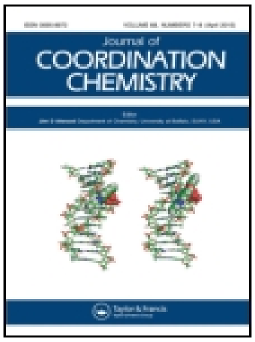

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Metal complexes with N-(trifluoromethylbenzyl) iminodiacetate chelators (x-3F ligands). Part I. Copper(II) chelates of p-3F, m-3F, and o-3F with or without imidazole-like ligands

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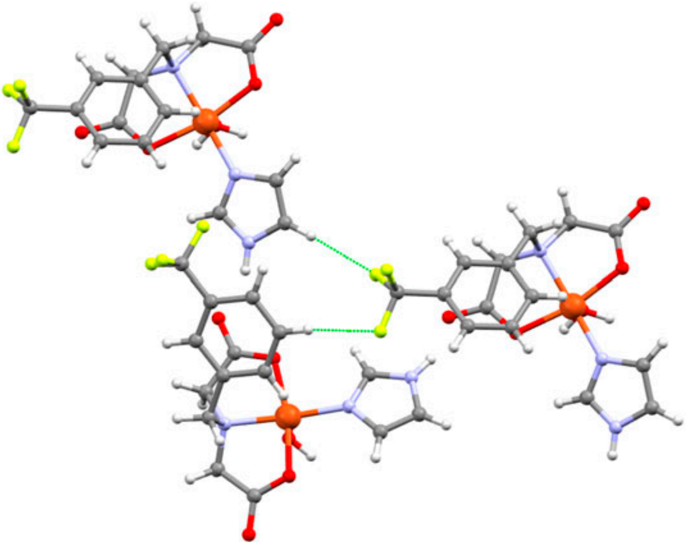

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Eight Cu(II) complexes with N-(p-, m- or o-trifluoromethylbenzyl)iminodiacetate chelators (x-3F ligands) have been synthesized to promote C–F/H interligand interactions involving the F_3C-group: $\{[Cu(\mu_2\text{-p-3F})(H_2O)]\cdot 3H_2O]\}_n$ (**1**), $[Cu(m\text{-3F})(H_2O)_2]$ (**2**), $[Cu(p\text{-3F})(Him)(H_2O)]$ (**3**), $[Cu(m\text{-3F})(Him)(H_2O)]$ (**4**), $[Cu(o\text{-3F})(Him)(H_2O)]$ (**5**), $[Cu_2(p\text{-3F})_2(H5Meim)_2(H_2O)_2]$ (**6**), $[Cu(m\text{-3F})(H5Meim)(H_2O)]$ (**7**), and $[Cu(o\text{-3F})(H5Meim)(H_2O)]$ (**8**) [Him and H5Meim = imidazole and the "remote" tautomer 5-methylimidazole, respectively]. The compounds were studied by single-crystal X-ray diffraction, FT-IR, electronic spectra and coupled thermogravimetric + FT-IR methods. The conformation of the iminodiacetate chelating moiety (IDA group) is *fac*-NO + O(apical) in **1** and *mer*-NO_2 in **2**–**8**. The *fac*-IDA conformation observed in **1** is related to its polymeric structure and the coordination of a O'-carboxylate donor, from an adjacent complex unit, *trans* to the Cu–N(IDA) bond. The *mer*-IDA conformation in **2** is in agreement with similar compounds with an aqua ligand *trans* to the corresponding Cu–N(IDA) bond. As expected, the ternary complexes **3**–**8** feature a *mer*-IDA conformation. Some of the studied complexes exhibit disorder in the $–CF_3$ group and C–H···F interligand interactions along with conventional N–H···O and O–H···O interactions. The thermal decomposition of all studied compounds under air flow produces variable amounts of trifluorotoluene.

Keywords: Copper(II) complexes; N-(Trifluoromethylbenzyl)iminodiacetate; Imidazole; Crystal structure; C–H/F interactions; FT-IR spectra; Electronic spectra; Coupled TG + FT-IR analysis; Trifluorotoluene

1. Introduction

Fluorinated compounds have gained technical [1], chemical [2], and therapeutic [3–5] relevance. It is easy to find them in a large variety of daily life products. The fluorine is characterized by small size, high electronegativity, low polarizability, and bond strength. The replacement of hydrogen by fluorine in organic compounds alters their physical, chemical, and biological properties [6]. Fluorine can promote different inter- and/or intra-molecular interactions, such as C–F···H, C–F···F, or C–F···π [6–9]. These interactions are normally weak, such as van der Waals forces, nevertheless they have proved to be important in defining the molecular and/or crystal structure of different compounds [6, 8, 9]. In contrast, fluorine directly bonded to electron-withdrawing aromatic rings does not participate in such interactions. The role of fluoromethyl moieties attached to aromatic rings seems to be also different and are indeed assumed to have the ability of taking part in C–F···H, C–F···F, or C–F···π interactions [10].

Herein, the synthesis of three N-(x-trifluoromethylbenzyl)iminodiacetate(2-) ligands, with x- being p-, m-, or o-substitution in x-3F ligands, is reported. In addition, the corresponding binary and ternary copper(II) complexes, involving one N-heterocyclic imidazole-like ligand, were also studied. The formulas of the ligands used in this work are shown in scheme 1. This work involves two main aims. First, to evaluate the structure of the obtained compounds. Special attention is paid to the conformation of the chelating iminodiacetate moiety (IDA) both in binary and ternary compounds. Second, to investigate the involvement of the trifluoromethyl group in intermolecular interactions and their role in the crystal architecture. Therefore, single-crystal X-ray diffraction is a crucial tool [11–15]. Syntheses of the metal complexes have been carried out in water or in methanol:water mixtures. Considering the active H-donor character of the N–H group of imidazole ligands, we anticipate structural frameworks where a competition or cooperation between O–H···O and/or N–H···O interactions as well as C–F···H, and related weak interactions, will be operative [6–9]. In addition, the tautomerism of H(4/5)-methylimidazole (HMeim) offers possibilities to isolate the "remote isomer" (more stable, with H5Meim) and/or the "adjacent isomer" (more hindered, with H4Meim) in the corresponding ternary complexes [16, 17].

2. Experimental and methods

2.1. *Chemicals*

Blue-greenish $Cu_2CO_3(OH)_2$, imidazole, 4(5)-methylimidazole, chloroacetic acid, methanol, and KOH were supplied by Merck, Aldrich or Acros. p-, m- and o-(Trifluoromethylbenzyl) amines were purchased from Alfa Aesar. All reagents and solvents were used as received. *Caution: all the solutions used to prepare the chelating ligands in their acid form (section 2.2) were prepared with CO_2-free distilled water.*

2.2. *Synthesis of chelating ligands*

In a three-necked round bottom flask, chloroacetic acid (0.12 mol, 11.34 g) was dissolved in 150 mL of water, placed in an ice-salt bath (temperature < 0 °C) under N_2 stream and stirred. KOH (0.29 mol, 16.3 g) was dissolved in 50 mL of cool water (about 0 °C) and then added dropwise to the chloroacetic solution. To the alkaline solution of potassium chloroacetate, a 5-mL ethanol solution of x-(trifluoromethylbenzyl)amine (x = p-, m- or o-, 0.0571 mol, 10 g) was dropwise added. The three-necked flask with the resulting reaction mixture was then placed inside a water bath at 85 °C, maintaining regular stirring and N_2 flow during 4 h. After condensation, the pH of the mother liquor was ~11–12. This solution was cooled in ice, neutralized with HCl 6N, and concentrated in a Büchi evaporator (~50 °C) to a volume of 100 mL. After that, the solution was cooled again and finally acidified to pH ~2–2.5 to induce precipitation of a white powder corresponding to the N-(x-trifluoromethylbenzyl)iminodiacetic acids (H_2p-3F, H_2m-3F or H_2o-3F). The H_2x-3F products ($C_{12}H_{12}F_3NO_4$, MW 291.22) were collected in several fractions by filtration, washed with cool water, acetone and ether, and air-dried. Yields were *ca.* 50–60%. NMR and FT-IR spectra of the organic products are shown in Supplementary Material (SM1 and SM2.1, respectively). The aforementioned procedure of acidification must be carried out with care, gradually reducing the addition of acid after the mother liquors have pH ~ 7. This is especially critical in the case of the H_2o-3F acid, where the solution becomes turbid near neutrality. For instance, when the mother liquor of H_2o-3F acid is cooled in an ice bath close to pH 7, precipitation of a different white product is induced. This product was collected by filtration, washed with cool water and iPrOH, and dried under air flow. This intermediate product was identified as N-carboxymethyl-(o-trifluoromethyl)benzylamine or o-(trifluoromethyl)tolyl-glycine (HoTTG). Yield: 2.56 g, 19.3%.

H_2p-3F; relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3437, $\nu_s(H_2O)$ 3241, $\nu_{as}(CH_2)$ 2923, $\nu_s(CH_2)$ 2854, ν(C=O) 1733, $\delta(H_2O)$ 1621, $\delta(CH_2)$ 1470, $\delta_w(CH_2)$ 1451, ν(C-O) + δ(OH) 1399, $\nu_s(COO^-)$ 1382, δ(OH) 1226, $-CF_3$ 1332, 1182, and 1140, π(CH)(2 adjacent aromatic H) 826, π(OH) 739. ^1H NMR (300 MHz, D_2O) δ 7.84 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 4.61 (s, 2H), 3.98 (s, 4H).

H_2m-3F; relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3432, $\nu_s(H_2O)$ 3245, $\nu_{as}(CH_2)$ 2930, $\nu_s(CH_2)$ 2855, ν(C=O) 1730, $\delta(H_2O)$ 1622, $\delta_w(CH_2)$ 1452, ν(C–O) + δ(OH) 1402, $\nu_s(COO^-)$ 1385, δ(OH) 1248, $-CF_3$ 1329, 1177 and 1128, π(CH)(1 aromatic H) 898, π(CH)(3 adjacent aromatic H) 752. ^{1}H NMR (300 MHz, D_2O) δ 7.79 (m, 4H), 4.62 (s, 2H), 4.01 (s, 4H).

H_2o-3F; relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3434, $\nu_s(H_2O)$ 3251, $\nu_{as}(CH_2)$ 2936, $\nu_s(CH_2)$ 2848, ν(C=O) 1716, $\delta(H_2O)$ 1637, $\nu_{as}(COO^-)$ 1609, $\delta(CH_2)$ 1468, $\delta_w(CH_2)$ 1453, $\nu_s(COO^-)$ 1383, δ(OH) 1238, $-CF_3$ 1311, 1171 and 1114, π(CH)(4 adjacent aromatic H) 772, π(OH) 739. ^{1}H NMR (300 MHz, D_2O) δ 7.80 (m, 4H), 4.80 (s, 2H), 4.06 (s, 4H).

HoTTG ($C_{10}H_{10}F_3NO_2$, MW 233.19); relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3433, $\nu_s(H_2O)$ ~3250, $\nu(C{-}H)_{arom}$2992, $\nu_{as}(CH_2)$ 2927, $\nu_s(CH_2)$ 2853, $\nu(NH_2^+)$ 2580, $\delta(H_2O) + \delta(NH_2^+)$ 1637, ν_{as}(COO) 1605, $\delta(NH_2^+)$1507, $\delta(CH_2)$ 1472, $\delta_w(CH_2)$ 1456, ν_s(COO) 1403 or 1385, $-CF_3$ 1315, 1182 and 1119, π(CH)(4 adjacent aromatic H) 778. ^{1}H NMR (300 MHz, D_2O) δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.70 (m, 3H), 4.50 (s, 2H), 3.72 (s, 2H).

2.3. *Synthesis of coordination compounds*

$\{[Cu(\mu_2\text{-p-3F})(H_2O)]\cdot 3H_2O]\}_n$ (**1**). In a Kitasato flask, $Cu_2CO_3(OH)_2$ (0.15 mmol, 33.2 mg) was reacted with H_2p-3F acid (0.3 mmol, 87.4 mg) in 50 mL of water, heating (~50 °C), and stirring for 1.5 h. The resulting clear blue solution was left to cool at room temperature and then filtered, without vacuum, on a crystallizing dish. The solution was allowed to stand at room temperature, covered with a film to control the evaporation. After one week, blue needle-like crystals were collected. These crystals were recrystallized in 30 mL of a methanol:water mixture (2 : 1). After one month, blue square crystals were obtained. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ ~3450, $\nu_s(H_2O)$ ~3250 (shoulder), $\nu_{as}(CH_2)$ 2943, $\nu_s(CH_2)$ 2850, $\delta(H_2O)$ ~1620 (shoulder), $\nu_{as}(COO^-)$ 1596, $\delta(CH_2)$ 1446, $\nu_s(COO^-)$ 1384 and 1374, (F_3C–) 1327, 1173 and 1127, π(CH)(2 adjacent aromatic H of p-3F) 811. Electronic spectrum (diffuse reflectance): ν_{max} 11,900 cm^{-1}.

$[Cu(m\text{-3F})(H_2O)_2]$ (**2**). A similar synthesis to that described for **1** was performed using H_2m-3F acid (0.3 mmol, 87.4 mg), instead of H_2p-3F acid, and methanol as solvent. After one week, a white precipitate was collected. The solution was filtered on a small crystallizing dish and allowed to evaporate at room temperature, covered with a plastic film. Four weeks later, parallelepiped blue crystals were obtained. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ ~3425, $\nu_s(H_2O)$ ~3275, $\nu(C{-}H)_{arom}$ 2991, $\nu_{as}(CH_2)$ 2965, 2936 and 2923, $\nu_s(CH_2)$ 2866 and ~2840 (shoulder), $\delta(H_2O)$ ~1630 (shoulder), $\nu_{as}(COO^-)$ 1603, $\delta(CH_2)$ 1472 $\delta_w(CH_2)$ 1454, $\nu_s(COO^-)$ 1396 and 1375, (F_3C–) 1329, 1169 and 1140, π(CH)(1 aromatic H from m-3F) 872. Electronic spectrum (diffuse reflectance): ν_{max} 11,900 cm^{-1}. Electronic spectrum (diffuse reflectance): ν_{max} 13,890 cm^{-1}.

$[Cu(p\text{-3F})(Him)(H_2O)]$ (**3**). In a Kitasato flask, $Cu_2CO_3(OH)_2$ (0.15 mmol, 33.2 mg) was reacted with H_2p-3F acid (0.3 mmol, 87.4 mg) in 50 mL of distilled water under mild heating (~50 °C) and stirring. Two hours later, a clear blue solution was obtained. The solution was cooled at room temperature, and then imidazole (0.3 mmol, 20.4 mg) was slowly added to the binary chelate solution. The reacting mixture was stirred for 1 h until an intense blue solution was obtained. Finally, the solution was filtered without vacuum on a crystallizing dish and covered with a plastic film to control the evaporation at room temperature. After four weeks, blue square crystals were collected. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ ~3400, $\nu_s(H_2O)$ ~3250, ν(N–H) 3148, $\nu_{as}(CH_2)$ 2952, $\nu_s(CH_2)$ 2851, $\delta(H_2O)$ 1626, $\nu_{as}(COO^-)$ 1614, δ(N–H) 1534, $\delta_w(CH_2)$ 1447, $\nu_s(COO^-)$ 1396 and 1384, (F_3C–) 1330, 1161 and 1134, π(CH)(1 aromatic H from Him) 900, π(CH)(2 adjacent aromatic H from Him and p-3F) 824, π(OH) 753. Electronic spectrum (diffuse reflectance): ν_{max} 14,800 cm^{-1}.

[Cu(m-3F)(Him)(H_2O)] (**4**). A similar synthesis to that described for **3** was carried out using H_2m-3F acid (0.3 mmol, 0.0874 g) instead of H_2p-3F acid. Blue square crystals were obtained in one week. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ ~3400, $\nu_s(H_2O)$ ~3250, ν(N–H) 3148, $\nu_{as}(CH_2)$ 2941, $\nu_s(CH_2)$ 2855, $\delta(H_2O)$ 1629, $\nu_{as}(COO^-)$ 1609, δ(N–H) 1501, $\delta(CH_2)$ 1501, $\delta_w(CH_2)$ 1447, $\nu_s(COO^-)$ 1397, (F_3C–) 1331, 1166, and 1123, π(CH)(1 aromatic H from Him and m-3F) 899 and 877, π(CH)(2 adjacent H from Him) 854, π(CH)(3 adjacent aromatic H from m-3F) 802, π(OH) 756. Electronic spectrum (diffuse reflectance): ν_{max} 14,300 cm^{-1}.

[Cu_2(o-3F)$_2$(Him)$_2$(H_2O)$_2$] (**5**). A similar synthesis to that reported for **3** and **4** was performed but using H_2o-3F acid. Four days later, blue parallelepiped crystals were collected. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3431, $\nu_s(H_2O)$ ~3250, ν(N–H) 3157, $\nu_{as}(CH_2)$ 2932, $\nu_s(CH_2)$ 2851, $\delta(H_2O)$ 1635, $\nu_{as}(COO^-)$ 1610, δ(N–H) 1507, $\delta(CH_2)$ 1465, $\delta_w(CH_2)$ 1454, $\nu_s(COO^-)$ 1384, (F_3C–) 1315, 1167 and 1123, π(CH)(1 aromatic H from Him) 881, π(CH)(2 adjacent aromatic H from Him) 824, π(CH)(4 adjacent aromatic H from o-3F) 767, π(OH) 743. Electronic spectrum (diffuse reflectance): ν_{max} 14,350 cm^{-1}.

[Cu_2(p-3F)$_2$(H5Meim)$_2$(H_2O)$_2$] (**6**). In a Kitasato flask, $Cu_2CO_3(OH)_2$ (0.15 mmol, 0.0332 g) was reacted with H_2p-3F acid (0.3 mmol, 0.0874 g) in 50 mL of a MeOH : H_2O mixture (10 : 1), heating (~50 °C), and stirring. Two hours later, a clear blue solution was obtained. Once the solution cooled to room temperature, H5Meim (0.3 mmol, 0.0246 g) was slowly added to the binary chelate solution and the reaction mixture was stirred for 1 h. The resulting solution, intense blue, was filtered without vacuum on a crystallizing dish and covered with plastic film to control the evaporation. One week later, blue square crystals were collected. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3419, $\nu_s(H_2O)$ ~3250, ν(N–H) ~3150, $\nu_{as}(CH_3)$ 2976, $\nu_{as}(CH_2)$ 2927, $\nu_s(CH_3)$ ~2870, $\nu_s(CH_2)$ 2850, $\delta(H_2O)$ 1624, $\nu_{as}(COO^-)$ 1616, δ(N–H) 1506, $\delta(CH_2)$ 1473, $\delta(CH_3)$ 1456, $\delta_w(CH_2)$ 1447, $\nu_s(COO^-)$ 1394 or 1384, (F_3C–) 1322, 1160 and 1133, π(CH)(1 aromatic H from H5Meim) 859, π(CH)(2 adjacent aromatic H from p-3F) 824, π(OH) 737. Electronic spectrum (diffuse reflectance): ν_{max} 14,685 cm^{-1}.

[Cu(m-3F)(H5Meim)(H_2O)] (**7**). A similar synthesis to that described for **5** was carried out using H_2m-3F acid (0.3 mmol, 0.0874 g) instead of H_2p-3F acid. In one week, blue rhomboid crystals were collected. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3410, $\nu_s(H_2O)$ ~3250, ν(N–H) 3148, $\nu_{as}(CH_3)$ 2976, $\nu_{as}(CH_2)$ 2939, $\nu_s(CH_3)$ 2876, $\nu_s(CH_2)$ 2850, $\delta(H_2O)$ 1628, $\nu_{as}(COO^-)$ 1615, $\delta(CH_2)$ 1479, $\delta(CH_3)$ 1454, $\delta_w(CH_2)$ 1445, $\nu_s(COO^-)$ 1397, (F_3C–) 1334, 1165, and 1133, π(CH)(1 aromatic H from H5Meim and m-3F) 872, π(CH)(3 adjacent aromatic H from m-3F) 806, π(OH) 761. Electronic spectrum (diffuse reflectance): ν_{max} 14,750 cm^{-1}.

[Cu(o-3F)(H5Meim)(H_2O)] (**8**). In a Kitasato flask, $Cu_2CO_3(OH)_2$ (0.1 mmol, 22.1 mg) was reacted with H_2o-3F acid (0.2 mmol, 58.3 mg) in 30 mL of H_2O with mild heating (~50 °C) and stirring. Two hours later, a clear blue solution was obtained. The solution was cooled at room temperature, and then H5Meim (0.2 mmol, 16.4 mg) was slowly added to the binary chelate solution. The reaction mixture was further stirred for 1 h. The final intense blue solution was filtered without vacuum on a crystallizing dish. The solution was left at room temperature covered with a plastic film to control the evaporation of the solvent. One week later, blue square crystals were obtained. Relevant bands FT-IR (cm^{-1}) and assignments: $\nu_{as}(H_2O)$ 3427, $\nu_s(H_2O)$ ~3250, ν(N–H) 3143, $\nu_{as}(CH_3)$ 2976, $\nu_{as}(CH_2)$ 2933, $\nu_s(CH_3)$ 2874, $\nu_s(CH_2)$ 2850, $\delta(H_2O)$ 1622, $\nu_{as}(COO^-)$ 1615, δ(N–H) 1507, $\delta(CH_2)$ 1472,

$\delta(CH_3)$ 1457, $\delta_w(CH_2)$ 1446, $\nu_s(COO^-)$ 1384, $(F_3C–)$ 1314, 1177 and 1132, π(CH) (1 aromatic H from H5Meim) 883, π(CH) (4 adjacent aromatic H from o-3F) 742, π(OH) 737. Electronic spectrum (diffuse reflectance): ν_{max} 14,680 cm^{-1}.

FT-IR (SM2.2–SM2.4) and electronic spectra (diffuse reflectance, SM3) of all copper(II) complexes are provided in Supplementary Material.

2.4. *Crystal structure determinations*

Suitable crystals were prepared for X-ray diffraction by immersion in perfluoropolyether, as protecting oil for manipulation, and mounted on a MiTeGenMicromounts™ under inert conditions. These samples were used for data collection. Data were collected with a Bruker D8 Venture diffractometer (120.0 K for **1** and 100.0 K for **2–8**). Data were processed with APEX2 [18] and corrected for absorption using SADABS [19]. The structures were solved by direct methods [20], which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters. All hydrogens were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. Geometric calculations were carried out with PLATON [21], and drawings were produced with OLEX2 [22] and MERCURY [23]. A summary of crystal data as well as structure and refinement parameters is given in table 1.

2.5. *Other physical measurements*

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). FT-IR spectra (KBr pellets) were recorded on a Jasco FT-IR 6300 spectrometer. Electronic (diffuse reflectance) spectra were obtained in a Varian Cary-5E spectrophotometer. Thermogravimetric (TG) analyses were carried out under dry air flow (100 mL/min), from RT-800 °C, at 10 °C/min in a Shimadzu thermogravimetric analyzer (TGA)-50H instrument, coupled to a FT-IR Nicolet Magma 550 spectrometer. A series of 20–35 FT-IR spectra were time-spaced recorded during each TG experiment. These spectra enable the qualitative identification of the gasses evolved during the experiment. The TG experiments always start after stabilization of the balance, i.e., once reached a stable weight for each sample is placed under dry air flow. It should be emphasized that, under these conditions, compounds can lose a variable amount of water before each TG experiment actually starts. The fitting of the formula and the starting material is assumed to be correct if the experimental and the calculated data for the final residue (expected to be CuO in the studied metal complexes) are in agreement within the experimental error, ≤1%.

2.6. *Criteria to evaluate intermolecular interactions involving the trifluoromethyl group*

The criteria reported by Reichenbächer and Süss [7] were followed to explore the intermolecular interactions involving the trifluoromethyl group. The van der Waals radii of fluorine (1.50–1.60 Å) and hydrogen (1.20–1.45 Å) have some uncertainties, and thus, the averaged value was assumed as 2.67 Å [7]. On this basis, C–F···H interactions were only considered if the interatomic F···H distance was shorter than 2.9 Å and the angle C–F···H

Table 1. Summary of crystal data, structure solution, and refinement of **1–8**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_{12}H_{18}CuF_3NO_8$	$C_{12}H_{14}CuF_3NO_6$	$C_{15}H_{16}CuF_3N_3O_5$	$C_{15}H_{16}CuF_3N_3O_5$	$C_{30}H_{32}Cu_2F_6N_6O_{10}$	$C_{32}H_{36}Cu_2F_6N_6O_{10}$	$C_{16}H_{18}CuF_3N_3O_5$	$C_{16}H_{18}CuF_3N_3O_5$
Formula weight	424.81	388.78	438.85	438.85	877.69	905.75	452.87	452.87
T (K)	120.2	100.0	100.0	100.0	100.0	299.7	99.9	100.0
Wavelength (Å)	0.71073	0.71073	1.54178	1.54178	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P12_1/n1$	*Pbca*	*Pbca*	$P2_1$	$P2_1/c$	*Pbca*	*Pbca*
Unit cell dimensions								
a (Å)	9.235(1)	7.384(4)	11.972(2)	11.821(4)	10.790 (9)	11.943 (2)	11.953(9)	11.880(4)
b (Å)	9.965(1)	26.841(19)	12.210(3)	12.861(5)	11.201(9)	12.451 (2)	12. 483(8)	12.442(3)
c (Å)	18.744(3)	7.533(3)	25.398(3)	22.500(8)	13.876(11)	25.855(4)	24.838(2)	24.838(2)
α (°)	90	90	90	90	90	90	90	90
β (°)	90.688(7)	92.149(10)	90	90	92.682(3)	90.011(4)	90	90
γ (°)	90	90	90	90	90	90	90	90
Z	4	4	8	8	2	4	8	8
$F(0\ 0\ 0)$	868	788	1784	1784	892	1848	1848	1848
Indep. reflections	2986	2582	3260	3499	4189	7833	3787	5176
GOF on F^2	1.083	1.047	1.069	1.019	1.060	1.066	1.044	1.060
Final $R1$ [$I > 2\sigma$]	0.049	0.050	0.042	0.034	0.037	0.042	0.033	0.046
Final $wR2$	0.126	0.095	0.111	0.074	0.082	0.105	0.079	0.112
Largest diff. peak /hole	1.083/−0.981	0.767/−0.608	0.618/−0.510	0.533/−0.403	1.197/−0.771	0.399/−0.488	0.449/−0.360	0.776/−0.819

fell in the range 70-180°; F···F interactions were assumed to give interatomic distances shorter than 3 Å. In C(1)–F···F–C(2) moieties, two types of interactions can be distinguished according to the C–F···F angles (φ_1 and φ_2): $\varphi_1 = \varphi_2$ (Type I) or $\varphi_1 \sim 90°$ and $\varphi_2 \sim 180°$ (Type II). Due to the negative charge density at F and the aromatic rings, C–F/π interactions should not be expected. The geometric criteria used to search these interactions were similar to those used for C–H/π (C-H···centroid < 3 Å, angle C–H···centroid ~ 180°).

3. Results and discussion

3.1. *Molecular and/or crystal structure of binary copper(II) chelates (1 and 2)*

Table 2 summarizes data concerning the copper(II) coordination of **1** and **2**. Compound **1** $\{[Cu(\mu_2\text{-p-3F})(H_2O)]\cdot 3H_2O\}_n$ is a hydrated coordination polymer. This polymeric nature is related to the chelating plus bridging role of the p-3F ligand (figure 1), involving an *anti, syn*-carboxylate. The Cu(II) is best described as a distorted square-based pyramid, type 4 + 1. The four closest donors to the metal are N and one O (from the monodentate carboxylate group) of the p-3F chelator, the O-aqua and one O' from a p-3F chelator of an adjacent complex unit within the chain. Thus, the tridentate chelating role of the p-3F ligand implies the contribution of one O-carboxylate as apical/distal donor, and therefore, the IDA moiety of the p-3F chelating ligand can be defined as *fac*-NO + O(apical). Note that, in this polymeric structure, the O'-donor is located *trans* to the Cu–N(p-3F) bond. No disorder was observed on the trifluoromethyl group in p-3F. In **1**, the 1-D polymeric chains extend parallel to the *b* axis. The aqua ligand acts twice as H-donor for two different solvent molecules. Additional H-bonds involving non-coordinating water and O-carboxylate acceptors build H-bonded 2-D frameworks parallel to the *ab* plane. These 2-D layers have the hydrophobic p-trifluoromethylbenzyl moieties of p-3F oriented toward their external faces and connect along the *c* axis by van der Waals forces, including some C–H···F interactions (see section 3.3).

Compound **2** agrees with the formula $[Cu(\text{m-3F})(H_2O)_2]$. The tridentate chelating ligand m-3F supplies the N-amino and two O-donors (from the monodentate carboxylate group) to the base surrounding of the 4 + 1 copper(II) coordination polyhedron (figure 2), which is

Table 2. Selected copper(II) coordination data in the binary compounds (bond lengths (Å), trans-basal angles (°)).

Compound	**1**	**2**
Chelator	μ_2-p-3F	m-3F
IDA group conformation	fac-NO + O(apic)	mer-NO_2
Cu–N(x-3F chelator)	2.048(3)	2.012(4)
Cu–O(x-3F chelator)	1.950(2)	1.926(3)
Cu–O(x-3F chelator)	2.239(2)!	1.938(3)
Cu–O#1(x-3F adjacent chelator)	1.947(2)	–
Cu–OW1(aqua, basal)	1.985(2)	1.942(3)
Cu–O2(aqua, apical)	–	2.281(4)
Trans–N–Cu–O\`[a]	171.83(11)	157.45(14)
Trans–O(carboxylate)–Cu–O(aqua, basal)	158.45(11)	171.28(12)
Addison–Reedijk parameter (τ)	0.22	0.23

[a] O' is a carboxylate atom from the p-3F chelator of the adjacent complex unit in the polymeric chain.

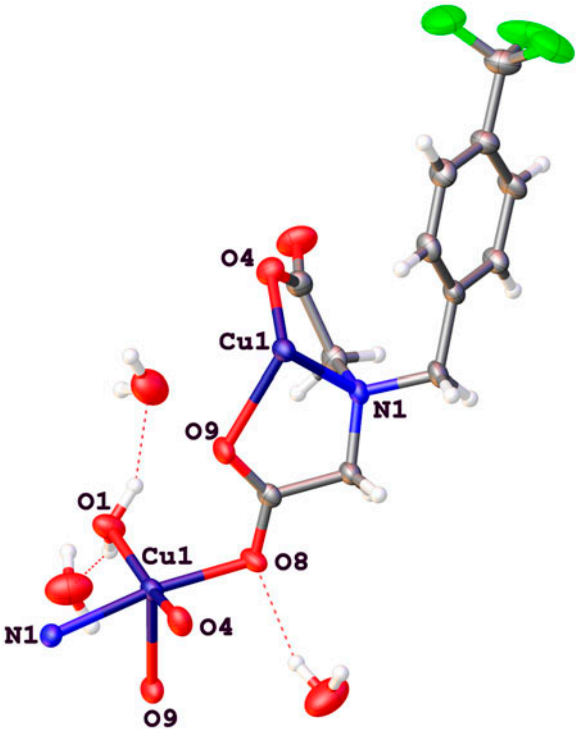


Figure 1. Fragment of **1** showing the 4 + 1 Cu(II) coordination. The O9 donor is at the apical site. The p-3F chelator adopts a *fac*-NO + O conformation. The *anti,syn*-bridging carboxylate is shown.

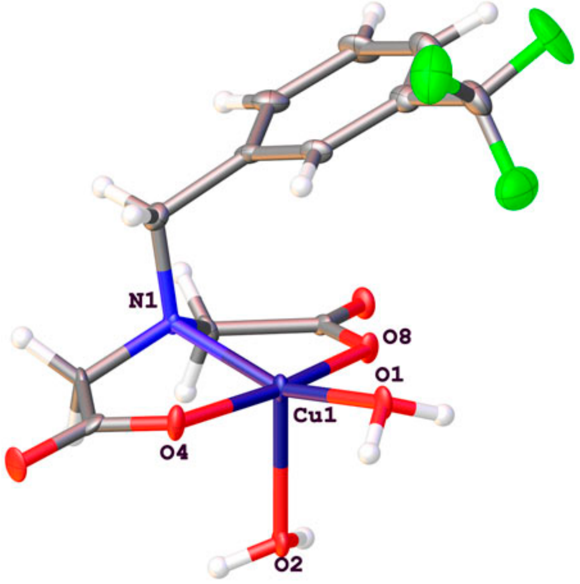


Figure 2. Asymmetric unit of **2** showing the *mer*-NO_2 conformation of the IDA moiety of the m-3F chelator.

further accomplished by the O-basal/proximal and the O-apical/distal donors of two aqua ligands. Hence, the IDA moiety of the m-3F ligand exhibits a *mer*-NO_2 conformation, in which the aqua ligand is *trans* to the Cu–N(m-3F) bond. The crystal of **2** is built by H-bonded 2-D bi-layers of complex molecules extending parallel to the *ac* plane. Each aqua ligand builds two O–H···O(carboxylate) interactions with the non-coordinated O5 and O9 carboxylate atoms from two distinct adjacent m-3F ligands. Thus, each complex molecule is H-bonded with two neighboring ones. In these 2-D frameworks, the m-trifluoromethylbenzyl moieties of m-3M ligands are also oriented toward their external faces. These layers are piled up along the *b* axis, connected by van der Waals forces. The m-trifluoromethyl group is not involved in C–F···H (see section 3.3), F···F or C–F/π interligand interactions.

3.2. *Molecular and crystal structure of mixed-ligand copper(II) complexes (3–8)*

The ternary complexes **3–8** crystallized as molecular compounds, according to the general formula [Cu(x-3F)(imidazole-like ligand)(H_2O)] (figures 3 and 4). All these compounds exhibit similar square-based pyramidal coordination, type 4 + 1, with lower Addison–Reedijk parameter (τ) values than those of **1** and **2** ($\tau = \varphi - \theta/60$, with θ and φ being the trans-basal coordination angles in a 4 + 1 surrounding, table 3). Compounds **3–8** also build crystals with rather similar architectures. All five ternary complexes (**3–8**) consist of H-bonded 2-D networks of complex molecules, layered parallel to the *ab* plane, where the hydrophobic x-(trifluoromethylbenzyl) arms of the x-3F chelators orient toward their external faces. To achieve the 3-D framework, the 2-D layers are piled up. Further C–F···H interactions connect the 2-D layers in **4–7**, but these connections are missing in **3** and **8**.

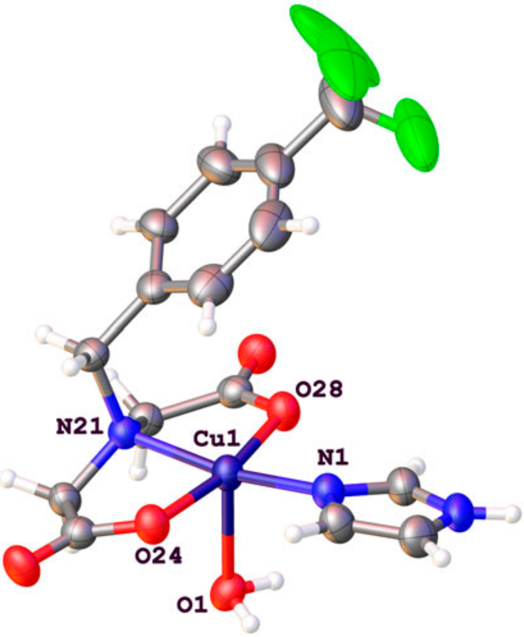


Figure 3. Asymmetric unit of **3** showing the IDA-*mer*-NO_2 conformation of the p-3F chelator and the apical aqua ligand.

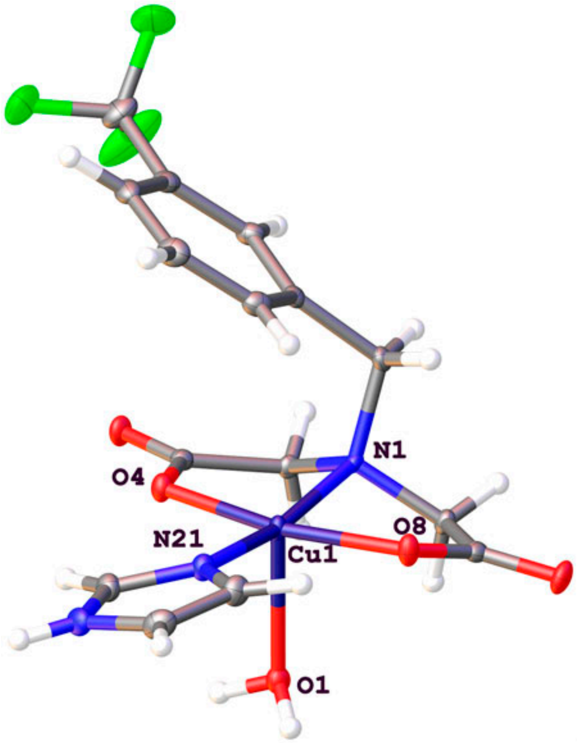


Figure 4. Asymmetric unit of **4** showing the IDA-*mer*-NO_2 conformation of the m-3F chelator and the apical aqua ligand.

In the crystals of **3**, **4**, **6,** and **7** (having the less hindered chelators p-3F or m-3F), the H-bonds involve two (aqua)O–H···O(carboxylate) (2.75–2.79 Å, 149–176°) and one (imidazole)N–H···O(carboxylate) (2.72–2.76 Å, 137–150°) interactions per complex molecule. In contrast, the two independent complex molecules in [Cu(o-3F)(Him)(H_2O)] (**5**) build shorter (aqua)O–H···O(carboxylate) (2.74 Å (average), 156 or 166°) and longer (imidazole) N–H···O(carboxylate) (2.84 Å (average), 166 or 169°) interactions (figure 5). It seems reasonable to state that the steric hindrance caused by the ortho-trifluoromethyl group in **5** and **8** is mainly tied to larger and more linear intermolecular (imidazole)N–H···O(carboxylate) interactions, compared to the corresponding compounds having p-3F or m-3F chelators.

3.3. *Interligand interactions involving the trifluoromethyl group of x-3F chelators*

In the studied crystals, F···F and C–F/π interactions were not observed. In contrast, C–F···H interligand interactions were found in five of the eight reported compounds (table 4). In these crystals, C–F···H interactions are always accompanied by H-bonds, type N–H···O and/or O–H···O. In **1–8**, the F···H distances fall in the range 2.43–2.72 Å, and thereby rather below the 2.9 Å limit value. The C–F···H angles broadly extend in the range between 70 and 180° (i.e., 95–170°). The data also reveal that these interactions are present regardless of (a) the binary (**1** and **2**) or ternary (**3–8**) nature of the copper(II) complexes and (b)

Table 3. Selected copper(II) coordination data in the ternary compounds (bond lengths (Å), trans-basal angles (º)).

Compound	**3**	**4**	**5**		**6**		**7**	**8**
Chelator	p-3F	m-3F	o-3F		p-3F		m-3F	o-3F
IDA group conformation	mer-NO_2	mer-NO_2	mer-NO_2		mer-NO_2		mer-NO_2	mer-NO_2
N-coligand	Him	Him	Him		H5Meim		H5Meim	H5Meim
Cu–N(imidazole-like ligand)	1.954(2)	1.945(2)	1.948(5)	1.952(5)	1.944(3)	1.944(3)	1.949(2)	1.953(3)
Cu–N(x-3F chelator)	2.000(2)	2.003(2)	2.017(5)	2.009(5)	1.993(2)	1.993(2)	2.002(2)	2.005(2)
Cu–O(x-3F chelator)	1.959(2)	1.962(2)	1.956(4)	1.954(4)	1.955(2)	1.954(2)	1.964(2)	1.973(2)
Cu–O(x-3F chelator)	1.976(2)	1.972(2)	1.992(4)	1.982(4)	1.977(2)	1.974(2)	1.975(2)	1.982(2)
Cu–O2(aqua, apical)	2.344(2)	2.313(2)	2.231(5)	2.214(4)	2.328(2)	2.327(2)	2.293(2)	2.321(2)
Trans–N–Cu–N(imidazole-like ligand)	168.71(9)	169.04(8)	169.5(2)	165.5(2)	169.56(12)	169.51(12)	169.87(7)	168.64(11)
Trans–O(carboxylate)–Cu–O(aqua, basal)	168.37(8)	167.74(7)	166.56(16)	166.81(17)	168.18(9)	168.04(9)	167.74(6)	168.45(9)
Addison–Reedijk parameter (τ)	0.01	0.02	0.05	0.02	0.02	0.03	0.04	0.003

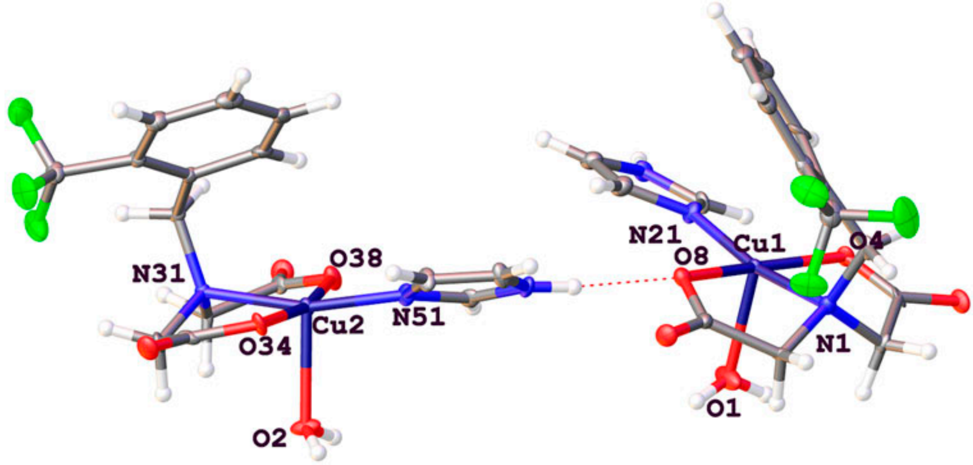


Figure 5. Two non-equivalent complex molecules in the asymmetric unit of the crystal of **5**. The IDA-*mer*-NO_2 conformation of the o-3F chelator is shown as well as the (Him)N–H···O(coordinated, o-3F) interaction connecting these molecules.

Table 4. Interligand C–F···H interactions, including F···H bond lengths (<2.9 Å) and C–F···H angles (º).

Compound	Chelator	N-coligand	–CF_3 disorder	Distance F···H	Angle C–F···H
1	μ_2-p-3F	–	no	F18···H6B 2.603 F19···H2B 2.543 F20···H2A 2.661	C17–F18···H6B 117.83 C17–F19···H2B 166.04 C17–F20···H2A 123.34
2	m-3F	–	no	–	–
3	p-3F	Him	no	–	–
4	m-3F	Him	no	F18···H13 2.488 F20···H24 2.461	C17–F18···H13 112.84 C17–F20···H24 176.12
5	o-3F	Him	no	F15···H48 2.719 F15···H49 2.712 F16···H40B 2.363 F45···H10A 2.532 F45···H49 2.616 F46···H10A 2.431	C13–F15···H48 142.07 C13–F15···H49 166.33 C13–F16···H40B 106.52 C43–F45···H10A 96.21 C43–F45···H49 136.26 C43–F46···H10A 102.10
6	p-3F	H5Meim	yes	F18A···H56C 2.547 F46A···H26C 2.632	C15–F18A···H56C 119.23 C45–F46A···H26C 118.30
7	m-3F	H5Meim	yes	F1A···H10A 2.561 F2A···H8 2.565 F2A···H26C 2.661	C12–F1A···H10A 113.54 C12–F2A···H8 158.94 C12–F2A···H26C 117.58
8	o-3F	H5Meim	no	–	–

the position (p-, m- or o-) of the –CF_3 group in the aromatic ring of the x-3F chelators. Only crystals of **6** and **7** feature disorder of the trifluoromethyl group (with p-3F and m-3F chelators, respectively – see figures 6 and 7). Short contact analysis of CIFs files of **6** and **7** revealed that only one of the two disordered forms of the trifluoromethyl groups is involved in C–F···H interactions. This fact strongly suggests the weakness of these interactions with respect to the O–H···H and N–H···O·H–bonding interactions. No structural correlation is further observed between the presence of C–F···H interligand interactions and the disorder of the trifluoromethyl group.

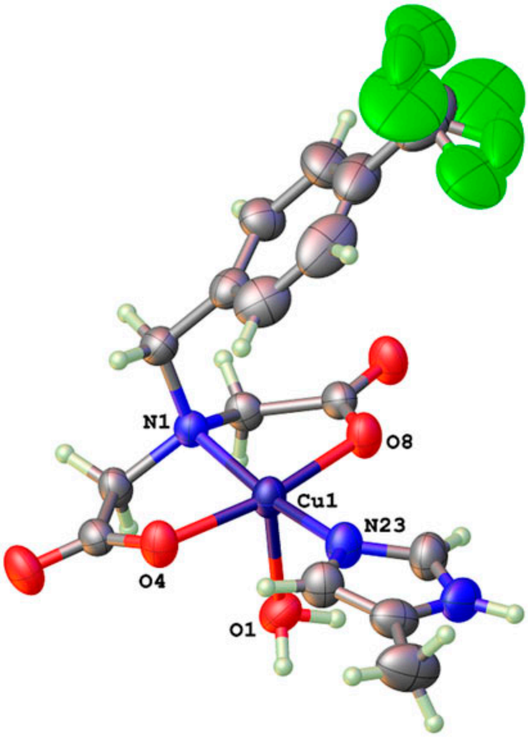


Figure 6. Asymmetric unit of **6** showing the disorder of the trifluoromethyl group and the *mer*-NO_2 conformation of the IDA moiety in p-3F.

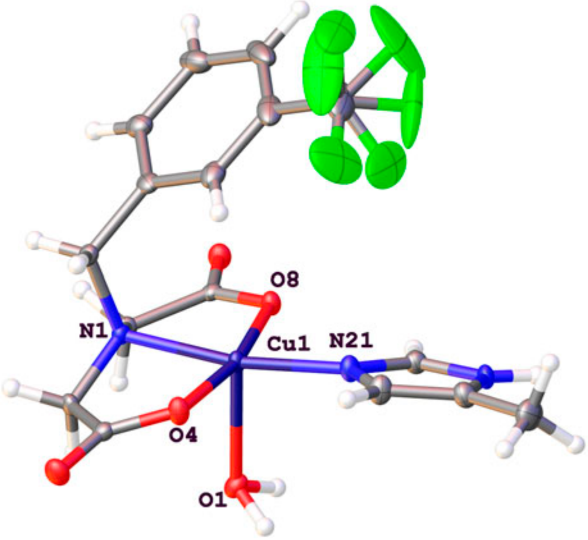


Figure 7. Asymmetric unit of **7** showing the disorder of the trifluoromethyl group and the *mer*-NO_2 conformation of the IDA moiety in m-3F.

3.4. *Chelating ligand conformation of the IDA group in 1–8 and related copper(II) iminodiacetates*

Another aspect to be discussed in this work concerns the conformation of the iminodiacetate moiety within the x-3F chelating ligands. This question must be addressed differently regarding binary and ternary complexes.

Table 5 summarizes examples of mononuclear and binuclear copper(II) chelates where the IDA moiety exhibits a *fac*-NO + O(apical) conformation, with the two metal-glycinate rings nearly perpendicular to each other and sharing the Cu–N bond. The *fac*-tridentate conformation of the chelator yields two short and one long coordination bonds within the 4 + 1 or 4 + 1 + 1 metal surrounding (square pyramidal or asymmetrical elongated octahedron, respectively). This conformation is directly related to the Jahn–Teller distortions caused by the $3d^9$ electronic structure of copper(II) centers. The *fac*-NO + O(apical) IDA conformation is usually found in polymeric compounds where the Cu–N(IDA) and the O'-carboxylate donors (with O'-being an O-carboxylate appertaining to the chelator of one adjacent metallic center) are *trans* to each other. This is the case for **1** (figure 1). Note that in table 5, three different kinds of polymers are found as follows: (i) polymers having their own iminodiacetate ligand; (ii) complexes with binucleating chelators (such as HDTA, with a 1,6-hexamethylene spacer, or p-PhDTA, with a p-phenylene spacer); (iii) and also 1,3-thiazolidine-2,4-dicarboxylate (1,3-thiadc, a C,C'-disubstituted IDA chelator). One compound out from this general trend is the binary Cu(II) chelate of N-carboxymethyl-S-prolinate(2-) (cm-S-Pro, a N,C-disubstituted IDA ligand). In this case, the Cu–N(IDA) bond and one aqua ligand (instead of an O'-carboxylate donor) are *trans* to each other.

Table 5. Copper(II) iminodiacetate-like chelates with the IDA moiety in *fac*-NO + O (apical) conformation.

Compound or CSD ref. code	Chelator[a]	R[a] group	Formula	Cu(II) coord.	Trans–donor to the Cu–N bond	Apical donor(s)	Reference
Compound **1**	p-3F	p-(tfm)Bz	$\{[Cu(p\text{-}3F)(H_2O)]\cdot 3H_2O\}_n$	4 + 1	O'	O(carboxyl)	This work
CUBMER	IDA	H	$\{[Cu(\mu_2\text{-}IDA)(H_2O)_2]\}_n$	4 + 1 + 1	O'	OW2 and O (carboxyl)	[24]
CUIMAC							[25]
CUIMAC01							[26]
YADVUW	IDA	H	$\{[Cu(\mu_2\text{-}IDA)(H_2O)]\}_n$	4 + 1	O'	O(carboxyl)	[27]
YEWJIT	HDTA	C6-alkyl	$\{[Cu_2(\mu_4\text{-}HDTA)(H_2O)_2]\cdot 4H_2O\}_n$	4 + 1	O'	O(carboxyl)	[28]
BODYID	p-PhDTA	p-phenylene	$\{[Cu_2(\mu_4\text{-}PhDTA)(dmso)_2]\cdot 4dmso\}_n$	4 + 1	O'	O(carboxyl)	[29]
SENTOW	1,3-thiadc	1,3-thia	$\{[Cu(\mu_{2-1},3\text{-}thiadc)(H_2O)_2]\cdot H2O\}_n$	4 + 1 + 1	O'	O(carboxyl) and OW2	[30]
REDWEE	1,3-thiadc	1,3-thia	$\{[Cu(\mu_{2-1},3\text{-}thiadc)(DMF)]\}_n$	4 + 1	O'	O(carboxyl)	[31]
WITRUM	cm-S-Pro		$\{[Cu(\mu_2\text{-}cm\text{-}S\text{-}Pro)(H_2O)]\cdot 2H_2O\}_n$	4 + 1	OW!	O(carboxyl)	[32]

[a] Abbreviations for some chelators and groups: p-(tfm)Bz, p-(trifluoromethyl)benzyl; HDTA, 1,6-hexamethylenedianinotetraacetate (4-) ligand; C6-alkyl, n-hexamethylene spacer; p-PhDTA, p-phenylenediamine-N,N,N',N'-tetra-acetato(4-) ligand; p-phenylene, 1,4-phenylene spacer, 1,3-thiadc, 1,3-thiazolidine-2,4-dicarboxylato(2-) ligand; 1,3-thia, 1,3-thiazolidine; cm-S-Pro, N-(carboxymethyl)-S-prolinato(2-) ligand.

Table 6 summarizes structural information on binary copper(II) compounds where the IDA moiety of the chelator adopts a *mer*-NO_2 conformation, that is two nearly coplanar Cu-glycinate rings that share the Cu–N bond. This IDA conformation is more frequent than the *fac*-NO + O(apical). The *mer*-NO_2 conformation is found in a remarkable variety of binary monomeric or polymeric compounds, with 4 + 1 and 4 + 1 + 1 copper(II) coordination. It is noticeable that the IDA-*mer*-NO_2 conformation is always present in molecular compounds with Cu(II) coordination type 4 + 1 having two aqua ligands. Compound **2** agrees with this criterion (figure 2). The *mer*-NO_2 conformation is also present in polymeric compounds where the Cu–N(IDA) bond and an aqua ligand are *trans* to each other, and an additional aqua or a neighboring O'-carboxylate is on the apical/distal coordination site. Other binary Cu(II) compounds showing the IDA-*mer*-NO_2 conformation are polymers where the chelators have two bridging carboxylate groups or a tridentate carboxylate group. Regarding ternary complexes, the IDA-*mer*-NO_2 conformation is also well documented. For instance, this conformation has been previously described for a variety of ternary copper(II) complexes having an iminodiacetate-like tridentate chelator and a coligand which supplies one N-heterocyclic donor per metal center. No exception has been reported to this

Table 6. Copper(II) iminodiacetate-like chelates with the IDA moiety in *mer*-NO_2 conformation.

Compound or CSD ref. code	Chelator[a]	R[a] group	Formula	Cu(II) coord.	Trans–donor to Cu–N bond	Apical donor(s)	Reference
2	m-3F	m-tfmBz	[Cu(m3F)(H_2O)]	4 + 1	OW1	OW2	This work
SUCXET	o-tolIDA	o-tolyl	[Cu(o-tIDA)(H_2O)$_2$]	4 + 1	OW1	OW2	[33]
VAMJUP	TEBIDA	tert-Bu	[Cu(TEBIDA)(H_2O)$_2$]	4 + 1	OW1	OW2	[34]
VUSHOG	p-tolIDA	p-tolyl	[Cu(p-tolylIDA)(H_2O)$_2$]	4 + 1	OW1	OW2	[35]
YIPWEA	BCAA	1-adamantyl	[Cu(BCAAA)(H_2O)$_2$]	4 + 1	OW1	OW2	[36]
ZAMBUK	2EtPhIDA	N2-Et-phenyl	[Cu(2EtPhIDA)(H_2O)$_2$]	4 + 1	OW1	OW2	[37]
LIRMIK	L	Diarylalkyl	[Cu$_2$(mu$_2$-Q)(H_2O)$_4$]·4H_2O	4 + 1	OW1	OW2	[38]
VENBEV	p-PhDTA	p-phenylene	{[Cu$_2$(μ_4-p-PhDTA)(H_2O)$_4$]·2H_2O}$_n$	4 + 1 + 1	OW1	OW2 and O'	[39]
CUEDTA01	EDTA	1,2-ethylene	{]Cu$_2$(μ_4-EDTA)(H_2O)$_2$]·2H_2O}$_n$	4 + 1	OW	O'	[40]
ONAMAS	MIDA	Me	{[Cu(μ_3-MIDA)]}$_n$	4 + 1	O'	O"	[41]
SOSWAZ	1pheida	2MeBz	{[Cu(μ_{3-1}pheida)]}$_n$	4 + 1 + 1	O'	O' y O"	[42]
DINFOX	p-tm-XDTA	tm-xyl	{[Cu$_2$(μ_{6-}p-tm-XDTA)]}$_n$	4 + 1	O'	O"	[43]
ZUFSEY	CMThreo	C-(hydroxyethyl)	{[Cu(μ_2-CMT)(H_2O)]}$_n$	4 + 1 + 1	O'	OW and O"	[44]
SISCUS	cm-L-Phe	C-benzyl	{[Cu(cm-L-Phe)(H_2O)]}$_n$	4 + 1 + 1	O'	OW and O"	[45]
SENTIQ	1,3-thiadc	1,3-thia	{[Cu(1,3-thiadc)(H_2O)]}$_n$	4 + 1 + 1	O'	O' and O"	[32]

[a]Abbreviations for some N-substituent of IDA groups (unless indicated a C-substitution): m-(tfm)Bz, m-(trifluoromethyl)benzyl; Diarylalkyl, 4.4'dimethylene-1,1'-diphenyl spacer; 2MeBz, o-tolyl-methyl; tm-xyl, 2,4,5,6-tetramethyl-p-xylyl spacer; 1,3-thia, 1,3-thiazolidine.

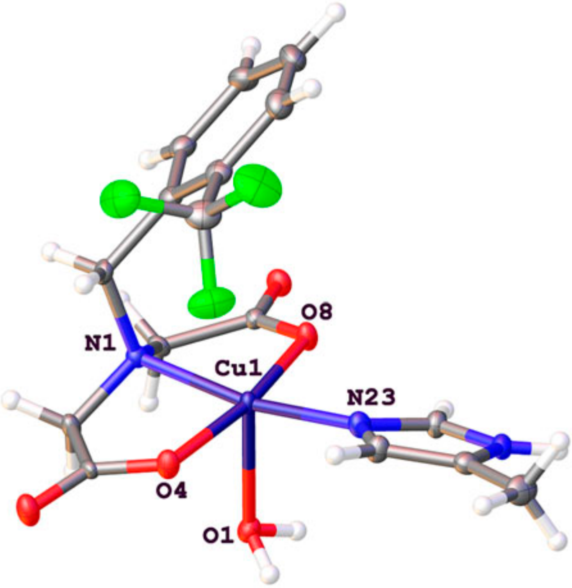
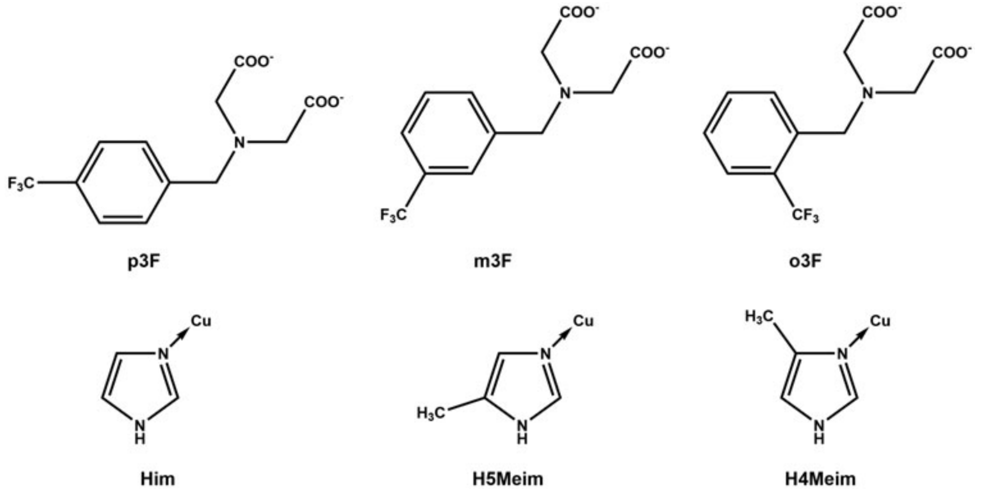


Figure 8. Asymmetric unit of **8** showing the IDA-*mer*-NO_2 conformation of the chelator o-3F.



Scheme 1. Chelating and imidazole-like ligands used in this work (the two tautomers of H(4/5)Meim are shown).

structural correlation, including **3–8** (figures 3–8). Other examples of ternary copper(II) complexes with typical N-heterocyclic ligands have benzimidazole [24], H(4/5)methylimidazole [16, 17], 2,4-diaminopyrimidine [11], adenine [46] and related N-heterocyclic bioligands [13–15, 47] such as hypoxanthine [48] or the synthetic acyclic–nucleoside acyclovir [49].

3.5. *Vibrational and electronic spectra and thermal analyses by coupled TG + FT-IR spectroscopy*

The infrared spectra of trifluoromethyl-aryl compounds exhibit at least three bands related to the F_3C-group, expected at 1321 ± 9, 1179 ± 7, and 1140 ± 9 cm^{-1}. The origin of these bands has been controversial, probably because they are non-pure stretching bands. The last two bands can be essentially attributed to the ν_{as} and ν_d modes, while the absorption near 1321 cm^{-1} could be a combined band of the stretching and deformation modes of this group. The aforementioned bands appear in spectra of the four reported organic ligands at 1322 ± 11, 1178 ± 7, and 1125 ± 15, the latter value being out of the expected range (1140 ± 9 cm^{-1}). The averaged values of these bands in the corresponding spectra of the copper (II) complexes are 1325 ± 10, 1167 ± 12, and 1134 ± 11 cm^{-1}. The band near 1325 cm^{-1} is similar in the spectra of both the organic ligands and the copper(II) complexes. In most of the metal complexes, the other two absorptions occur with a smaller difference in wavenumber (30–45 cm^{-1}) compared to the organic ligands. The highest shift at lower frequencies was observed for the band near 1179 cm^{-1}.

The electronic (diffuse reflectance) spectra of studied compounds exhibit, as expected, a broad and asymmetric absorption with maxima ranging between 11.9 and 14.8 kK. Spectra of binary chelates **1** and **2** had their maxima below 14,000 cm^{-1}, whereas the maximum absorption in **3–8** (with one Him-like ligand instead of the proximal aqua ligand in the 4 + 1 Cu(II) coordination) was registered at 14,300–14,750 cm^{-1}. The O-aqua substitution by N-imidazole is performed in solutions where the H_2O/imidazole molar ratio is 55.5 M/0.01 M. This is possible due to the strong affinity of the N-imidazole donor, a borderline Pearson base, to the copper(II) center, a borderline Pearson acid. Thus, the coordination of an imidazole instead of an O-donor increases the ligand field and for compounds with similar coordination geometry (type 4 + 1 in **1**–**8**) consequently increases the ν_{max} values, as indeed is observed (see SM3).

All compounds reported in this work, binary (**1** and **2**) and ternary compounds (**3–8**), have also been studied by coupled TG + IR spectroscopy. Their thermal behavior can be exemplified in the spectra of **2** and **4**. Detailed information on the TG + FT-IR measurements of both complexes as well as additional data from **1**, **3,** and **5–8** can be found in the Supplementary Material SM4. Compound **2** (see SM4.2 and table 7) decomposes in three rather different steps. The first step is mainly characterized by the loss of both aqua ligands (the FT-IR spectra recorded at this time also revealed the loss of some CO_2). Afterward, the decomposition of the m-3F organic ligand occurs in a quite sharp event (weight loss

Table 7. Thermogravimetric study of **2** under dry air flow (sample 7.064 mg). Evolved gasses were identified by a series of 30 time-spaced FT-IR spectra along 90 min of experiment. The final CuO residue was formed about min. 55.

			Weight		
Step or residue	Temperature (ºC)	Time (min)	Experimental %	Calculated %	Gasses or residue
1	50–155	2–13	8.727	9.268	2 H_2O, CO_2 (t)
2	155–330	13–32.5	63.569	–	H_2O, CO_2, CO, TFT, TMA
3	330–595	32.5–54	7.320	–	H_2O, CO_2, CO, TFT, N_2O, NO
Residue	595	~55	20.377	20.460	CuO

Notes: t = traces, TFT = trifluorotoluene, TMA = trimethylamine.

Table 8. Thermogravimetric study of **4** under dry air flow (sample 8.090 mg). Evolved gasses were identified by a series of 25 time-spaced FT-IR spectra along 90 min of experiment. The final CuO residue was formed at min. 45.

Step or residue	Temperature (ºC)	Time (min)	Weight Experimental %	 Calculated %	Gasses or residue
1a + 1b	95–125–160	7–10.5–14	4.832	4.105	1 H_2O, CO_2 (t)
2	160–220	4–19.5	18.693	–	H_2O, CO_2
3	220–260	19.5–23	14.608	–	H_2O, CO_2
4	260–370	23–35	18.657	–	H_2O, CO_2, CO, TFT (t)
5	370–495	35–47	24.657	–	H_2O, CO_2, CO (t), N_2O, NO, NO_2
Residue	495	~45	19.015	18.126	CuO

Notes: t = traces, TFT = trifluorotoluene, TMA = trimethylamine.

~63.5%). This process is related with the production of CO_2, H_2O, CO, trifluorotoluene (TFT) and trimethylamine (TMA) as evolving gasses. At higher temperatures (>330 °C), during the last step, N_2O and NO gasses instead of TMA are observed. The weight of the final residue is in excellent agreement to that calculated for a CuO residue (table 7).

Compound **4** (SM4.3 and table 8) exhibits an overall aqua loss process (~4.8%) divided into two similar steps (Ia and Ib, with a ~2.4% loss per step). Again, the corresponding FT-IR spectra revealed the loss of some CO_2 during this initial step. In this case, the formation of TFT is weakly observed (step 4) while that of TMA can be neglected. In contrast, the formation of the three N-oxides gasses (N_2O, N_2O and NO) are observed in the last step (370–500 °C), mainly related to the decomposition of the 5-methylimidazole ligand. The weight of the final residue (about 600 °C) agrees to that calculated for a non-pure CuO residue within an experimental error <1%.

The formation of different amounts of TMA and TFT is also observed in all the p-3F, m-3F and o-3F derivatives here reported. This fact strongly suggests that the decarboxylation of the x-3F chelators can be followed by the appropriate recombination process. This singularity should be only understood as one decomposition possibility, among others, also associated to the well-known thermodynamic stability of the C–F bonds. In this regard, similar TG experiments also revealed the formation of TMA during the thermal decomposition of Cu(II) complexes with N-methyl-IDA [46] or N-benzyl-IDA (unpublished results).

4. Concluding remarks

Binary **1** showed a polymeric nature and the iminodiacetate chelating moiety in *fac*-NO + O conformation. In contrast, **2–8** have a molecular nature and exhibit a *mer*-NO_2 conformation. All copper(II) complexes have in common the coordination of aqua ligands (**1–8**). The formation of rather strong N–H···O and/or O–H···O interactions does not preclude the formation of C–H···F interactions (**1**, **4–7**). However, C–F/π or F···F interactions are missing. Appropriate comparisons revealed that the C–H···F interactions occur irrespective of (a) the dimensionality of the compounds (polymeric (**1**) or molecular (**2–8**) structures) and (b) the binary (**1** and **2**) or mixed-ligand nature (**3–8**) of the compounds. No further structural correlation was observed between the presence of C–F···H interligand interactions and the disorder on the trifluoromethyl group.

Supplementary material

^{1}H NMR spectra of the chelating H_2x-3F ligands and the HoTTG by-product are given in SM1. FT-IR spectra of the organic acids (SM2.1) and metal complexes **1–8** (SM2.2–SM2.3), electronic spectra of **1–8** (SM3), coupled TG + FT-IR results on **2** and **4** are provided. Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Center, CCDC 1040268–1040275 (**1–8**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (0) 1223336033; E-mail: deposit@ccdc.cam.ac.uk).

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1062092].

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