = trifluorotoluene, TMA = trimethylamine

SM4.3. Thermogravimetric results for compound **4**: $[\text{Cu}(\text{m3F})(\text{Him})(\text{H}_2\text{O})]$

Sample C-775: 8.090 mg.

Air-dry flow: 100.0 mL/minute.

Increasing rate of temperature: 10 °C/minute.

a) The TG plot of compound **4** as a function of the time (bottom axis) and temperature (right axis). Weight sample is indicated at the left axis.

b) The TG-plot of compound **2** with weight loss as a function of the temperature (bottom axis)

c) The five sheets below show a time-spaced sequential series of thirty FT-IR spectra, recorded at increasing times (minutes) which enable the identification of the evolved gases.

Sheet 1:

Sheet 2:

Sheet 3:

Sheet 4:

Sheet 5:

d) Additional amplification of the FT-IR spectrum at 48.992 minutes (see sheet 4) ending the step 5. The absorptions at 1306, 1178, 1149 and 1078 cm^{-1} revealed the production of trifluorotoluene.

e) Summary the TG-data and interpretation of results.

	Temperature	Time	Weight		
Step or residue	°C	Min.	Experimental %	Calculated %	Gases or residue
1a+1b	95-125-160	7-10.5-14	4.832	4.105	1H ₂ O, CO ₂ (t)
2	160-220	14-19.5	18.693	-	H ₂ O, CO ₂
3	220-260	19.5-23	14.608	-	H ₂ O, CO ₂
4	260-370	23-35	18.657	-	H ₂ O, CO ₂ , CO, TFT (t)
5	370-495	35-47	24.657	-	H ₂ O, CO ₂ , CO (t), N ₂ O, NO, NO ₂
Residue	495	-	19.015	18.126	CuO

t = trace or low amounts, TFT = trifluorotoluene, TMA = trimethylamine