# Trifluoromethylated enaminones and their explorative coordination chemistry with Cu(II): synthesis, redox properties and structural characterization of the complexes<sup>†</sup>

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The syntheses of three original trifluoromethylated enaminones **L1H–L3H**, an unexplored type of ligand with possible multiple coordination centres, their redox properties and explorative coordination chemistry with copper(II) are presented. The ability of these ligands to coordinate copper(II) and then to form new mono- and dinuclear complexes is presented and discussed. The consequences of this metal coordination on redox properties are also explored.

# Introduction

The discovery just over twenty years ago that some metallic hybrid inorganic–organic clusters may behave as single-molecule magnets (SMMs)<sup>1</sup> is currently stimulating abundant research in relation to potential applications in information processing and storage.<sup>2</sup> In that context and relevant to the work presented here, one of us recently reported several examples of molecular clusters exhibiting interesting magnetic properties (like SMM ones) involving N,N,O or O,N,O enaminoketone ligands (Fig. 1).<sup>3-7</sup>

It appeared that ligands coordinating the metal cation could play an important role in the magnetic properties. With this in mind, and as part of our work on polynuclear metal complexes,<sup>8</sup> we chose the trifluoromethylated enaminone ligand which may exhibit interesting redox properties as a "noninnocent" ligand<sup>9</sup> and which could be a magnetic coupler for propagating interactions between paramagnetic ions.

Trifluoromethylated  $\beta$ -aminovinyl ketones are known and have been frequently used as valuable building blocks, to prepare various trifluoromethylated aromatics and heterocycles.<sup>10</sup> The ability of enaminones to coordinate with a variety of transition metals has been used with success to prepare a number of metallomesogens with interesting liquid crystal properties,<sup>11-14</sup> highly-active catalysts for olefin polymerization, including recently fluorinated enaminones.<sup>15-17</sup> However a detailed study of the redox properties of fluorinated enaminones and their useful coordination



Fig. 1  $[Dy_3Cu_6]$  single molecule magnet.

chemistry with broad applications in materials science has scarcely been studied.<sup>18-22</sup> Recently a series of fluorinated enaminones bearing two independent coordination centers have been obtained and the crystal structure of a Cu(II) complex was revealed.<sup>18</sup> The crystal structure of a Mn(II) complex with a trifluoromethylated enaminone derivative of 3-imidazoline nitroxide was also published with a weak ferromagnetic property;19 in addition crystal structures of Cu(II), Ni(II) and Pd(II) bischelates with a trifluoromethylated enaminoketone derivative of 2-imidazoline nitroxide were also known.<sup>20</sup> As far as we know there are only two reports of the electrochemistry of fluorinated enaminones and their Cu(II) and Ni(II) complexes.<sup>21-22</sup> These two studies showed that the reduction of the ligands in dimethylformamide were irreversible, giving unstable radical anions as reduction products and that the corresponding Cu(II) and Ni(II) chelates were characterized in most cases by a quasi-reversible one-electron transfer; most of the enaminones presented in these two papers did not feature possible mulliple coordination centers, and no further extension with potential applications in materials science have appeared in the literature.

As part of our ongoing efforts in search of novel polynuclear metal complexes with potential involvement in catalysis, magnetism and biology, we wish to report in this paper our preliminary results with the synthesis of three trifluoromethylated

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 $<sup>\</sup>dagger$  CCDC reference numbers 682201–682203 for [Cu(L1)<sub>2</sub>], [Cu<sub>2</sub>(L2)<sub>4</sub>] and [Cu(L3)<sub>2</sub>] respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b805071f

enaminones (L1H–L3H) (Fig. 2) including their redox properties and the synthesis, structural characterization and electrochemical behavior of the resulting Cu(II) complexes.



Fig. 2 Structures of the trifluoromethylated enaminone ligands L1H–L3H.

# **Results and discussion**

### Syntheses of the ligands

The enaminone ligands **L1H–L3H** were prepared in good yields in two straightforward steps: trifluoroacetylation of commercially available ethyl vinyl ether [trifluoroacetic anhydride (TFAA)/pyridine in anhydrous dichloromethane], followed by O–N exchange reaction of the resulting crude (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one,<sup>23</sup> with the corresponding amines (slight excess) in anhydrous acetonitrile (Scheme 1).



Scheme 1 General access to the ligands L1H-L3H.

The benzylic substrate L1H<sup>24</sup> was obtained in a 81% isolated yield through the dropwise addition of the benzyl amine to a cooled (0 °C) anhydrous acetonitrile solution containing the crude (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one, followed by warming the reaction mixture to room temperature for one hour (TLC monitoring). The aromatic L2H and heterocyclic L3H substrates were also obtained in very good yields (84% for L2H and 75% for L3H) under refluxing conditions for one hour (TLC monitoring). All the enaminone ligands were obtained as Z isomers, as determined by <sup>1</sup>H NMR (small coupling constant of the olefinic protons of 7–8 Hz and a deshielded peak of the amino proton  $\delta_{\rm H} > 10.0$  ppm) due to hydrogen bonding between NH and C=O. The three enaminones were obtained as solids; L1H was purified by silica gel chromatography whereas L2H and L3H were recrystallized from the crude product.

# Syntheses of the Cu(II) complexes

L1H was first chosen as a model ligand and the corresponding copper(II) complex was prepared through dropwise addition of a

methanolic solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.0 equiv.) to a methanolic solution of the ligand. After stirring at room temperature for ten minutes, Et<sub>3</sub>N (in excess) was then added and the resulting green solution stirred for an additional two hours. Single crystals suitable for X-ray characterization were obtained after three days of evaporation. The complex was obtained as green needles in a 43% isolated yield. Copper(II) complexes of **L2H** (green plates, 63%) and **L3H** (brown needles, 75%) were prepared in a similar way.

### Single crystal X-ray diffraction studies

**Data collection.** The data were processed using the KappaCCD analysis programs.<sup>25</sup> The lattice constants were refined by least-squares refinements. For all complexes, no absorption correction was applied to the data sets. All the data collections have been performed at 293 K.

Structure solution and refinement.  $[Cu(L1)_2]$  and  $[Cu_2(L2)_4]$  complexes crystallize in the monoclinic system. According to the observed systematic extinctions, their structures have been solved and refined in the  $P2_1/c$ ,  $P2_1/n$  space groups respectively.  $[Cu(L3)_2]$  complex crystallizes in the triclinic system. Due to the observed systematic extinctions, its structure has been solved and refined in the  $P\overline{1}$  space group.

All the structures have been solved by direct methods using the SIR97 program<sup>26</sup> combined with Fourier difference syntheses and refined against *F* using the CRYSTALS program.<sup>27</sup> The hydrogen atoms have been either found by Fourier difference and located theoretically based on the conformation and environment of the supporting atom. Hydrogen atoms were introduced in calculated positions and refined riding on their parents atoms. All the atomic displacement parameters for non-hydrogen atoms have been refined anisotropically.

## Crystal structure descriptions<sup>†</sup>.

[ $Cu(L1)_2$ ]. The complex is built from one copper atom surrounded by two L1 ligands (see Fig. 3a). No solvent molecules or counter-ions have been found in the structure during the refinement. The complex entity appears then to be neutral with one Cu(II) and two (L1)<sup>-</sup> deprotonated ligands. The metal is located in an almost perfect square planar environment with Cu–O and Cu–N bond lengths which are equal to 1.913(3) and 1.994(4) Å respectively. N–Cu–N and O–Cu–O angles, due to the inversion center located on the metal position, are equal to 180°. N–Cu– O range from 88.9(1) to 91.1(1)°. The structural packing can be viewed as columns of complexes running along the *a* axis



**Fig. 3** (a)  $[Cu(L1)_2]$  entity; (b) structural packing of the structure along the *b* axis of the unit cell (hydrogen atoms have been omitted for clarity).

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of the unit cell (see Fig. 3b). As no hydrogen bond has been found, the structural cohesion inside the columns is assumed by  $\pi$ - $\pi$  interactions between phenyl rings which stack perfectly (distance between two consecutive phenyl rings is equal to 3.8 Å). The structural cohesion between two neighbouring columns is assumed by van der Waals interactions.

 $[Cu_2(L2)_4]$ . The asymmetric unit of this structure is built from one copper atom surrounded by two  $(L2)^{-}$  ligands. One of these L2 ligands has an asymmetric unit with its CN moiety connected to a neighbouring and crystallographically equivalent copper atom, forming then the dimer, whereas the second L2 ligand stays free. The final entity can be then described as a copper(II) dimer with the following refined formula:  $[Cu_2(L2)_4]$  (see Fig. 4a). The copper atom exhibits a distorted square pyramidal environment. The square base of this is composed by two nitrogen atoms and two oxygen atoms belonging to the two L2 ligands of the  $\{Cu(L2)_2\}$  unit (half of the dimer). The Cu–O bond lengths (1.914 Å and 1.919 Å) are a bit shorter than the Cu-N bond lengths (1.981 (3) Å and 1.986 (3) Å) but in good agreement with those previously reported in the literature.<sup>5</sup> O-Cu-N angles range from 88.7 (1)° to 92.6 (1)° and from 164.5 (1)° to 170.1 (1)°. Inside a dimer, the Cu-Cu distance is equal to 6.727(1) Å. This distance appears to be too long to expect any interesting magnetic properties for this complex. As no hydrogens and counter-ions have been found in the structure, the structural cohesion is assumed by van der Waals interactions. The structural packing can be considered as columns of dimers running along the *a* axis of the unit cell.



**Fig. 4** (a)  $[Cu_2(L2)_4]$  entity; (b) structural packing of the structure along the *a* axis of the unit cell (hydrogen atoms have been omitted for clarity).

 $[Cu(L3)_2]$ . The structure contains three complexes per unit cell. This complex is formed from one copper(II) cation surrounded by two deprotonated L3 ligands forming then a neutral mononuclear entity as no counter-ion has been found in the structure (see Fig. 5a). The metal is located in a distorted octahedral environment and is connected to four nitrogen atoms (two per ligand) and two oxygen atoms (one per ligand). Cu-N and Cu-O bond lengths range from 1.945(7) to 2.221(6) Å and from 2.058(6) to 2.258(6) Å respectively. The Cu-L3 bond lengths (three nitrogen atoms and one oxygen atom) in the square plane of the bipyramid range from 1.945(7) Å to 2.089(7) Å. Cu-L3 bond lengths in the equatorial direction are longer than those in the square plane and are equal to 2.221(6) Å and 2.258(6) Å. X-Cu-Y (with X and Y = N or O) range from 78.1(3)° to 97.8(3)° and from 167.2(2) to  $175.5(3)^{\circ}$  illustrating that the octahedral metal environment is distorted (Addison parameter equal to 0.08, 0.12 and 0.10 for the three complexes of the unit cell).<sup>28</sup>



**Fig. 5** (a)  $[Cu(L3)_2]$  entity; (b) structural packing of the structure along the *a* axis of the unit cell (hydrogen atoms have been omitted for clarity).

The structural packing can be viewed as independent clusters (see Fig. 5b). As no hydrogen bonds has been found in the structure, the structural cohesion is assumed by van der Waals interactions.

# **Electrochemical studies**

**Ligands L1H–L3H.** The redox properties of ligands **L1H–L3H** were explored by cyclic voltammetry (see Experimental for details). The three ligands were found to be irreversibly reduced in a single step at potentials between -1.52 and -1.89 V in dichloromethane and between -1.36 V and -1.89 V in DMF (Table 1). In both solvents the reduction step remains irreversible up to 3 V s<sup>-1</sup> demonstrating that the radical anion is quite unstable.<sup>29</sup> **L1H** was found to be irreversibly oxidized at a rather high oxidation potential close to 2.10 V in dichloromethane. No clear oxidation steps could be detected for **L2H** and **L3H**.

**Copper(II) complexes in dichloromethane.** First, we can note that, for each complex, no reduction peak corresponding to the free ligand in solution was detected. The cyclic voltammetry of the Cu(L1)<sub>2</sub> and the Cu<sub>2</sub>(L2)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> exhibited an irreversible reduction wave around -1.0 V (Table 2). The formation of an irreversible anodic wave is observed around 0.3 V for the two complexes and they are connected to the reduction process. The exhaustive electrolysis at -1.4 V gave a consumption of 2 F mol<sup>-1</sup> for complex Cu(L1)<sub>2</sub> and 4 F mol<sup>-1</sup> for complex Cu<sub>2</sub>(L2)<sub>4</sub>. The cyclic voltammetry recorded after the exhaustive electrolysis showed only the reduction peak of the free ligand. The working electrode when removed from the electrolytic solution was characterized by the formation of a Cu mirror. From these observations, the reduction mechanism for these two complexes can be summarized as follows:

$$Cu(L1)_2 + 2e \rightarrow Cu^0 + 2L1^-$$
$$Cu_2(L2)_2 + 4e \rightarrow Cu^0 + 4L2$$

 Table 1
 Electrochemical data<sup>a</sup> for the reduction of the ligands L1H–L3H

Compound	$E_{\rm pc}{}^{b}/{ m V}$
L1H	$-1.89 (-1.89^{\circ})$
L2H	$-1.52 (-1.36^{\circ})$
L3H	$-1.53 (-1.53^{\circ})$

<sup>*a*</sup> Peak potential recorded in dichloromethane at 293 K with a glassy carbon electrode, with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte; all potentials are *versus* SCE, scan rate 0.1 V s<sup>-1</sup>. <sup>*b*</sup> Cathodic peak potential. <sup>*c*</sup> In dimethylformamide with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte.

Table 2 Electrochemical data" for the copper(11) complexes in dichloromethane

Complex	$E_{ m pc}{}^{b}/{ m V}$	$E_{\mathrm{pa}}{}^{c}/\mathrm{V}$
Cu(L1) <sub>2</sub>	-1.00	0.35
$Cu_2(L2)_4$	-0.80	0.40
$Cu(L3)_2$	-0.73/-0.96	-0.10

<sup>*a*</sup> Peak potential recorded at 293 K with a glassy carbon electrode, with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte; all potentials are *versus* SCE, scan rate 0.1 V s<sup>-1</sup>. <sup>*b*</sup> Cathodic peak potential. <sup>*c*</sup> Anodic peak potential only appears after scanning through the first reduction step.

In contrast, the Cu(L3)<sub>2</sub> complex gave two irreversible waves with the same intensity at -0.73 V and -0.96 V. However as observed for the previous two complexes, exhaustive electrolysis at a potential corresponding to the second reduction step gave a Cu mirror on the surface of the glassy carbon electrode with a concommitant anodic peak close to -0.1 V. It appears reasonable to propose that the two reduction steps do correspond to two monoelectronic transfers, with the first one corresponding to the formation of the copper(1) complex and the second transfer to the further reduction into copper(0).

**Copper(II) complexes in** *N*,*N*-**dimethylformamide.** The reduction of our complexes is found to occur at more positive potentials than their corresponding ligands, and the reduction processes were found to be irreversible. We can note that our results are different from the literature,<sup>22</sup> as it was observed (although with different enaminoketone ligands and corresponding complexes) that the reduction processes were monoelectronic and quasi-reversible for copper and nickel complexes indicating some stability with the copper(I) and nickel(I).

With our systems we have obtained for each complex a first monoelectronic irreversible wave with a more complicated redox pathway. This first reduction step is located at potentials between -0.38 V and -0.78 V, with the dimer Cu<sub>2</sub>(L2)<sub>4</sub> the easier to reduce. In addition the first reduction is connected to a quasi-reversible [Cu(L3)<sub>2</sub>] or irreversible oxidation [Cu(L1)<sub>2</sub>] wave at -0.25 and +0.12 V (Table 3). The exhaustive electroysis at a potential corresponding to the first reduction step gave 1 F mol<sup>-1</sup> for Cu(L1)<sub>2</sub> and Cu(L3)<sub>2</sub> complexes. From these observations, it seems consistent to propose that the first reduction generates a copper(I) species stabilized by *N*,*N*-dimethylformamide as opposed to dichloromethane. The second reduction wave with

Table 3 Electrochemical data<sup>*a*</sup> for the copper(II) complexes in N,N-dimethylformamide

Complex	$E_{\rm pc}{}^b/{ m V}$	$E_{\rm pa}{}^f/{ m V}$
$ \frac{\operatorname{Cu}(\mathbf{L1})_2}{\operatorname{Cu}_2(\mathbf{L2})_4}\\\operatorname{Cu}(\mathbf{L3})_2 $	$-0.65/-1.92^{c}$ $-0.38/-1.85^{d}$ $-0.78/-1.10^{e}$	0.12 0.06 -0.25

<sup>*a*</sup> Peak potential recorded at 293 K with a glassy carbon electrode, with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte; all potentials are *versus* SCE, scan rate 0.1 V s<sup>-1</sup>. <sup>*b*</sup> Cathodic peak potential. <sup>*c*</sup> An additional reduction step is observed at -2.7 V (irreversible). <sup>*a*</sup> Two additional reduction steps are observed at -2.4 V (irreversible) and -2.7 V (reversible). <sup>*c*</sup> Four additional reduction steps are observed at -1.9 V (irreversible), -2.1 V (irreversible) and -2.7 V (irreversible), -2.3 V (irreversible) and -2.7 V (irreversible). <sup>*c*</sup> Anodic peak potential only appears after scanning through the first reduction step.

a same intensity could be the copper(0) formation (Table 3). For the dimer  $Cu_2(L2)_4$ , the redox process seems more complicated. Although the cyclic voltammetry behavior was similar to the previous complexes, the coulometry at the first reduction step was not clear to determine the electron number exchange in this redox process. In addition other reduction steps were observed at more negative potentials for all the complexes (Table 3). The elucidation of the redox mechanism is in progress in our laboratories.

# Conclusions

The synthesis of three trifluoromethylated enaminone ligands, their redox behaviors and their coordination chemistry with copper(II) was presented. The copper(II) complexes were characterized by X-Ray single crystal structure analysis and cyclic voltammetry; two of these complexes were found to be monomeric species and one is a dimeric species. The redox behavior of these complexes were found to be different in dichloromethane and in N,Ndimethylformamide; in the former solvent for all the complexes copper(II) was directly reduced to copper(0), but in the latter solvent copper(I) species seem to be more stabilized since the two redox transitions copper(II)/copper(I) and copper(I)/copper(0) could be detected. These preliminary studies on the coordination potential of these new enaminones ligands will give an access to other heteromultinuclear complexes. Following a precise strategy, it will be then possible to associate ligand redox properties to magnetic properties of these future complexes in order to obtain molecular electro-magnetic switches.

# Experimental

# General comments

All operations and manipulations were performed under inert atmosphere. Solvents were distilled before use. Reagents were obtained commercially and used without further purification except for benzylamine which was distilled. <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance 300 spectrometer in CDCl<sub>3</sub> at 300 MHz, 282 MHz and 75 MHz respectively. Chemical shifts are given in ppm relative to residual peak of solvent ( $\delta_{\rm H} = 7.26$  ppm for CHCl<sub>3</sub>,  $\delta_{\rm C} = 77.0$  ppm for CDCl<sub>3</sub>) or CFCl<sub>3</sub> (<sup>19</sup>F). Coupling constants are given in Hertz. Silica gel chromatography was performed on Macherey-Nagel Silica gel 60M (0.04-0.063 mm). Solvents for chromatography are: ethyl acetate (EA), and petroleum ether (PE) (bp 30-60 °C). Mass spectra were recorded using a FINIGAN MAT 95 (EI). Melting points (uncorrected) were determined in capillary tubes on a Buchi apparatus. Electrochemical measurements were performed using an EG & G-Princeton Applied Research 263A all-in-one potentiostat, using a standard three-electrode setup with a glassy carbon electrode, platinum wire auxiliary electrode and SCE (saturated calomel electrode) as the reference electrode;  $CH_2Cl_2$ or DMF solutions of the compound under the study were 1.0 mM and 0.1 M in the supporting electrolyte  $n-Bu_4NPF_6$  with the voltage scan rate of 0.1 V s<sup>-1</sup>. Under these experimental conditions the ferrocene/ferricinium couple, used as internal reference for potential measurements, was located at  $E_{1/2} = 0.421$  V in CH<sub>2</sub>Cl<sub>2</sub> and 0.445 V in DMF. (E)-4-Ethoxy-1,1,1-trifluorobut-3-en-2-one was prepared according to literature.23

# Syntheses

General procedure for the synthesis of the enaminone ligands. To a stirred solution of (E)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (1.81 g, 9.8 mmol) in anhydrous acetonitrile (30 mL) was added dropwise the appropriate amine (10.8 mmol) at 0 °C. The solution turned red or pink and was stirred at room temperature (L1H) or heated at reflux for 1 h (L2H and L3H). The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (L1H) or recrystallization (L2H and L3H).

(Z)-4-Benzylamino-1,1,1-trifluorobut-3-en-2-one L1H<sup>24</sup>.



Pale pinkish crystals, yield 81%, mp 48 °C. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 178.3 (q, J = 33.5, C-2), 157.9 (C-4), 136.1 (C-6), 129.2 (C-9), 128.4 (C-8), 127.5 (C-7), 117.5 (q, J = 288.7, C-1), 87.6 (q, J = 1.5, C-3), 53.3 (C-5). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 10.52 (1H, br s, NH), 7.44–7.25 (4H, m, H-7, H-8 and H-9), 7.23 (1H, dd, J = 13.4, 7.2, H-4), 5.42 (1H, d, J = 7.2, H-3), 4.50 (2H, d, J = 6.0, H-5). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$  (ppm): -77.2 (s). MS EI: m/z = 229 (M<sup>++</sup>), 160 ([M – CF<sub>3</sub>]<sup>++</sup>), 138 ([M – C<sub>7</sub>H<sub>7</sub>]<sup>++</sup>), 91 (C<sub>7</sub>H<sub>7</sub><sup>++</sup>). HRMS for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>NO [M+] calc., 229.0714; found, 229.0711.

(Z)-2-(4,4,4-Trifluoro-3-oxobut-1-enylamino)benzonitrile L2H.



Pale yellow crystals (CH<sub>2</sub>Cl<sub>2</sub>), yield 84%, mp 126 °C. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 180.7 (q, J = 33.5, C-2), 148.2 (C-4), 141.8 (C-5), 134.7 (C-7), 133.6 (C-9), 125.1 (C-8), 116.6 (q, J =288.9, C-1), 115.7 (C-6), 102.5 (C-10), 92.5 (m, C-3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 12.02 (1H, br s, NH), 7.73 (1H, dd, J = 12.4, 7.7, H-4), 7.68–7.55 (2H, m, H-7 and H-9), 7.36 (1H, d, J = 8.1, H-6), 7.27–7.21 (1H, m, H-8), 5.80 (1H, d, J = 7.7, H-3). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$  (ppm):  $\delta$  –77.8 (s). MS EI: m/z =240 (M<sup>++</sup>), 171 ([M – CF<sub>3</sub>]<sup>++</sup>). HRMS for C<sub>11</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>O [M+] calc., 240.0510; found, 240.0507.

(Z)-1,1,1-Trifluoro-4-(quinolin-8-ylamino)but-3-en-2-one L3H.



Ochre crystals (CH<sub>2</sub>Cl<sub>2</sub>–hexane), yield 75%, mp 124 °C. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 179.6 (q, J = 33.8, C-2), 149.8 (C-4), 146.8 (C-12), 138.5 (C-9), 136.0 (C-10), 135.5 (C-5), 128.7 (C-13), 126.6 (C-8), 123.5 (C-7), 122.5 (C-11), 117.1 (q, J = 287.7, C-1), 110.8 (C-6), 91.5 (m, C-3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 13.17 (1H, br s, NH), 9.01 (1H, dd, J = 4.1, 1.7, H-12), 8.19 (1H, dd, J = 8.28, 1.5, H-10), 7.92 (1H, dd, J = 13.7, 7.6, H-4), 7.51–7.61 (4H, m, H-6, H-7, H-8 and H-11), 5.81 (1H, d, J = 7.6, H-3). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$  (ppm):  $\delta$  -77.5 (s). MS

EI:  $m/z = 267 (M^{+})$ , 198 ([M - CF<sub>3</sub>]<sup>+</sup>). HRMS for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O [M+] calc., 267.0745; found, 267.0743.

# General procedure for the syntheses of the Cu(II) complexes

A methanolic solution (5 mL) of  $CuCl_2 \cdot 2H_2O$  (28.2 mg, 0.21 mmol) was added dropwise to a methanolic solution (15 mL) of the ligand (0.21 mmol) at room temperature. After 10 min of stirring, 0.2 mL of Et<sub>3</sub>N was added and the resulting dark green (for L1H and L2H) or brown solution (for L3H) was stirred for an additional 2 h. Single crystals for X-ray characterization were obtained by slow evaporation of the solvent (3 d).

### Crystallography

Structure refinement results for [Cu(L1)<sub>2</sub>]. C<sub>22</sub>H<sub>18</sub>Cu<sub>1</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>,  $M = 519.9 \text{ g mol}^{-1}$ , monoclinic, a = 4.9303(3) Å, b = 9.2242(4) Å, c = 23.976(1) Å,  $\beta = 92.432(2)^{\circ}$ , U = 1089.4(1) Å<sup>3</sup>, T = 293 K, space group P2<sub>1</sub>/c (no. 14), Z = 2, 5070 reflections measured, 2581 unique ( $R_{\text{int}} = 0.051$ ),  $R(F, I/\sigma(I) > 3) = 0.0382$ , w $R(F, I/\sigma(I) > 3) = 0.0444$ , S = 1.18,  $\Delta \rho_{\text{max}} = 0.32 \text{ e}^{-}$  Å<sup>-3</sup>,  $\Delta \rho_{\text{min}} = -0.25 \text{ e}$  Å<sup>-3</sup>, 1108 reflections used to refine 180 parameters.

Structure refinement results for  $[Cu_2(L2)_4]$ .  $C_{44}H_{24}Cu_2F_{12}N_8^{-1}$  $O_{42}$ , M = 1083.8 g mol<sup>-1</sup>, monoclinic, a = 10.2689(4) Å, b = 10.2371(4) Å, c = 21.489(1) Å,  $\beta = 92.757(2)^\circ$ , U = 2256.4(2) Å<sup>3</sup>, T = 293 K, space group  $P2_1/n$  (no. 14), Z = 2, 8447 reflections measured, 5027 unique ( $R_{int} = 0.044$ ),  $R(F, I/\sigma(I) > 3) = 0.0402$ , w $R(F, I/\sigma(I) > 3) = 0.0457$ , S = 1.14,  $\Delta \rho_{max} = 0.26$  e Å<sup>-3</sup>,  $\Delta \rho_{min} = -0.42$  e Å<sup>-3</sup>, 2283 reflections used to refine 316 parameters.

Structure refinement results for [Cu(L3)<sub>2</sub>]. C<sub>26</sub>H<sub>16</sub>Cu<sub>1</sub>F<sub>6</sub>N<sub>4</sub>O<sub>2</sub>,  $M = 594.0 \text{ g mol}^{-1}$ , triclinic, a = 12.0582(7) Å, b = 16.326(1) Å, c = 20.279(1) Å,  $\alpha = 68.198(4)^{\circ}$ ,  $\beta = 80.075(3)^{\circ}$ ,  $\gamma = 78.876(4)^{\circ}$ , U = 3614.7(4) Å<sup>3</sup>, T = 293 K, space group  $P\overline{1}$  (no. 2), Z = 6, 22 876 reflections measured, 13 648 unique ( $R_{\text{int}} = 0.092$ ),  $R(F, I/\sigma(I) > 1) = 0.0683$ , wR ( $F, I/\sigma(I) > 1$ ) = 0.0556, S = 1.15,  $\Delta \rho_{\text{max}} = 0.49$  e Å<sup>-3</sup>,  $\Delta \rho_{\text{min}} = -0.50$  e Å<sup>-3</sup>, 5871 reflections used to refine 1054 parameters.

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