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ARTICLE TYPE

# Cu(II)-Specific Metallogel Formation by an Amido-Anthraquinone-Pyridyloxalamide Ligand in DMSO-water.<sup>†</sup>

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This study on the CuCl<sub>2</sub>-induced and water-mediated metallo-gel formation by a pyridine containing anthraquinone-based ligand in DMSO provides significant insights on the relation between coordination geometry and metallo-gelation aptitude for a series of variably substituted pyridyloxalamide ligands.

## Introduction

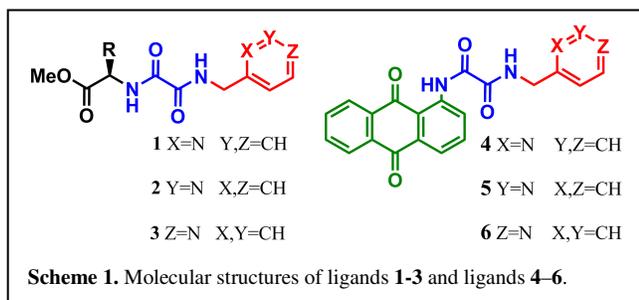
Supramolecular gels derived from low-molecular-weight gelators (LMWGs) are fascinating chemical systems and they have recently attracted considerable interest.<sup>1</sup> Their unique physico-chemical features are thought as potentially valuable for developing innovative applications<sup>1,2</sup> and for preparing intriguing new materials.<sup>3</sup> Supramolecular gels are formed by the assembly of smaller units into fibrillar networks which trap a multitude of solvent molecules, generally several hundreds of times the gelator unit in weight (good gelators work at < 1% w/w). A variety of different non-covalent interactions drives the aggregation process which, importantly, must not lead to high degree of order which favours crystallization. Gel systems containing metal ions incorporated in the fibrous networks, or made of metal complexes, are referred to as metallogels.<sup>4</sup> These systems, designed on the basis of metal–ligand interactions, are quite promising for they could successfully integrate the spectroscopic and catalytic properties of metal ions with the bulk gel materials. However, despite increasing efforts in the rationalization of gelation data based on a constantly updated collection of molecular gel-systems, and on the discovery of structure-properties relationships,<sup>5</sup> the identification of a metallo-gelator molecule remains a big challenge and, very often, it does not rely on *a priori* design, but rather on serendipity.

in that only 3-pyridyloxalamide derivative **2** showed the ability to form three component CuCl<sub>2</sub>-metallogels. The other two derivatives, **1** and **3** (2- and 4-pyridyloxalamide derivatives), under the same conditions, yielded a blue solution or a fine precipitate, respectively.

This behaviour was rationalized by taking into consideration the different coordination ability of the three isomers towards the metal ion. Indeed, compound **2** (R=isobutyl) was believed to be able to establish a set of interactions which could lead to a *coordination polymer* entrapping solvent molecules and hence forming the gel state. Having recognized some of the elements which selected the stable state of **1-3**, we were deeply interested in gathering more information on the system. In general, intermolecular hydrogen bond (HB) interactions are often crucial to obtain gelation, however π–π stacking and hydrophobic interactions can also be important in such aggregation processes. With this in mind, we synthesized and tested ligands **4-6** in Scheme 1. They are endowed with large aromatic anthraquinone units and possess a pyridyl group substitution pattern as in **1-3**. Here, we report on the gelation attitude and metal affinity of **4-6** in DMSO:water mixtures by the use of several spectroscopic techniques (<sup>1</sup>H-NMR, FT-IR, and UV-vis spectroscopy) along with the analysis of the X-ray determined structure of [(**2**)<sub>2</sub>CuCl<sub>2</sub>] (R= isobutyl). Guiding principles that could avail rationalization of the observed behaviour and prediction for similar compounds are presented.

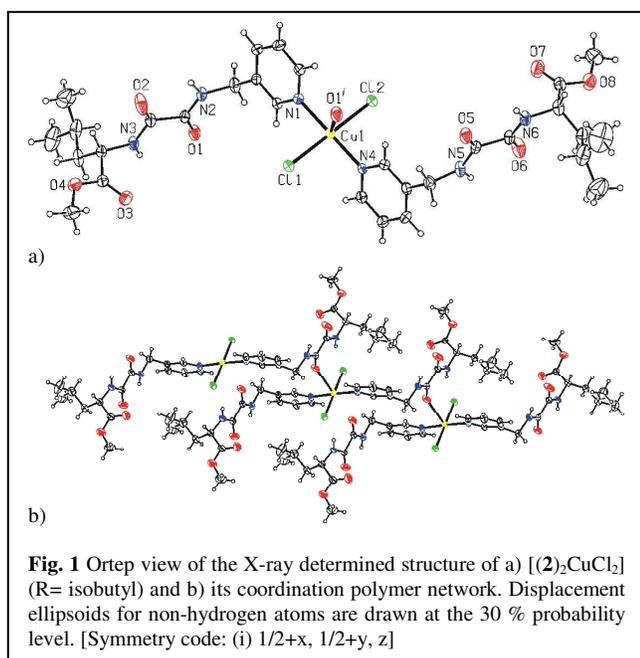
## Results and Discussion

By slow evaporation of a methanol solution of **2** (R=isobutyl) in the presence of CuCl<sub>2</sub> salt, we were able to obtain good quality single crystals of its Cu(II) complex amenable to structural characterization by X-ray diffraction. As shown in Fig. 1a, in the solid state, the complex can be thought as a 1:2 metal to ligand (M:L) complex, where the coordination geometry of each Cu atom can be best described as a slightly distorted square-pyramidal (Table S3, ESI). The metal penta-coordination, common for Cu(II) ions, is filled by the pyridine ring nitrogen atoms of two leucine derivatives, by two chlorides and, interestingly, by one oxalylic oxygen atom from a neighbouring



Very recently,<sup>6</sup> we have reported on the series of pyridyloxalamide ligands **1-3** which solely differ in the position of the N atom on the pyridine ring (Scheme 1). Their aptitude for gelling alcohols in the presence of Cu(II) salts was interesting,

ligand which occupies the apical position. This latter coordinative interaction is responsible for the formation of the coordination network in the solid state (as seen in Fig. 1b). More detailedly, two N–H...Cl and two C–H...O HBs also participate in the formation of such coordinative chains (Table S4 and Fig. S15a, ESI) which are mutually linked by two strong N–H...O HBs. These bonds are reinforced by other three weaker C–H...Cl HBs, one C–H...O HB, as well as by one C–H... $\pi$  interaction, thus forming two-dimensional sheets (Fig. S15b, ESI) which are spreading in the *ab* plane. Inter-chain distance of neighbouring Cu–Cu is shorter (*ca.* 7.02 Å) than that of intra-chain Cu atoms (9.12 Å).



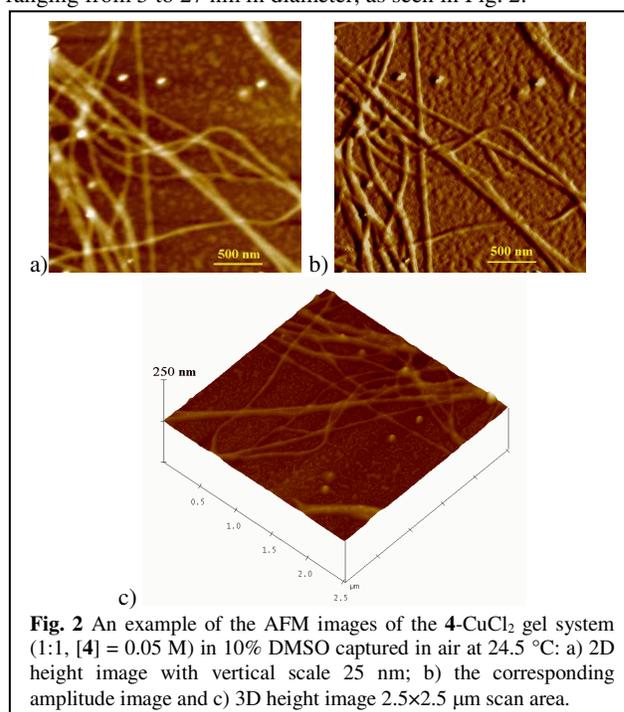
**Fig. 1** Ortep view of the X-ray determined structure of a)  $[(2)_2\text{CuCl}_2]$  (R= isobutyl) and b) its coordination polymer network. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level. [Symmetry code: (i)  $1/2+x, 1/2+y, z$ ]

The above solid state characterization corroborates our view on the behaviour of the Cu(II) complex with **2** in terms of its gelation ability in alcoholic solutions. Indeed, ligand **2** is incapable to form a more classical NNO coordination as seen with **1**,<sup>6</sup> and instead employs the combination of one of its carbonyl and the pyridyl group to establish an effective network of interactions.

As said a variety of intermolecular interactions can be responsible for gelation and  $\pi$ - $\pi$  stacking and hydrophobic interactions are among them. Ligands **4-6** in Scheme 1 (see ESI for the synthetic procedure) are endowed with large aromatic anthraquinone units known to possess substantial tendency to aggregate,<sup>7</sup> and were tested for their gelation abilities in various solvents and with different metal salts. As ligands **4-6** maintain the pyridyl group substitution pattern, as in **1-3**, this study also allowed us to test our understanding on the principles needed to design pyridyloxalamide based metallo-gelators.

Gelation tests performed by adding to ligands **4-6** a variety of transition metal cations, such as  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{PdCl}_2$  and  $\text{AgCl}$  under different conditions (ESI), showed that among the three derivatives only **4** is able to form metallo-gels in DMSO-water mixtures, and only in the presence of  $\text{CuCl}_2$  (or  $\text{CuBr}_2$  to some degree, vide infra). A distinctive colour change, from dark yellow to light green, is also observed in the gel formation process (Fig. S1, ESI). The

morphological features of these metallo-gels were investigated by TEM and AFM. TEM images revealed the formation of a network of entangled nanofibers of several micrometers in length (ESI), while detailed AFM study for a diluted sample of  $4\text{-CuCl}_2$  in 9:1 (v/v) DMSO-water mixture shows the presence of fibers ranging from 5 to 27 nm in diameter, as seen in Fig. 2.



**Fig. 2** An example of the AFM images of the  $4\text{-CuCl}_2$  gel system (1:1,  $[4] = 0.05 \text{ M}$ ) in 10% DMSO captured in air at  $24.5^\circ \text{C}$ : a) 2D height image with vertical scale 25 nm; b) the corresponding amplitude image and c) 3D height image  $2.5 \times 2.5 \mu\text{m}$  scan area.

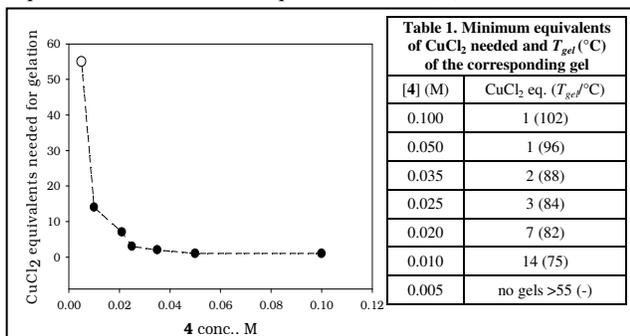
The presence of water as a co-solvent is important for metallo-gelation. When anhydrous DMSO was used, no gel was formed; also when the % v/v of water in DMSO was less than 10%, the formation of the gel was far from optimal. Higher % v/v of water (*i.e.*, 20% and 30%) led to less stable and less homogeneous gel material as visually exemplified by Figure 3. The role of water in organogelation has been studied in several occasions,<sup>8</sup> and it can be related to specific solvation of polar groups in gelator molecule, to an enhancement of aggregation due to hydrophobic effect, or to a polarity modulation of the bulk solvent. In our case, 10% water in DMSO was found to be the best choice to obtain stable and strong gel materials (this solvent mixture is hereafter referred to as 90% DMSO).



**Fig. 3** Pictures of metallo-gels upon mixing of ligand **4** and 1 equivalent of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in DMSO:water mixtures (0.05 M) at room temperature containing, from left to right: 0, 5, 10, 20 and 30% water (v/v).

In cases where a single component is responsible for the gel formation, gelation experiments easily allow to determine the minimum gelation concentration (*mgc*) for a gelator in a given

solvent. In cases where a metal complex of defined M:L stoichiometry is responsible for the process, as with **4**, the stability of the metal complex formation is decisive. In order to determine the actual M:L ratio of the gelating Cu(II)-**4**, several gelation attempts at different ratios and concentrations have been performed. Our data shows that the ratio at which the gelation in 90% DMSO occurs depends on the concentrations used (Fig. 4). The highest concentration tested was  $[4] = 0.1$  M. At this concentration, 1 equivalent of Cu(II) is sufficient. While by halving the concentration of **4**, the minimum required metal concentration does not change, a further reduction has indeed an effect. For example, decreasing the concentration of **4** to 1/10, requires the addition of 14 equivalents of Cu(II) in order to obtain



**Fig. 4** Visual representation of the data in Table 1, indicating the minimum equivalents of CuCl<sub>2</sub> which should be added to **4**, at various concentrations to obtain a gel.

a gel material. More so, at  $[4] = 0.005$  M, no gel is formed upon addition of up to ca. 55 equivalents of metal salt. Since the M:L ratio at which a gel is observed more closely approaches that of the actual gelator  $M_xL_y$  complex at higher concentration (associated species are favoured), we got a strong indication that a 1:1 complex, of moderate stability, constitutes the gelating unit. Hence, we can reasonably assume that the  $mgc$  for the system is between 0.01 and 0.005 M. Notably, we also monitored the temperature at which the gel collapse to a solution ( $T_{gel}$ ). These experiments (Table 1) confirm that the more robust gel is formed at higher  $[4]$ , which require only 1 eq. of CuCl<sub>2</sub>, and can withstand the highest temperature, ca. 102 °C. Decreasing the  $[4]$  the gel formation requires more equivalents of metal and the  $T_{gel}$  decrease accordingly, in line with the considerations above. A similar behaviour was found for CuBr<sub>2</sub> whose gel however displays a lower thermal stability (Table S1, ESI).

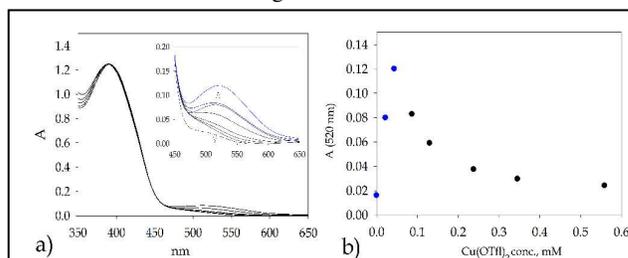
The data just presented also show an important feature of this system. At variance with the majority of cases,<sup>3d,9</sup> where the use of slightly higher than optimal amount of metal ions inhibits the gel formation, this system withstands the presence of a significant excess of Cu(II) ions. For example, at  $[4] = 0.01$  M, gel is formed making use of 14 times higher concentration of CuCl<sub>2</sub>. This unusual feature can be exploited. Indeed, a new [Cu(DMSO)<sub>2</sub>Cl<sub>2</sub>] polymorph is produced spontaneously upon aging the Cu(II)-**4** metallogel (7:1 M/L ratio) for one week at room temperature without any sign of deterioration of the material.<sup>10</sup>

A more detailed phenomenological description of the behaviour of **4** as a pro-gelator should also mention that the formation of a stable gel from **4** not only requires the presence of Cu(II), but also that of Cl<sup>-</sup> ions.<sup>11</sup> To demonstrate this fact, we performed a series of experiments that involved mixing ligand **4**

with different combinations of metal and organic salts in 90% DMSO. We started by testing different Cu(II) salts, such as sulphate, nitrate, acetate, and triflate. None of these salts lead to gelation with **4** in a wide range of metal salt:gelator ratios ( $[4] = 0.025$  M). When a source of Cl<sup>-</sup> anions was added to the mixture of the ligand and one of the above metal salts, the gel state could be obtained again. For example, the addition of NaCl to a 4:1 mixture of CuSO<sub>4</sub> and compound **4** was able to produce a stable gel when the 1:4:16 (Cl<sup>-</sup>/Cu<sup>2+</sup>/L) proportions were reached. The need of approx. three times the quantity of Cl<sup>-</sup> than expected (it is reminded that gel is formed at a M:L ratio of 3:1 at  $[4] = 0.025$  M) implies a certain level of disturbance of SO<sub>4</sub><sup>2-</sup> ions to the process. A similar behavior was observed by replacing NaCl with (TBA)Cl. In any case, the experiment confirms the necessity of the presence of the three components in order to form the gel. Notably, the only exception to this general behaviour, is represented by the case of Cu(OAc)<sub>2</sub>, whose addition turns the solution to a reddish colour. This colour change, also observed by addition of TBA salts of relatively basic anions (acetate, fluoride) to a DMSO solution of **4**, is attributed to the deprotonation of the aromatic amidic NH group (UV-vis absorption spectral changes upon deprotonation of **4** are reported in Fig. S4, ESI). The above experiments demonstrate that specificity is not remarkable only in terms of the metal identity, but also in terms of the anion's.

On the other hand, the position of the pyridyl N-atom is also a crucial aspect for the formation of a supramolecular metallo-gel. Surprisingly, based on the data on ligands **1-3** and on the apparent relation between the ligands coordination ability and their gelating aptitude,<sup>6</sup> we would have expected ligand **5**, and not **4**, to be the best metallo-gelator. We thus embarked in a series of detailed spectroscopic studies to gather more information on the system.

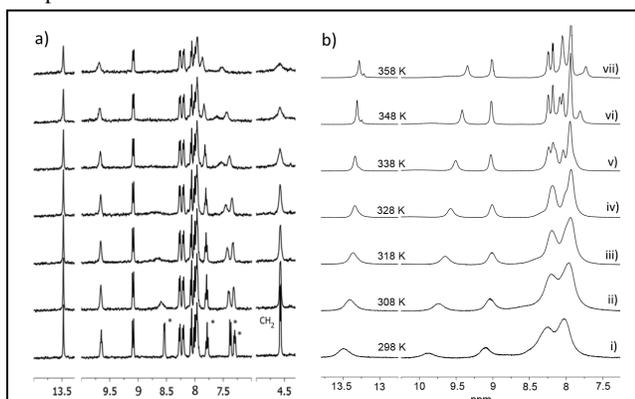
An UV-vis absorption spectroscopy investigation on the system was also performed. Ligand **4**, and its isomers **5** and **6**, all obey to a linear Abs vs. concentration relationship (Fig. S5-S7, ESI) showing no signs of aggregation in DMSO at 25 °C within the tested concentration range.



**Fig. 5** a) Family of Absorption spectra obtained upon addition of increasing aliquots of concentrated solution of Cu(OTf)<sub>2</sub> to a 0.24 mM solution of **4** in DMSO at 25 °C; inset: magnification of the 450-650 nm region; b) Absorption changes at 520 nm vs. Cu(II) concentration.

Addition of Cu(OTf)<sub>2</sub> to a  $2.5 \times 10^{-4}$  M solution of **4** in DMSO causes absorption changes to occur in the 470-650 nm region (Fig. 5a).<sup>12</sup> While at low Cu(II) concentration a broad band centred approx. at 520 nm starts to appear, by increasing the Cu(II) concentration, a decrease of the absorption is observed which eventually leads to a plateau (Cu(OTf)<sub>2</sub> does not absorb at  $\lambda > 400$  nm). No significant changes were observed in the region of maximum absorbance of the ligand ( $\lambda_{max} = 395$  nm,  $\epsilon = 5600 \pm$

30 M<sup>-1</sup> cm<sup>-1</sup>). Despite being not conspicuous at all (see Fig. 5a), these absorption variations provide some insights on the interactions between Cu(II) ion and ligand **4**. Due to the fact that coordination of the metal centre to the pycolilamine region does not produce absorption changes in the 500 nm region, we are led to think that the interaction responsible for the initial response is that of Cu(II) with the anthraquinone moiety;<sup>13</sup> also, given that the initial absorption change is occurring under conditions of ligand excess, the formation of a labile 1:2 M:L complex is a plausible explanation for the observed data. Clearly, the increase of Cu(II) concentration shifts the equilibrium toward a 1:1 complex.



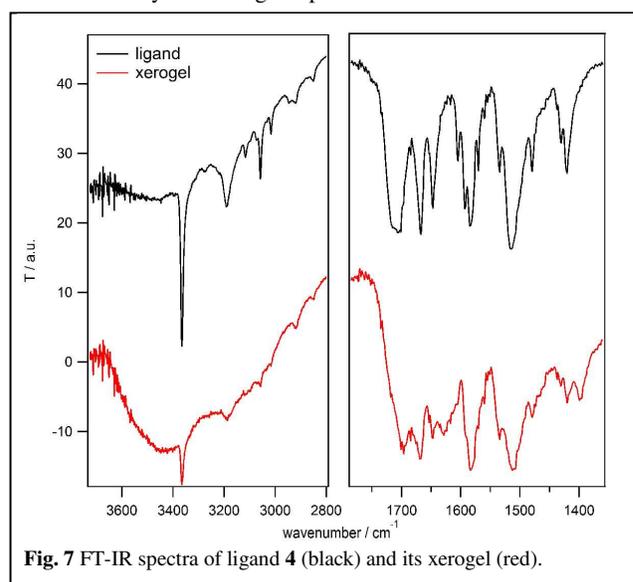
**Fig. 6** a) Selected portions of the <sup>1</sup>H-NMR spectrum of **4** (1x10<sup>-3</sup> M, in DMSO-*d*<sub>6</sub>) upon addition of CuCl<sub>2</sub> (0, 1/3, 2/3, 1, 2, 3, 5 equivalents from bottom to top). Signals belonging to the pyridine group are marked (\*); b) Selected portions of the <sup>1</sup>H-NMR spectrum of **4** (0.01 M in the presence of 1 eq. of CuCl<sub>2</sub>, in 90% DMSO-*d*<sub>6</sub>) at 298 K and at various increasing temperature: ii-vii) 308 - 358 K.

The behaviour of ligand **4** in the presence of Cu(II) is even richer, in that we collected evidence on the possibility of the 2:1 M:L complexes (under condition of excess Cu(II) with respect to **4**, see Fig. S10, ESI). Although informative on the lack of a strongly favoured complex stoichiometry for the **4**-Cu(II) adduct, we also note that the gelation process occurs at much higher concentrations than that employed in the UV-vis studies and, therefore, the above analyses could only be taken as a hint of what might be happening in the process of gel formation. As said, evidence for NNO coordination of similar ligands to Cu(II) has been already found in the solid state.<sup>6,14</sup> However, the coordination mode could not be inferred by these UV-vis data alone and, thus, additional analyses were undertaken in order to have a better insight on the process at higher concentration range.

Hence, we set out <sup>1</sup>H-NMR experiments where we titrated a 1x10<sup>-3</sup> M solution of **4** in DMSO-*d*<sub>6</sub> with small concentrated aliquots of CuCl<sub>2</sub> (0-5 equivalents). The result of the experiment is shown in Fig. 6a. Upon addition of Cu(II) ions, a certain degree of broadening is observed for all signals, however, the effect is significantly more pronounced for the signals belonging to the pyridine group and the methylene spacer. This indicated proximity between the paramagnetic Cu(II) ion and the pyridine ring of **4** in solution. However, based on the presence of the modest effect observed on the amidic NHs, the formation of a complex with **4** acting as NN bidentate or NNO tridentate ligand, which presupposes deprotonation of the NH group, seems not to occur under these conditions.

The observed weak propensity for deprotonation of the NH group may be explained by the presence of a strong intramolecular NH...O=C hydrogen bond established with the beta carbonyl of the oxalyl moiety, clearly visible in the solid state for similar compounds.<sup>6,15</sup> This observation gives a rationale on the multi-faceted behaviour shown by the ligand based on the UV-vis data, in that **4** lacks of any strongly favoured binding site for the Cu(II) ion in DMSO.

Dynamic <sup>1</sup>H-NMR experiment in the 298-358 K temperature range is shown in Fig. 6b. The broad signals observed in the gel state gradually become sharper upon raising temperature. However, they remain broad due to the paramagnetic relaxation effect exerted by the Cu(II) ions. The only evident changes are observed for the amidic NH groups which show an upfield shift from gel state at 298 K to solution at 358 K. The temperature induced shift for the aliphatic amidic NH is more evident (from 9.89 ppm to 9.34 ppm, ca. 0.5 ppm compared to ca. 0.2 ppm for the aromatic NH). This difference indicates a different involvement of the two NHs in the HB interaction network which is gradually destabilized upon transition from the gel to the solution state by increasing temperature.



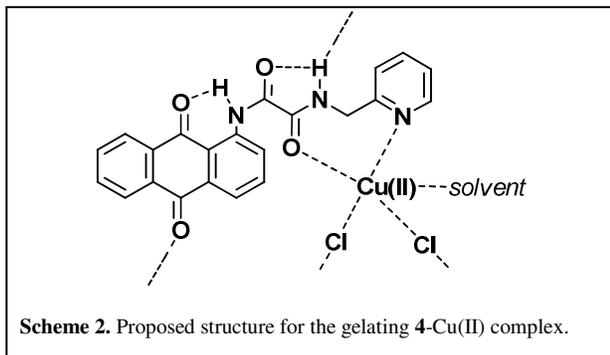
**Fig. 7** FT-IR spectra of ligand **4** (black) and its xerogel (red).

Finally, additional information on the Cu(II)-**4** gel system was obtained by comparison between the FT-IR spectrum of ligand **4** and that of the corresponding CuCl<sub>2</sub> xerogel (Figure 7). In the xerogel, the amide I band (C=O stretching) and the C=N band of the pyridyl ring in the region 1647-1700 cm<sup>-1</sup> both shift to lower frequencies, indicating metal ion coordination by the carbonyl and the pyridyl groups. Furthermore, amide N-H stretching bands (amide A band) at 3364 cm<sup>-1</sup> and 3188 cm<sup>-1</sup>, related to intramolecular as well as intermolecular HB interactions between oxalamide units, are present in both free ligand and xerogel. This points to the participation of this group in HB interaction rather than in metal coordination during metallogel formation.

In the literature, Cu(I)-metallogels are known,<sup>16</sup> and some cases of ligand induced Cu(II)-to-Cu(I) reduction in gel systems are reported.<sup>15a,b</sup> In order to rule out this possibility for the system presented here, Electron Paramagnetic Resonance (EPR) measurements were performed in 90% DMSO solution. They

confirm the presence of Cu(II) ions even under conditions of ligand **4** excess. Furthermore, paramagnetic line broadening is observed in the  $^1\text{H-NMR}$  spectrum of the gel and in those acquired during the titration experiments presented in Fig. 6a, where no oxidative degradation of the ligand is observed.

Based on these evidences, we propose the binding mode depicted in Scheme 2, where the Cu(II) ion is coordinated by a bidentate **4** by the pyridyl nitrogen and by an oxalamidic carbonyl. Some examples of such coordinative behaviour can be found in the literature for similar ligands.<sup>17</sup> Chloride ions and solvent molecules complete the coordination sphere of the metal ion.<sup>18</sup>



## Conclusions

Complete control over LMWG gel systems and all the subsequent technological applications will only be attained when a comprehensive understanding of all the factors which govern their formation will be fully achieved. Nowadays, despite an extensive collection of notable examples of supramolecular gel systems and several attempts towards data rationalization, this stage is not still reached. Here, we presented a detailed study of a series of isomeric compounds **4-6**, whose behaviour in terms of gelating properties was surprisingly different from what we would have expected based on previous results on compounds **1-3**,<sup>6</sup> and on the novel X-ray characterization of the **2**-Cu(II) complex (Fig. 1). Indeed, ligand **4**, but not **5** or **6**, is able to form stable three component gel in 90% DMSO in the presence of Cu(II) and chloride ions, showing quite a selectivity in terms of salt composition. Although ligand **4** does not show high propensity for metal coordination, it is capable to form Cu(II)-complexes. Studies by  $^1\text{H-NMR}$ , FT-IR, EPR and UV-vis spectroscopy were conducted in order to gain insights into the coordination ability of **4**. UV-vis absorption data collected in DMSO are consistent with the formation of labile 2:1 and 1:2 complexes, in addition to the more stable 1:1 adduct which forms at higher concentrations. This latter species, as also indicated by gelation tests data, represents the actual gelator compound. The complex features a direct Cu(II) interaction with its pyridinic moiety, as evidenced by the  $^1\text{H-NMR}$  data in DMSO- $d_6$ . Interestingly, the expected deprotonation of the neighbour aliphatic amidic NH does not occur. Finally, despite the large aromatic moiety in **4**, there is no indication of strong stacking interactions, while amidic NHs are still involved in establishing the gel interaction network, as shown by  $^1\text{H-NMR}$  and FT-IR analyses. The role of water has also been investigated as its presence in a range of concentration close to 10% v/v seems to be

crucial for the obtainment of stable and robust gels. Based on the above, we envisage ligand **4** acting as bidentate making use one oxalamidic carbonyl and the pyridyl nitrogen, as shown in Scheme 2. The weak propensity to form the classical and more stable NNO tridentate complex, probably due to intramolecular HB which persist in DMSO solution, is a key element.

Drawing general conclusions based on a limited set of compounds can easily expose to risks of over-simplification. Guiding principles, however seems to emerge here. Indeed, based also on previous work,<sup>6</sup> we can affirm that in order to obtain Cu(II) induced metallo-gelation by the series of pyridyloxalamide ligands **1-6**, the NH deprotonation must be prevented; ligand acts as bidentate with metal coordination exerted by one oxalyl C(=O) group and by a pyridine ring; and coordination geometry of the ligand is not the only factor to be taken into account, however, it is determinant in that it dictates the stoichiometry of the final gelating species. Hydrophobic interactions have a role in the aggregative response of **4** given the needed presence of 10% water as co-solvent.

We believe that the presented data contribute to the improvement of the level of understanding on the behaviour of LMWG metallo-gel systems, which despite increasing attempts, still remain far from ideal. They also highlight the simple fact that similar systems might behave in completely different ways under slightly different conditions, thus suggesting that structure-gelation relationships should be considered with extreme care. The use of this system to grow crystals of a variety of Cu(II) complexes with organic compounds, also of pharmaceutical interest, is currently under exploration.

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## Notes and references

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: [Syntheses and characterization of ligands **4-6**, gelation tests, AFM and TEM images, additional UV/vis characterization, crystallographic details for [(**2**)<sub>2</sub>CuCl<sub>2</sub>] (CCDC 1037543)]. See DOI: 10.1039/b000000x/
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- 12 Cu(OTf)<sub>2</sub> was chosen in order to limit the UV-vis response to the presence of Cu(II) alone. The triflate counteranion can be considered as non-participating at these low concentrations in DMSO. However, similar spectral changes were also observed with CuCl<sub>2</sub>.
- 13 A similar behaviour is also found for ligands **5** and **6** (see Fig. S8-S9 ESI). These compounds, isomeric to **4**, feature a different position of the pyridyl nitrogen and coordination motifs.
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