

High Molecular Weight Cu^{II} Coordination Polymers and Their Characterisation by Electrospray Mass Spectrometry (ESMS)

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The ligands **L** and ligand **L**^{*} self-assemble with Cu^{II} in different solvents to give a mixture of coordination polymers. These artificial nanostructures have been characterised with the help of ESMS, the only analytical tool that allows their

unambiguous characterisation. Kinetic and thermodynamic ESMS studies have excluded the possibility that these compounds form aggregates during the ES process.

Introduction

The self-assembly of suitably designed organic ligands with transition-metal ions allows the generation of a wide range of polymetallic complexes possessing a variety of well-defined architectures (racks, ladders, grids, rings, etc.).^[1,2] These organised entities, and especially coordination polymers, may present interesting physical and chemical properties and are of much current interest within metallosupramolecular chemistry due to their potential applications in materials science.^[3] One of the challenges in this field resides in the preparation of high molecular weight coordination polymers that may possess good solubilities in order to characterise their properties in solution as well as in the solid state. Unfortunately, an unequivocal structural analysis of these metallosupramolecular compounds is often missing. Indeed, because of the complexity of the NMR spectra and because of the recurrent presence of paramagnetic metals, NMR spectroscopy is often unusable. In the same way, X-ray suitable crystals of sufficient quality are often difficult to obtain; the use of X-ray crystallography is therefore limited. The other classical analytical tools able to give any information are in most cases inconclusive with respect to the formulation (e.g., UV/Vis absorption and emission spectroscopy, infrared, etc.). An unambiguous characterisation is therefore highly compromised. Despite the problems and difficulties that often occur during the development of this chemistry (especially due to the increasing size of such molecules), encouraging

perspectives are offered by the use of electrospray mass spectrometry (ESMS)^[4] for an unequivocal characterisation. ESMS has been proven to be a very useful technique for the characterisation of biological^[5] and chemical^[6] assemblies. Moreover, this analytical method is particularly suitable for large, noncovalent species with high molecular masses. Indeed, when several parameters are carefully controlled, ESMS is a mild method, which causes minimum fragmentation and therefore allows molecular mass determination.

We describe here the characterisation in solution by ESMS of the largest reported Cu^{II} coordination polymers stable in solution up to a concentration of 10^{−4} M and soluble in common organic solvents (acetonitrile, methanol, nitromethane). In this present case, ESMS was the only analytical tool allowing an unambiguous characterisation. Therefore, kinetic and thermodynamic studies have been undertaken in order to exclude the possibility that these coordination polymers are aggregates resulting from the ES process.^[7]

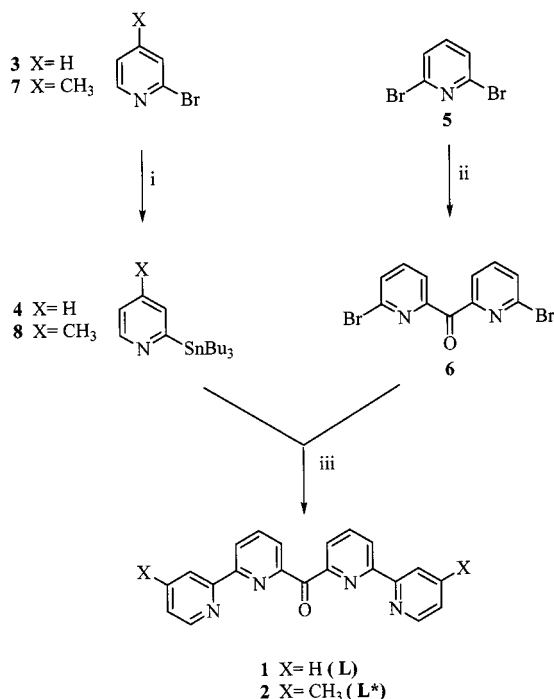
Results and Discussion

The ligand **L** was synthesised following the procedure outlined in Scheme 1. The self-assembly reaction to obtain the Cu^{II} coordination polymers was carried out as follows: an equimolar amount of the ligand **L** and Cu(CF₃SO₃)₂ were mixed together in anhydrous acetonitrile (ca. 10^{−4} M), the mixture was stirred at room temperature for five minutes and a clear blue solution was obtained.

The analysis of this solution by ESMS immediately after preparation has shown the presence of coordination complexes of general formula [LCu(CF₃SO₃)₂]_n, M_n, in equilibrium in solution (Figure 1). Ions observed in the ES mass spectrum (M_n^{x+}; 1 ≤ n ≤ 47 and 1 ≤ x ≤ 4) are interpreted

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Scheme 1. i, *n*BuLi, THF, -78°C ; Bu_3SnCl , -78°C , 96%; ii, *n*BuLi, ether, -90°C ; ClCO_2Et , 47%; iii, $\text{Pd}(\text{PPh}_3)_4$, toluene, 110°C , 50–76%

as the successive loss of x counter anions CF_3SO_3^- (^-OTf), leading to multiply charged ions, and correspond to molecular masses up to 32901.4 Da ($n = 47$).

The charge states of these ions were unambiguously determined owing to the high-resolution capability of a time of flight analyser (Figure 2). Charge states of these ions range from $x = 1+$ to $x = 4+$. The largest polymer ($n = 47$) has been identified owing to its $4+$ charged ion at $m/z = 8076.0$ (see the ES mass spectra, Figure 1). The ES

mass spectra obtained were reproducible ($\pm 10\%$) and identical in terms of relative intensities of the different peaks on four different instruments [Quattro II, LC-Tof, Q-Tof (Micromass, Altrincham, UK) and ESQUIRE-LC (Bruker-Franzen Analytik GmbH, Bremen, Germany)]. All the ions observed were interpreted and are summarised with their m/z values and their charge states in Table 1.

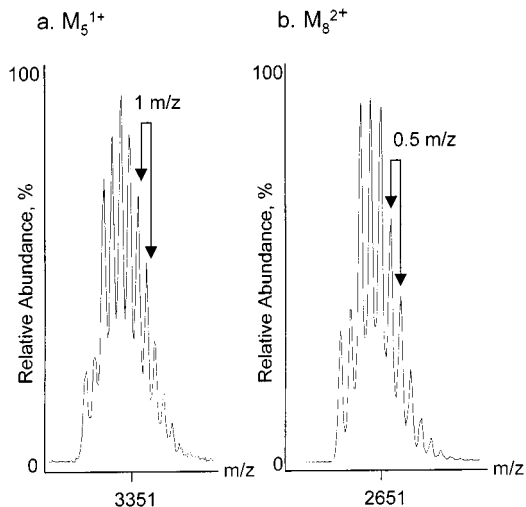


Figure 2. High resolution spectrum, obtained on an LC-Tof spectrometer

These ESMS results in acetonitrile and the stoichiometries determined suggest that in all complexes four nitrogen donor atoms coordinate one Cu^{II} . The IR analysis showed only a slight change in the $\text{C}=\text{O}$ vibration frequency between the ligand and the mixture of complexes — from 1686 cm^{-1} to 1679 cm^{-1} — suggesting that the carbonyl group does not participate in the coordination with Cu^{II} . Since Cu^{II} is normally pentacoordinated, if we assume

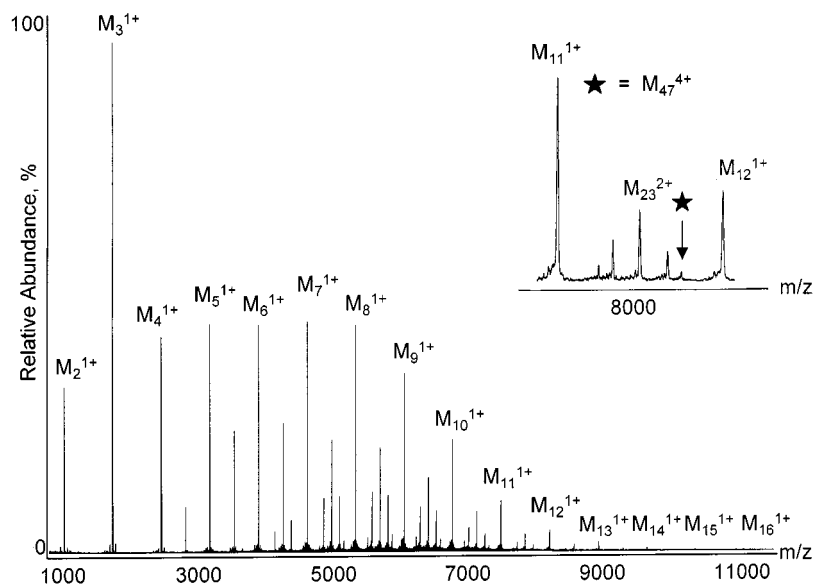


Figure 1. ES mass spectrum (obtained on an LC-Tof spectrometer) of an equimolar mixture of L and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in anhydrous acetonitrile at 10^{-4} M

Table 1. Identification of the M_n (1 < n < 47) ions detected by ESMS^[a]

M ₁	M ₂	M ₃	M ₄	M ₅	M ₆	M ₇	M ₈	M ₉	M ₁₀
551.0 (1+) <i>550.97</i>	1250.9 (1+) <i>1251.0</i>	1950.9 (1+) <i>1951.03</i>	2650.9 (1+) <i>2651.06</i>	3351.3 (1+) <i>3351.09</i>	4050.9 (1+) <i>4051.12</i>	4751.1 (1+) <i>4751.15</i>	5451.2 (1+) <i>5451.18</i> 2650.9 (2+) <i>2651.06</i>	6150.3 (1+) <i>6151.21</i> 3000.8 (2+) <i>3001.08</i>	6851.9 (1+) <i>6851.24</i> 3351.3 (2+) <i>3351.10</i>
M ₁₁	M ₁₂	M ₁₃	M ₁₄	M ₁₅	M ₁₆	M ₁₇	M ₁₈	M ₁₉	M ₂₀
7550.6 (1+) <i>7551.27</i>	8250.9 (1+) <i>8251.30</i>	8949.8 (1+) <i>8951.33</i>	9650.1 (1+) <i>9651.36</i>	10353.1 (1+) <i>10351.39</i>	11048.1 (1+) <i>11051.42</i>	5801.1 (2+) <i>5801.19</i>	6150.3 (2+) <i>6151.21</i>	6500.3 (2+) <i>6501.22</i>	6851.9 (2+) <i>6851.24</i>
3700.7 (2+) <i>3701.91</i>	4050.9 (2+) <i>4051.12</i>	4400.4 (2+) <i>4401.14</i>	4751.1 (2+) <i>4751.15</i>	5100.6 (2+) <i>5101.16</i>	5451.2 (2+) <i>5451.18</i>	3817.5 (3+) <i>3817.77</i>	4050.9 (3+) <i>4051.12</i>	4284.6 (3+) <i>4284.46</i>	4517.4 (3+) <i>4517.80</i>
M ₂₁	M ₂₂	M ₂₃	M ₂₄	M ₂₅	M ₂₆	M ₂₇	M ₂₈	M ₂₉	M ₃₀
7200.0 (2+) <i>7201.25</i>	7550.6 (2+) <i>7551.27</i>	7901.0 (2+) <i>7901.28</i>	8250.9 (2+) <i>8251.30</i>	8601.1 (2+) <i>8601.31</i>	8949.8 (2+) <i>8951.33</i>	9300.6 (2+) <i>9301.34</i>	9650.1 (2+) <i>9651.36</i>	10001.9 (2+) <i>10001.37</i>	10353.1 (2+) <i>10351.39</i>
4751.1 (3+) <i>4751.15</i>	4984.4 (3+) <i>4984.49</i>	5217.2 (3+) <i>5217.83</i>	5451.2 (3+) <i>5451.18</i>	5684.2 (3+) <i>5684.52</i>	5917.0 (3+) <i>5917.86</i>	6150.3 (3+) <i>6151.21</i>	6384.0 (3+) <i>6384.55</i>	6617.9 (3+) <i>6617.89</i>	6851.9 (3+) <i>6851.24</i>
M ₃₁	M ₃₂	M ₃₃	M ₃₄	M ₃₅	M ₃₆	M ₃₇	M ₃₈	M ₃₉	M ₄₀
7084.58 (3+) <i>7085.0</i>	7317.8 (3+) <i>7317.92</i>	7550.6 (3+) <i>7551.27</i>	7784.5 (3+) <i>7784.61</i>	8017.8 (3+) <i>8017.95</i>	8250.9 (3+) <i>8251.30</i>	8485.5 (3+) <i>8484.64</i>	8717.0 (3+) <i>8717.98</i>	8949.8 (3+) <i>8951.33</i>	6851.9 (4+) <i>6851.24</i>
5276.2 (4+) <i>5276.17</i>	5451.2 (4+) <i>5451.18</i>	5626.2 (4+) <i>5626.18</i>	5801.1 (4+) <i>5801.19</i>	5976.6 (4+) <i>5976.20</i>	6150.3 (4+) <i>6151.21</i>	6326.6 (4+) <i>6326.21</i>	6500.3 (4+) <i>6501.22</i>	6676.2 (4+) <i>6676.23</i>	
M ₃₁	M ₃₂	M ₃₃	M ₃₄	M ₃₅	M ₃₆	M ₃₇	M ₃₈	M ₃₉	M ₄₀
7084.58 (3+) <i>7085.0</i>	7317.8 (3+) <i>7317.92</i>	7550.6 (3+) <i>7551.27</i>	7784.5 (3+) <i>7784.61</i>	8017.8 (3+) <i>8017.95</i>	8250.9 (3+) <i>8251.30</i>	8485.5 (3+) <i>8484.64</i>	8717.0 (3+) <i>8717.98</i>	8949.8 (3+) <i>8951.33</i>	6851.9 (4+) <i>6851.24</i>
5276.2 (4+) <i>5276.17</i>	5451.2 (4+) <i>5451.18</i>	5626.2 (4+) <i>5626.18</i>	5801.1 (4+) <i>5801.19</i>	5976.6 (4+) <i>5976.20</i>	6150.3 (4+) <i>6151.21</i>	6326.6 (4+) <i>6326.21</i>	6500.3 (4+) <i>6501.22</i>	6676.2 (4+) <i>6676.23</i>	
M ₄₁	M ₄₂	M ₄₃	M ₄₄	M ₄₅	M ₄₆	M ₄₇			
7026.1 (4+) <i>7026.24</i>	7200.0 (4+) <i>7201.25</i>	7376.2 (4+) <i>7376.26</i>	7550.6 (4+) <i>7551.27</i>	7726.1 (4+) <i>7726.27</i>	7901.0 (4+) <i>7901.28</i>	8076.0 (4+) <i>8076.29</i>			

^[a] Measured *m/z* (charge state) and calculated *m/z* in italics.

that four nitrogen donor atoms coordinate one Cu^{II}, the fifth coordination position is probably occupied by a molecule of solvent in order to complete the metal coordination sphere. In fact an acetonitrile molecule is probably coordinated to the Cu^{II} in solution but is lost in the gas phase.

To confirm this possible coordination cell, ESMS studies in anhydrous MeOH have been undertaken. Indeed, it has already been observed in the case of metallic complexes that MeOH is a better coordinating solvent than acetonitrile in the gas phase.^[8] The ES mass spectrum (Figure 3) obtained in [D₄]MeOH has confirmed the presence of solvent molecules attached to these high-molecular-weight complexes. [D₄]MeOH was used in this case instead of MeOH to facilitate the resolution of the different adducts. In these conditions, for small oligomers (M_n, *n* = 1 to *n* = 5), the addition of one molecule of [D₄]MeOH to each Cu^{II} atom is observed from the *m/z* difference of 36 for singly charged peaks and 18 for doubly charged peaks. Unfortunately, for higher oligomers (M_n, *n* > 5) the ES mass spectrum is too complex at the resolution available (*R* = 8000) and no in-

formation could be obtained on the number of molecules of solvent attached to these large ions.

Slow crystallisation of these oligomers was unsuccessful and only crystals corresponding to the monomer (M₁) structure were found. Thanks to the ESMS and IR data a possible structure was deduced for these polymers in solution (Figure 4). Obviously, a cyclic form cannot be distinguished from a linear structure by mass measurement in our case. However, the 1:1:1 (L:Cu^{II}:MeOH) stoichiometry obtained for small oligomers (M_n, *n* = 1 to *n* = 5), suggests the formation of cyclic compounds in solution. On the other hand, considering the number of units, high polymers (M_n, *n* > 5) should be present as open structures (linear polymers). At both extremities the coordination sphere of Cu^{II} would be completed in solution by acetonitrile molecules, which are lost in the gas phase and not detected in the ESMS.

Considering that ESMS is the only analytical tool allowing an unambiguous characterisation in this case, kin-

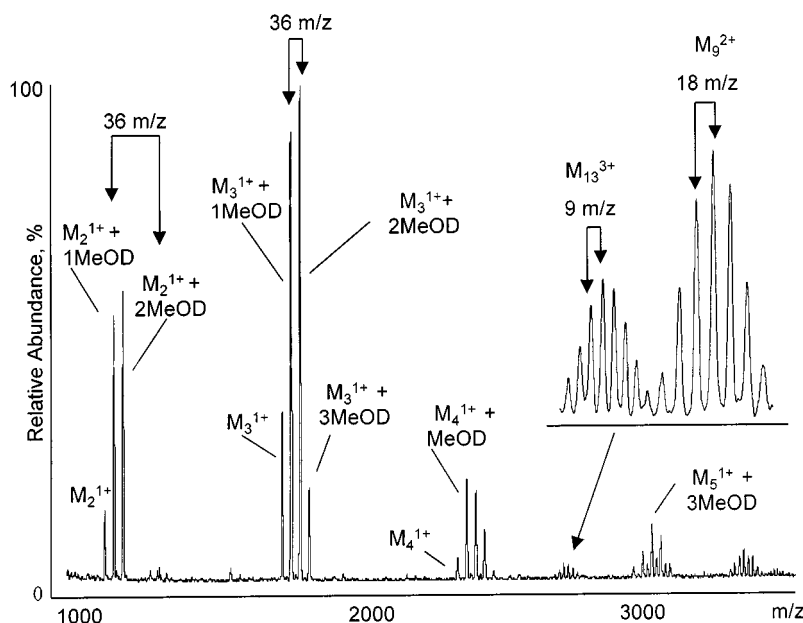


Figure 3. ES mass spectrum of an equimolar mixture of L and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in $[\text{D}_4]\text{MeOH}$

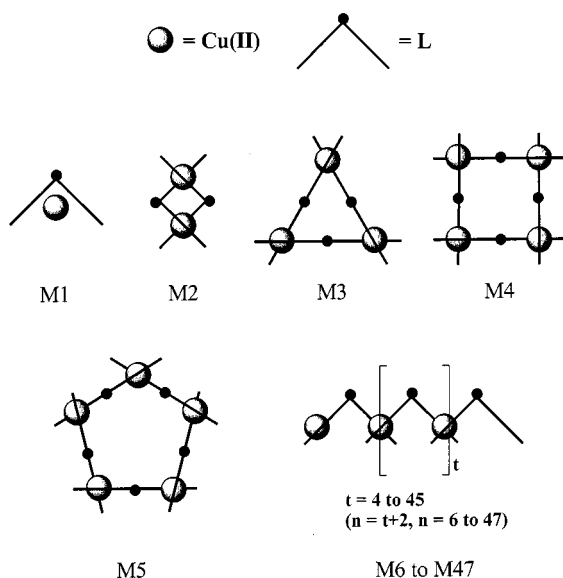


Figure 4. Possible structure of the coordination polymers $[\text{LCu}(\text{CF}_3\text{SO}_3)_2]_n$ deduced from ESMS and IR data (solvent adducts are omitted for clarity)

etic and thermodynamic studies were necessary in order to exclude the possibility of these oligomers being artefacts resulting from the ES process.

Kinetic Studies

The stability of the polymers in solution was tested during 40 days in several anhydrous solvents (acetonitrile, nitromethane, and methanol). ES mass spectra obtained from the same sample immediately after mixing (5 minutes) and after 40 days were found to be the same, showing the high stability of these compounds in solution. In the same

way, when 5% water was added to one of these solutions, the ES analysis after 5 minutes was unchanged. Later, peaks corresponding to the higher oligomers progressively disappeared and after 24 hours only one peak corresponding to the monomer complex (M_1^{1+}) was observed in the ES mass spectrum (Figure 5a, b, c).

The observation of this progressive dissociation is the definitive piece of evidence which shows that these high molecular weight coordination complexes are formed in solution and not during the ES process. Hence, the possibility for these polymers of being artefacts of the ES process can be definitely rejected.

Thermodynamic Studies

Attempts to isolate some of the oligomers using size exclusion sephadex chromatography (by classical column or by HPLC) were fruitless and unfortunately only the monomer (M_1) was obtained. This result indicates that all these components are in equilibrium in solution. In order to determine if ligand exchange took place in this high-molecular-weight system, the ligand L was first mixed with a stoichiometric amount of $\text{Cu}(\text{OTf})_2$ in anhydrous acetonitrile (ca. 10^{-4} M). Then, after stirring for 5 minutes, one equivalent of the methylated ligand L^* (Scheme 1) was added to this mixture. The resulting solution was stirred for 5 minutes at room temperature and analysed immediately. The ES mass spectrum (Figure 6) showed that all possible combinations of oligomers M_aM_b^* ($0 < a, b < 9$) of general formula $\text{L}_a\text{L}_b^*[\text{Cu}(\text{CF}_3\text{SO}_3)_2]_{a+b}$ were obtained statistically in solution. This observation clearly indicates that ligand exchange occurred in solution, and confirms that these coordination polymers are in equilibrium in solution. Interestingly, the methylated ligand L^* yielded a mixture of oligomers with $\text{Cu}(\text{OTf})_2$ in anhydrous acetonitrile in the same manner as obtained with the ligand L.

To complete the study of these compounds, other thermodynamic experiments were carried out. In order to obtain more information about the stability of the complexes

in solution, five solutions containing an equimolar amount of Cu(OTf)₂ and the ligand L in anhydrous acetonitrile at different concentrations (10⁻³, 10⁻⁴, 10⁻⁵, 10⁻⁶ and 10⁻⁷ M) were analysed by ESMS. The ES mass spectra obtained showed the presence of the oligomeric mixture for a concentration down to 10⁻⁴ M. For lower concentrations, these high-molecular-weight complexes disappear and only the monomer ion (M₁¹⁺) is detected, indicating that dissociation processes occur below a concentration of 10⁻⁴ M (Figure 7a, b).

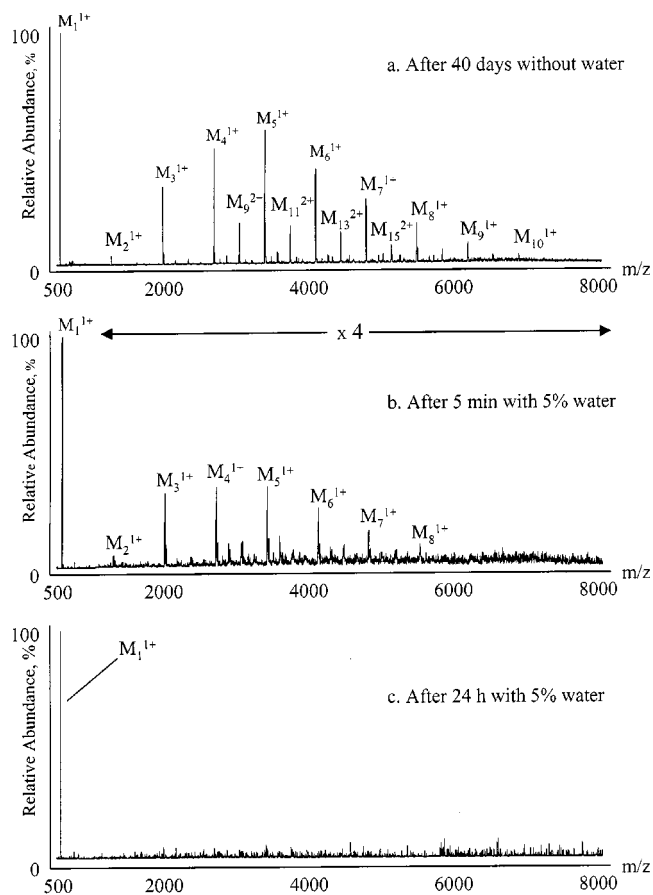


Figure 5a, b, c. Kinetic study: a. in anhydrous acetonitrile after 40 days; b. in acetonitrile with 5% water after 5 min; c. in acetonitrile with 5% water after 24 h; this study addresses the possibility that the compounds are ES process artefacts

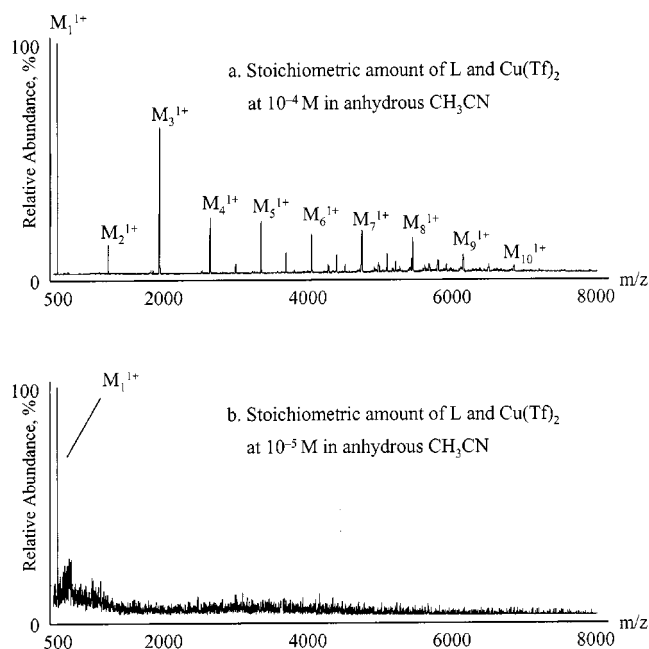


Figure 7a, b. Evaluation of the stability in solution of the coordination polymers at different concentrations

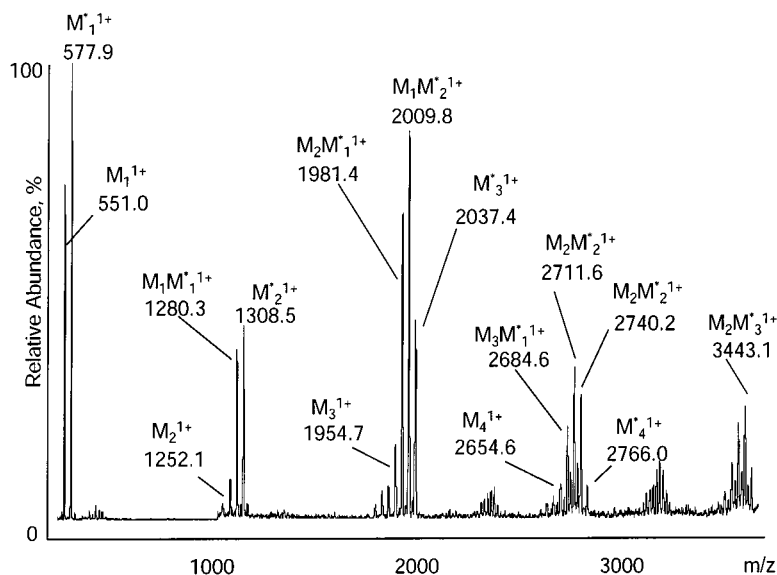


Figure 6. ES mass spectrum of an equimolar mixture of L and Cu(CF₃SO₃)₂ with one equivalent of L* in anhydrous acetonitrile at 10⁻⁴ M

Conclusion

We have shown that ligand **L** and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in a 1:1 ratio in anhydrous solvents generate a mixture of high molecular weight coordination polymers of general formula $[\text{LCu}(\text{CF}_3\text{SO}_3)_2]_n$ by self-assembly. The largest oligomer clearly identified contains 47 units and weighs 32901.4 Da. The structure (cyclic for small oligomers and linear for the highest one) has been deduced from the IR and the ESMS data.

The kinetic decomplexation observed in the presence of 5% water shows that these self-assembled polymeric species are formed in solution and are not artefacts due to the ES process. To complete this study, ESMS thermodynamic experiments have been carried out and have demonstrated that these oligomers are in equilibrium in solution, are stable over time and can be observed down to a concentration of 10^{-4} M.

ESMS may therefore be regarded as an extremely valuable tool to prove the existence of very large polynuclear transition metal complexes in solution, and encouraging perspectives are offered for the characterisation of species of nanometric dimensions.

Experimental Section

Materials: Unless otherwise noted, ^1H NMR spectra were measured at 200 MHz with a Bruker AC 200 spectrometer in CDCl_3 and referenced to the residual solvent peak. Melting points were obtained with a digital Thomas Hoover (Electrotherma) apparatus. Infrared absorption spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer in KBr, and electronic absorption spectra on a Cary 219 spectrometer in CHCl_3 with λ_{max} in nm and ϵ ($\times 10^4$) in $\text{M}^{-1} \text{cm}^{-1}$. Fast atom bombardment mass spectrometry (FAB-MS) was performed on a ZAB-HF VG spectrometer with *m*-nitrobenzyl alcohol as the matrix. Spectroscopic studies were performed in spectroscopic-grade solvents. All solvents were reagent-grade and used without further purification. The Cu^{II} triflate was purchased from Fluka (Buchs, Switzerland).

ESMS: Positive ES mass spectra were mainly obtained on an ES triple quadrupole mass spectrometer Quattro II with an *m/z* range extended to 8000 (Micromass, Altrincham, UK). The electrospray source was heated to 70 °C. The sampling cone voltage (V_c) was set to 70 V and the skimmer Lens Offset to 0 V to allow the transmission of ions with *m/z* > 4000 without fragmentation processes. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 5 $\mu\text{L}\cdot\text{min}^{-1}$. Calibration was performed using protonated horse myoglobin. Scanning was performed from *m/z* = 500 to 8000 in 20 s, and several scans were summed to obtain the final spectrum. ES mass spectra at higher resolution were obtained on an LC-Tof mass spectrometer (Micromass, Altrincham, UK).

Samples for ESMS were prepared by mixing the corresponding ligand and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in a 1:1 ratio to achieve a concentration of 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} or 10^{-7} M in anhydrous acetonitrile and a concentration of 10^{-4} M in $[\text{D}_4]\text{MeOH}$. After stirring at room temperature for 1 min, the clear blue solution was analysed directly by ESMS.

Synthesis of the Ligands **L and **L***:** The ligands were prepared as shown in Scheme 1. The stannylation of 2-bromopyridine (**3**) with butyllithium and tributylstannyl chloride gave 2-tributylstannylpyridine (**4**).^[9] The ketone **6** was prepared from 2,6-dibromopyridine (**5**) by monolithiation and reaction with ethylchloroformate as previously described.^[10] The cross coupling reaction between **4** and **6** or **8** and **6** in the presence of $\text{Pd}(\text{PPh}_3)_4$ yielded ligand **1** (**L**) or ligand **2** (**L***) which were completely characterised.

2-Tributylstannylpyridine (4): A 1.6 M solution of *n*-butyllithium in hexane (39.2 mL, 0.062 mol) was slowly added to a solution of 2-bromopyridine (**3**; 6 mL, 0.062 mol) in THF (120 mL) cooled to -78 °C under argon. After 30 min, Bu_3SnCl (16.8 mL, 0.062 mol) was added to give a dark solution which was stirred at -78 °C for one more hour. The solution was allowed to warm to room temperature and a saturated aqueous solution of NH_4Cl (60 mL) was added. The aqueous phase was extracted with ether (3×100 mL) and the combined organic layers were washed with brine (100 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by chromatography on alumina ($\text{EtOAc}/\text{hexane}$ 1:20) to obtain a pale yellow oil (22.1 g, 96%).^[9] ^1H NMR: δ = 8.73 (ddd, J = 4.9, 1.9, 1.0 Hz, 1 H, H_6), 7.48 (dt, J = 7.4, 1.8 Hz, 1 H, H_5), 7.39 (dt, J = 7.4, 1.6 Hz, 1 H, H_3), 7.10 (ddd, J = 6.9, 4.9, 1.7 Hz, 1 H, H_4), 1.70–1.05 (m, 18 H, CH_2), 0.85 (t, 9 H, J = 7.3 Hz, CH_3).

Bis(6-bromo-2-pyridyl)ketone (6): 1.1 Equiv. of *n*-butyllithium in hexane (29 mL, 0.046 mol) was added dropwise under argon to a solution of 2,6-dibromopyridine (**5**; 10 g, 0.042 mol) in diethyl ether (200 mL) cooled to -90 °C. After stirring vigorously for 20 min, a solution of ethyl chloroformate (2.02 mL, 0.021 mol) in diethyl ether (50 mL) was added. The deep blue solution was stirred for one hour and warmed to -40 °C for 30 min. Then, the reaction was quenched successively with methanol (50 mL) and water (50 mL). The organic phase was removed under vacuum and the aqueous layer was extracted with chloroform (3×50 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under low pressure. The residue was purified by flash chromatography on silica gel using $\text{EtOAc}/\text{hexane}$ (1:6) as eluent to give a white solid (3.4 g, 47%). M.p. 159–160 °C (ref.^[10] 155–156.5 °C). ^1H NMR: δ = 8.08 (dd, J = 7.1, 1.4 Hz, 2 H, H_3), 7.76 (dd, J = 8.0, 7.2 Hz, 2 H, H_4), 7.69 (dd, J = 8.0, 1.5 Hz, 2 H, H_5). ^{13}C NMR: δ = 189.5, 154.0, 141.5, 138.9, 131.4, 124.3.

2-Tributylstannyl-4-picoline (8): 1 Equiv. of a 1.6 M solution of *n*-butyllithium in hexane (18.15 mL, 29.066 mmol) was added at -78 °C under argon to a solution of 2-bromopicoline (**7**; 5 g, 29.066 mmol) in tetrahydrofuran (100 mL). After 30 min, Bu_3SnCl (7.9 mL, 29.066 mmol) was added and the reaction was monitored by TLC. The reaction was allowed to rise to room temperature and after 30 min a saturated aqueous solution of NH_4Cl was added (100 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under low pressure. The residue was purified by chromatography on alumina using $\text{EtOAc}/\text{hexane}$ (1:20) as eluent to obtain a pale yellow oil (11.1 g, 78%). B.p. 144 °C (0.6 Torr). ^1H NMR: δ = 8.58 (d, J = 5.0 Hz, 1 H, H_6), 7.22 (s, 1 H, H_3), 6.94 (d, J = 5.0 Hz, 1 H, H_5), 2.32 (s, 3 H, CH_3), 1.70–1.05 (m, 18 H, CH_2), 0.85 (t, J = 7.2 Hz, 9 H, CH_3). ^{13}C NMR: δ = 173.1, 150.2, 143.9, 133.4, 123.0, 29.1, 27.3, 13.7, 9.7, 8.7. EI-MS: *m/z* (%) = 383 (5) [$\text{M} + 1$], 326 (85) [$\text{M} - \text{Bu}$], 268 (45) [$\text{M} - 2\text{Bu}$], 212 (100) [$\text{M} - 3\text{Bu}$].

L [Bis(2,2'-bipyrid-6'-yl)ketone]: Toluene (20 mL) was added to a mixture of compound **4** (2.15 g, 5.84 mmol), the dibromo com-

pound **6** (0.50 g, 1.46 mmol) and tetrakis(triphenylphosphane)palladium (0.34 g, 20% mol) and the resulting mixture was stirred at 110 °C under argon for 24 hours. The toluene was then evaporated and the residue was chromatographed on silica gel eluting with acetone/hexane (2:5). The pale yellow solid was triturated with hexane to afford a white solid (0.38 g, 77%). M.p. 171–172 °C. ¹H NMR: δ = 8.68 (m, 2 H, H₃), 8.66 (dd, *J* = 7.8, 1.3 Hz, 2 H, H₃'), 8.33 (dt, *J* = 7.9, 1.0 Hz, 2 H, H₆), 8.16 (dd, *J* = 7.6, 1.3 Hz, 2 H, H₅'), 8.04 (t, *J* = 7.7 Hz, 2 H, H₄'), 7.70 (dt, *J* = 7.7, 1.8 Hz, 2 H, H₅), 7.30 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2 H, H₄). ¹³C NMR: δ = 192.8, 144.4 (2C), 153.7, 149.1, 137.3, 136.9, 125.0, 124.0, 123.4, 121.4. FAB-MS: *m/z* (%) = 339.1 (100) [*M* + 1], 155 (7) [*M* – 183 (bipy)]. C₂₁H₁₄N₄O (338.4): calcd. C 74.53, H 4.17, N 16.57; found C 74.45, H 4.41, N 16.68. IR (KBr): ν̄ = 1686, 1581, 1430, 1320, 1258, 1097, 992, 752, 667 cm⁻¹. UV/Vis: λ (ε_{max}) = 230 (1.0), 279 (0.9).

L* [Bis(2,2'-bipyrid-4-methyl-6'-yl)ketone]: Toluene (5 mL) was added to a mixture of compound **8** (0.17 g, 0.442 mmol), dibromo compound **6** (0.063 g, 0.184 mmol) and tetrakis(triphenylphosphane)palladium (0.043 g, 20% mol) and the resulting mixture was stirred at 110 °C under argon for 17 hours. The toluene was then evaporated and the residue was chromatographed on silica gel eluting with acetone/hexane (2:5). The pale yellow solid was triturated with hexane to afford a white solid (0.040 g, 59%). M.p. 149–150 °C. ¹H NMR: δ = 8.64 (dd, *J* = 1.2, 7.8 Hz, 2 H), 8.54 (d, *J* = 4.7 Hz, 2 H), 8.20–8.15 (m, 4 H), 8.03 (t, *J* = 7.8 Hz, 2 H), 7.12 (dq, *J* = 0.6, 6.1 Hz, 2 H), 2.25 (s, 3 H). FAB-MS: *m/z* (%) = 367.1 (100) [*M* + 1]. C₂₃H₁₈N₄O (366.4): calcd. C 75.39, H 4.95, N 15.29; found C 74.3, H 4.95, N 15.5.

Synthesis of the Cu^{II} Coordination Polymers: The Cu^{II} coordination polymers were obtained by mixing the ligand **L** or **L*** and Cu^{II} triflate [Cu(CF₃SO₃)₂] in a 1:1 ratio in anhydrous acetonitrile or in [D₄]MeOH. The resulting clear blue solution was stirred at room temperature for 1 min.

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