Metal Ion and Anion Based 'Tuning' of a Supramolecular Metallogel

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Supplementary Material

Synthesis

Synthesis of 1-(1-Methyl-1-{3-[1-methyl-1-(3-{(E)-1-[(Z)-vinyliminomethyl]-propenyl}-ureido)ethyl]-phenyl}-ethyl)-3-{(E)-1-[(Z)-vinyliminomethyl]-propenyl}-urea (1). A solution of 1,3bis(1-isocyanato-1-methylethyl)benzene (4.89 g, 20.0 mmol) in dry CHCl₃ (40 mL) was heated to reflux and stirred under N₂ atmosphere. A solution of 3-aminopyridine (3.80 g, 40.4 mmol) in dry CHCl₃ (40 mL) was slowly added dropwise to the reaction mixture over a period of several hours. After complete addition the reaction mixture was stirred at reflux for 72 h. After this period an off-white precipitate formed, which was filtered off and washed with CHCl₃ (3×30 mL) and diethyl ether (3×30 mL) to obtain the clean product as a white powder. Yield 7.20 g , 16.6 mmol, 83.3 %. ¹H NMR (400 MHz, DMSO) δ 8.57 (s, 2H, NH), 8.43 (d, *J* = 2.6, 2H, ArH), 8.07 (dd, *J* = 1.4, 4.6, 2H, ArH), 7.80 (ddd, *J* = 1.4, 2.6, 8.4, 2H, ArH), 7.44 (s, 1H, Ar-H), 7.35 (m, 3H, ArH) 7.19 (dd, *J* = 4.6, 8.4, 2H, ArH), 6.68 (s, 2H, NH), 1.60 (s, 12H, CH₃). ¹³C{¹H} NMR (101 MHz, DMSO) δ 153.87, 147.67, 141.88, 139.21, 137.03, 127.54, 124.08, 123.33, 122.48, 121.19 54.60, 29.63. IR v_{max}(cm⁻¹): 3316 (NH), 1622 (C=O). ES⁺-MS *m*/z 433.3 ([M+H]⁺, 100%). Anal. calc. for C₂₄H₂₈N₆O₂: C 66.65, H 6.53, N 19.43 % Found: C 66.98. H 6.38. N 19.37%.

Crystal Data

Crystal data for **2**: C₉₆H₁₁₂Cl₆Cu₃N₂₄O_{23.6}, M = 2383.02, $0.50 \times 0.14 \times 0.04 \text{ mm}^3$, triclinic, space group *P*-1 (No. 2), a = 9.1548(3), b = 14.8760(5), c = 22.3887(7) Å, $\alpha = 78.5570(10)$, $\beta = 84.283(2)$, $\gamma = 81.9150(10)^\circ$, V = 2950.65(17) Å³, Z = 1, $D_c = 1.341 \text{ g/cm}^3$, $F_{000} = 1234$, Smart 1000, MoK α radiation, $\lambda = 0.71073$ Å, T = 120(2)K, $2\theta_{\text{max}} = 50.0^\circ$, 22353 reflections collected, 10353 unique (R_{int} = 0.0583). Final *GooF* = 1.040, RI = 0.0756, wR2 = 0.1874, *R* indices based on 5835 reflections with I >2 σ (I) (refinement on F^2), 893 parameters, 228 restraints. Lp and absorption corrections applied, $\mu = 0.746 \text{ mm}^{-1}$.

Crystal data for **5**: C₅₀H₆₈CuN₁₄O₁₄, M = 1152.72, $0.37 \times 0.09 \times 0.07$ mm³, triclinic, space group P-1 (No. 2), a = 8.9533(18), b = 9.5321(19), c = 16.993(3) Å, $\alpha = 76.234(4)$, $\beta = 86.011(4)$, $\gamma = 84.480(4)^{\circ}$, V = 1400.4(5) Å³, Z = 1, $D_c = 1.367$ g/cm³, $F_{000} = 607$, Smart 1000, MoK α radiation, $\lambda = 0.71073$ Å, T = 120(2)K, $2\theta_{max} = 46.7^{\circ}$, 12148 reflections collected, 4041 unique

($R_{int} = 0.0582$). Final *GooF* = 1.084, *R1* = 0.0432, *wR2* = 0.0897, *R* indices based on 3280 reflections with I >2 σ (I) (refinement on F^2), 381 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.466 \text{ mm}^{-1}$.

Gelation Behaviour

Ligand 1 gels methanol at above 0.5 % weight in the presence of 0.3 or more equivalents of copper(II) chloride. It was also found to gel MeOH: H_2O mixtures of compositions from 9:1 to 6:4. The ligand does not dissolve in a range of other solvents such as acetone or acetonitrile. No gels were observed in THF or THF/water mixtures, DMSO and DMSO/water mixtures.

For the methanol gels studied, after addition of $CuCl_2$ and heating to dissolve any precipitate the solution appears dark green. Over a period of 10 minutes the color changes to dark blue and the development of fibers can be observed. At this stage the material still flows freely although the consistency is viscous. Over a period of a few days the color becomes lighter and the translucency decreases. The final gels are only slightly translucent (sometimes with domains of greater opacity). For rheological measurements gels were left to settle for 1 week and the resulting gels proved to be stable at least over several months.

Thermal Stability. The thermal stability of the gels was determined using the dropping ball method wherby 10 mL of gel were prepared as described above in a sample vial (diameter 21 mm). A steel ball (diameter 7 mm, mass 1.39 g) was carefully placed in the middle of the surface of the gel and the vial was then sealed and immersed in a water bath. Upon heating the gel-sol transition temperature (T_{gel}) was recorded when the ball had completely sunk into the gel.



Figure S1 CuCl₂ metallogels of ligand 1 (1 wt%) in MeOH using (from left to right) 0.1, 0.2, 0.3,

0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equivalents of CuCl₂·2H₂O.



Figure S2 SEM images of xerogels derived from the copper(II) chloride metallogel of **1** obtained from MeOH using 0.3 equivalents of CuCl₂ at magnifications of (a) \times 13,000 and (b) \times 50,000.



Figure S3 X-ray crystal structure of $[Cu_3(1)_4Cl_4]Cl_2 \cdot nH_2O(2)$ obtained from a 1:1 solution of 1 and $CuCl_2 \cdot 2H_2O$ in MeOH:H₂O 7:3 – extended coordination polymer structure.



Figure S4 PXRD patterns for selected samples of (from top to bottom) pure ligand 1, and with 0.1, 0,3, 0.5, 0.8, and 1.0 equivalents of added $CuCl_2$. The bottom pattern is obtained from the sample used in the single crystals analysis and matches the calculated pattern from the single crystal data.



Figure S5 Elastic modulus and yield stress (taken as the point where the G'' plot crosses that of G') as a function of concentration of CuCl₂ with respect to a ligand concentration of 1 wt%. The lines are a guide to the eye only.



Figure S6 Solid state MAS ¹³C NMR spectra of dried samples of ligand **1** using (from top to bottom) pure ligand, 0.1, 0.3, 0.5, 0.6, 0.8, and 1.0 equivalents of CuCl₂, and isolated crystals of **2**. The square brackets indicate spinning side bands, the arrows indicate the appearance of a new urea peak.