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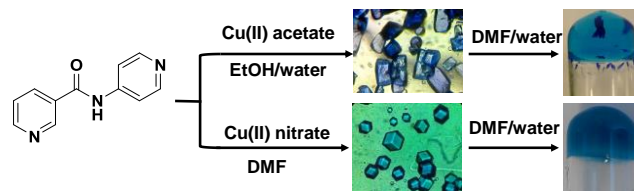
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Graphical Abstract**Selective gelation of N-(4-pyridyl)nicotinamide by copper(II) salts**

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We report the gelation properties of copper(II) complexes of *N*-(4-pyridyl)nicotinamide (**4PNA**). Gelation was observed for copper(II) complexes of **4PNA** whereas the manganese(II), iron(II), cobalt(II), nickel(II), cadmium(II) and zinc(II) complexes were not able to form metallogels.



ARTICLE

Selective gelation of *N*-(4-pyridyl)nicotinamide by copper(II) salts

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We report the selective gelation properties of copper(II) complexes of *N*-(4-pyridyl)nicotinamide (4PNA). The morphology of the xerogels was examined by scanning electron microscopy (SEM). Correlation of X-ray powder diffraction (XRPD) pattern of the xerogels and single crystal structure of copper(II) acetate complex suggests that the single crystal X-ray data represents a good structural model for the gel fibers themselves and that gelation arises from the presence of a 1D hydrogen bonded chain between gelator amide groups and coordinated anions, while the presence of strongly bound water in non-gelator systems results in the formation of more extensively hydrogen bonded crystalline networks. The selective gelation of all the copper(II) salts compared to the other metal salts may be attributed to Jahn-Teller distorted nature of copper(II), which weakens water binding in all copper(II) salts.

Introduction

Supramolecular gels based on low molecular weight gelators (LMWGs)¹⁻¹⁰ have emerged as a prolific area of current research due their potential applications as functional soft materials for separation,¹¹ drug delivery,¹²⁻¹⁴ templating of inorganic and polymer materials^{15, 16} and as media to control crystal growth.¹⁷ Gels are formed by the immobilisation of solvent molecules in the 3-D fibrous network of the gelators, which self-assemble *via* non-covalent interactions^{18, 19} such as hydrogen bonding, van der Waals interactions, π - π stacking and halogen bonding. Recently, there has been an upsurge of interest in metal based supramolecular gels (metallogeles).^{8, 20} These metal-containing LMWGs have strong coordination interactions between the organic moiety and metal centre, which act as a key driving force in the formation of the gel fibre network in combination with the various non-covalent interactions.^{8, 21, 22} The gel fibres themselves can arise from the self-assembly of discrete complexes,²³⁻²⁸ coordination polymers,²⁹⁻³⁴ or cross-linked coordination polymers.³⁵ Non-coordinated metal ions or metallic nanoparticles may also be incorporated into the gel matrix.³⁶⁻³⁹ The inclusion of metal ions in LMWGs lead to multifunctional metallogeles which offer potential applications²⁰ in catalysis, sensing, optics and magnetic materials.

The understanding of the structure of LMWGs and metallogeles in the gel state is still in its infancy because of the low ordering of the gel as a whole and the wide range of length scales of the

gel structure, ranging from the nano- to microscale. Efforts have been made to determine gel structure by analysis of the X-ray diffraction pattern of the dried gel (xerogel). Nevertheless, removal of solvent to prepare a xerogel can result in artefacts due to dissolution and recrystallization, changes in morphology or polymorphic phase transition. However, the combination of crystal structure and the powder diffraction pattern of either native gel or the xerogel remains one of the most practical methods to gain insight to gelator structure and aggregation behaviour. Based on this approach efforts have been made to identify the key structural features of gel-network formation in LMWGs by analysis of potential using supramolecular synthons.⁴⁰

Scheme 1

Although, there are a few reports on structure-property correlation of metallogeles,⁴¹⁻⁴⁵ designing metallogeles with specified properties and structure is still a daunting task. We have shown that metal binding to functionality such as a pyridyl group can 'switch on' gelation by removing the competing urea-pyridyl hydrogen bonding interaction.^{18, 46} In previous

work one of us has reported a series of pyridyl amide compounds and established that *N*-(4-pyridyl)isonicotinamide can selectively form a hydrogel.⁴⁷ Other *N*-(pyridyl)isonicotinamide isomers do not gel water highlighting the importance of the relative position of ring nitrogen atoms for gel formation. In this work, we explore the ability of metal salts to bring about gelation in pyridyl amides. Specifically, we report the gelation properties of metal salts of *N*-(4-pyridyl)nicotinamide (**4PNA**) as depicted in Scheme 1.

Experimental

Materials and methods

All starting materials were purchased from commercial sources and were used as supplied. Dichloromethane was freshly distilled from calcium hydride prior to use for the synthesis of amide, other solvents were used without further purification. Deionized water was used for all the experiments. ¹H and ¹³C-NMR spectra were recorded on Bruker Advance 400 spectrometer (¹H-NMR: 400 MHz, ¹³C-NMR: 100 MHz). IR spectra were measured on a Nicolet iS10, SEM was performed on Leo Supra 25 microscope and PXRD was analysed using Bruker D8 Focus instrument.

Synthesis of ligand

The synthesis and characterisation of **4PNA** has been reported previously⁴⁷ and the analytical and spectroscopic data matched that reported in the literature.

Synthesis of complexes

[Cu(4PNA)₂(OAc)₂] (1): A solution of **4PNA** (25 mg, 0.125 mmol) in 5 mL of ethanol was layered over 5 mL of aqueous Cu(OAc)₂·2H₂O (12.4 mg, 0.062 mmol) solution. Blue crystals of **1** were obtained in a week (23 mg, 0.04 mmol). Yield: 64%. Anal. data for C₂₆H₂₄CuN₆O₆: Calc. C, 53.84; H, 4.17; N, 14.49. Found: C, 53.72; H, 4.04; N, 14.42. FT-IR (cm⁻¹): 3255m, 3171m, 3075m, 3002m, 1687vs, 1601vs, 1507vs, 1429vs, 1332s, 1298s, 1240w, 1209w, 1117s, 1065w, 1026s, 895m, 839s, 728s, 679m, 622m, 601m, 542s.

[Cd(4PNA)₂(OAc)₂(H₂O)]·2H₂O (2): The cadmium complex was synthesised by layering an ethanolic solution (1.5 mL) of **4PNA** (20 mg, 0.1 mmol) over an aqueous solution (1 mL) of Cd(OAc)₂·2H₂O (13.3 mg, 0.05 mmol). Colourless crystals suitable for X-ray analysis were obtained after a period of one week (8 mg, 0.012 mmol). Yield: 25%. Anal. data for C₂₆H₃₀CdN₆O₉: Calc. C, 45.72; H, 4.43; N, 12.31. Found: C, 45.87; H, 4.12; N, 12.30. FT-IR (cm⁻¹): 3247w, 3170w, 3069w, 1686s, 1597vs, 1523vs, 1421vs, 1333s, 1301s, 1212s, 1117s, 1065w, 1045m, 1015s, 936w, 896m, 834s, 730s, 711s, 672m, 622m, 591m, 538s.

[Zn(4PNA)₂(NO₃)₂(H₂O)₂] (3): Complex **3** was synthesized by layering an ethanolic solution (10 mL) of **4PNA** (39.8 mg, 0.2 mmol) over aqueous solution (10 mL) of Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol). After a period of two weeks X-ray quality single crystals were obtained (48.6 mg, 0.078 mmol) Yield: 78

% Anal. data for C₂₂H₂₂N₈O₁₀Zn: Calc. C, 42.36; H, 3.55; N, 17.96. Found: C, 42.27; H, 3.38; N, 17.79. FT-IR (cm⁻¹): 3430b, 2516w, 2427w, 2356m, 1858w, 1678vs, 1620s, 1568s, 1492vs, 1426m, 1384vs, 1341m, 1315m, 1292s, 1108m, 1063s, 1023s, 920m, 900s, 873w, 842w, 828m, 811m, 756m, 700vs, 651s, 602m, 528m, 420m.

[Cd(4PNA)₂(NO₃)₂(H₂O)₂] (4): An ethanolic solution (10 mL) of **4PNA** (39.8 mg, 0.200 mmol) was layered over an aqueous solution of Cd(NO₃)₂·4H₂O (30.8 mg, 0.1 mmol). After a period of one week, X-ray quality single crystals were obtained. (36.0 mg, 0.053 mmol) Yield: 54%. Anal. data for C₂₂H₂₂CdN₈O₁₀: Calc. C, 39.39; H, 3.31; N, 16.70. Found: C, 39.22; H, 3.26; N, 16.64. FT-IR (cm⁻¹): 3668w, 3391b, 3306b, 2446w, 2361s, 1929b, 1769w, 1681vs, 1596vs, 1523vs, 1418m, 1384vs, 1333vs, 1297vs, 1208s, 1115s, 1065m, 1047m, 1021vs, 930m, 897s, 822vs, 729m, 699vs, 596m, 530s, 418m.

Gel Preparation

Copper(II) acetate gel: Gels were prepared at various wt% by dissolving the required amount of Cu(OAc)₂·2H₂O in water (0.5 mL) and mixing with the corresponding amount (1:2 metal:ligand ratio) of **4PNA** in DMF (0.5 mL). The mixture was sonicated for 2–4 minutes and allowed to stand. The blue copper(II) acetate-**4PNA** gel was obtained overnight and was confirmed by tube inversion test. Yield: 45%. The spectroscopic data of the xerogels matched with that of **1**.

Copper(II) chloride gel: The gelation experiments were performed by mixing an aqueous solution of CuCl₂ (0.5 mL water) with corresponding amount (1:2 metal:ligand ratio) of **4PNA** in DMF (0.5 mL). The resulting solution was sonicated for one minute and allowed to stand overnight to yield green gel. Yield: 38%. Anal. data for C₁₇H₂₃Cl₂CuN₅O₃: Calc. C, 42.55; H, 4.83; Cu, 13.24; N, 14.60. Found: C, 42.72; H, 4.49; Cu, 13.49; N, 13.84. FT-IR (cm⁻¹): 3303m, 3228m, 3152m, 3066m, 1693vs, 1600vs, 1512vs, 1428s, 1331s, 1297vs, 1209s, 1117s, 1049m, 1024m, 896m, 835s, 725w, 696m, 675w, 645w, 599w, 537m, 445w.

Copper(II) nitrate gel: Gelation was observed at 3–7 wt% and the gel was prepared by mixing Cu(NO₃)₂·3H₂O (in water, 0.5 mL) and mixing with corresponding amount (1:2 metal:ligand ratio) of **4PNA** in DMF (0.5 mL). The solution were mixed together, without sonication and allowed to stand overnight to yield greenish-blue gel. Yield: 19%. Anal. data for C₁₄H₁₈CuN₆O₉: Calc. C, 35.19; H, 3.80; Cu, 13.30; N, 17.59. Found: C, 35.51; H, 3.49; Cu, 12.59; N, 16.10. FT-IR (cm⁻¹): 3319m, 3084w, 1695s, 1600vs, 1513vs, 1429s, 1380vs, 1335s, 1295s, 1211s, 1117m, 1057w, 1029w, 897w, 832s, 738w, 690m, 653w, 599w, 536m, 450w.

Copper(II) perchlorate gel: The gelation experiments performed at various concentration of Cu(ClO₄)₂·6H₂O and **4PNA** in 1:2 DMF/water (v/v) resulted in partial gelation. Gelation was observed above 4 wt% at higher DMF concentration (9:1 DMF/water, v/v) and pure DMF. This was achieved by mixing a solution of Cu(ClO₄)₂·6H₂O (0.1 mL water or DMF) with corresponding amount (1:2 metal:ligand ratio) of **4PNA** in DMF (0.9 mL). The resulting solution was

sonicated for one minute and allowed to stand overnight to yield greenish-blue gel. Yield: 13%. Anal. data for $C_{25}H_{25}Cl_2CuN_7O_{11}$: Calc. C, 40.91; H, 3.43; Cu, 8.66; N, 13.36. Found: C, 41.86; H, 3.11; Cu, 9.69; N, 12.96. FT-IR (cm^{-1}): 3448b, 3069m, 1692s, 1600vs, 1514vs, 1476w, 1425s, 1395w, 1335s, 1298s, 1210s, 1116vs, 1029m, 898w, 834s, 734w, 687m, 627m, 599m, 535m.

Copper(II) sulphate gel: Copper(II) sulphate complexes of **4PNA** displayed similar properties as copper(II) perchlorate salts. In this case, the required amount of $Cu(SO_4) \cdot 5H_2O$ in water (0.2 mL) and mixing with the corresponding amount (1:2 metal:ligand ratio) of **4PNA** in DMF (0.8 mL). The mixture was sonicated for one minute and allowed to stand overnight to yield greenish-blue gel. Yield: 44%. Anal. data for $C_{22}H_{28}CuN_6O_{11}S$: Calc. C, 40.77; H, 4.35; Cu, 9.80; N, 12.97; S, 4.95. Found: C, 40.88; H, 3.94; Cu, 10.58; N, 12.96; S, 5.91. FT-IR (cm^{-1}): 3401b, 3084w, 1691s, 1654m, 1605vs, 1516vs, 1421s, 1387w, 1336s, 1302s, 1212s, 1120vs, 1029m, 899w, 839m, 738m, 698m, 652w, 619m, 541m.

Scanning electron microscopy

The copper(II) salt dissolved in water was mixed with a solution of **4PNA** in DMF in a 1:2 metal:ligand ratio. In case of copper(II) acetate, copper(II) chloride and copper(II) nitrate 1:1 DMF/water (v/v) was used, for copper(II) perchlorate and copper(II) sulphate 9:1 DMF/water (v/v) and 8:2 DMF/water (v/v) mixtures were used respectively. It was then allowed to stand overnight, the resulting blue gel was filtered and dried under high vacuum. The gels in pure water for copper(II) acetate and copper(II) chloride were also prepared in similar fashion and dried. A small portion of the dried gel was placed on the pin mount with graphite planchets on top and coated with gold in the SEM (Leo Supra 25 microscope).

Crystallography

X-ray quality single crystals were obtained by the slow evaporation of **4PNA** and metal salt solution such as $Cu(OAc)_2 \cdot 2H_2O$ (**1**), $Cd(OAc)_2 \cdot 2H_2O$ (**2**), $Zn(NO_3)_2 \cdot 6H_2O$ (**3**), $Cd(NO_3)_2 \cdot 4H_2O$ (**4**) and $Cu(NO_3)_2 \cdot 3H_2O$ (**5**); however, crystals of **5** did not diffract. The X-ray single crystal data have been collected using $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker D8 Venture (Photon100 CMOS detector, $I\mu S$ -microsource, focusing mirrors for complexes **2**, **3** and **4** and for complex **1** sealed tube, graphite monochromator) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2)K. All structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2⁴⁸ and SHELXTL⁴⁹ software. All non-disordered non-hydrogen atoms were refined anisotropically, hydrogen atoms in structure **1** was refined isotropically, the hydrogen atoms in the structures **2**, **3** & **4** (except those of amide groups and H_2O molecules) were placed in the calculated positions and refined in riding mode. Disordered atoms in the structures **3** and **4** were refined isotropically with fixed $SOF=0.5$. Crystal data and parameters

of refinement are listed in Table S14, ESI†. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1062590-1062592 and 1062883.

Figure 1: Reaction of copper(II) salts with **4PNA** at 1:2 metal:ligand ratio forming gels (a) Cu(II) acetate and **4PNA** at 3 wt% in 1:1 DMF/water (v/v); (b) Cu(II) chloride and **4PNA** at 3 wt% in 1:1 DMF/water (v/v); (c) Cu(II) nitrate and **4PNA** at 4 wt% in 1:1 DMF/water (v/v); (d) Cu(II) perchlorate and **4PNA** at 4 wt% in 9:1 DMF/water (v/v) and (e) Cu(II) sulphate and **4PNA** at 4.5 wt% in 8:2 DMF/water (v/v).

Results and discussion

Synthesis

The **4PNA** ligand was prepared by reacting nicotinoyl chloride and 4-aminopyridine in dichloromethane in presence of triethylamine.⁴⁷ The gelation ability of the free ligand was examined in various solvents (Table S2, ESI†) and gelation was observed only in water at higher concentration (3 wt%). The gelation ability of **4PNA** was further analysed in the presence of various metal ions such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) salts (Table 1). We have selected various anions of these metal salts with different hydrogen bonding properties such as acetate, chloride, nitrate, perchlorate and sulphate. The copper(II) acetate, cadmium(II) acetate, zinc(II) nitrate and cadmium(II) nitrate complexes of **4PNA** were also isolated and structurally characterised by single crystal X-ray diffraction (*vide infra* and ESI†).

Gelation studies

All of the metal salts were screened for gel formation with **4PNA** in a variety of solvents, however the starting metal complexes only proved to be soluble in highly polar solvents, particularly water, DMF and DMSO. Gelation tests were performed *in situ* by mixing the metal salt and ligand. In a typical experiment, the aqueous solution of metal salt was mixed with a DMF solution of **4PNA** (1:1 or 1:2 metal:ligand ratio), sonicated for a short period of time and left to stand overnight. The manganese(II), iron(II), cobalt(II), nickel(II), cadmium(II) and zinc(II) complexes of **4PNA** did not form gels; a clear solution was observed initially, further evaporation yield precipitate/crystals (Table 1). In contrast all copper(II) salts formed gels with **4PNA** at a 1:2 metal:ligand ratio (assessed by simple inversion test) in different DMF/water concentrations (Figure 1).

Table 1: Gelation studies with different metal salts 1:1 DMF/water (v/v)

Metal Salts	Initial Observations	Final observation	wt %
Cu(OAc) ₂ ·2H ₂ O	Blue solution (C)	Blue Gel (T)	2.0–6.0
Cu(OAc) ₂ ·2H ₂ O	Blue solution (C)	Blue Gel (O)	7.0–10.0
CuCl ₂	Light Green solution (O)	Green Gel (O)	2.6–10.0
Cu(NO ₃) ₂ ·3H ₂ O	Blue solution (O)	Blue Gel (O)	3.0–6.0
Cu(ClO ₄) ₂ ·6H ₂ O ^a	Greenish-blue solution (O)	Greenish-blue Gel (O)	4.0–11.7
CuSO ₄ ·5H ₂ O ^b	Blue solution	Blue Gel (O)	3.5–9.0
Zn(NO ₃) ₂ ·6H ₂ O	Clear solution	Clear solution	3.0–9.0
Zn(OAc) ₂ ·2H ₂ O	Clear solution	Clear solution	3.0–8.0
ZnCl ₂	Clear solution	Crystalline material	3.0–6.0
ZnSO ₄ ·7H ₂ O	Clear solution	White precipitate	3.0–6.8
Zn(BF ₄) ₂ ·H ₂ O	Clear solution	Clear solution	3.0–6.0
Cd(NO ₃) ₂ ·4H ₂ O	Clear solution	White precipitate	3.0–9.0
Cd(OAc) ₂ ·2H ₂ O	White solution	White precipitate	3.0–8.0
CdCl ₂	White solution	White precipitate	3.0–6.0
CdSO ₄ ·8/3H ₂ O	White solution	White precipitate	3.0–6.0
FeSO ₄ ·7H ₂ O	Green solution (C)	Yellow precipitate	3.0–6.0
FeCl ₂ ·4H ₂ O	Yellow solution (C)	Crystalline material	3.0–6.0
Ni(OAc) ₂ ·4H ₂ O	Green solution (C)	Green solution (C)	3.0–6.0
NiCl ₂ ·6H ₂ O	Green solution (C)	Green solution (C)	3.0–6.0
Ni(NO ₃) ₂ ·6H ₂ O	Green solution (C)	Green solution (C)	3.0–6.0
Co(OAc) ₂ ·4H ₂ O	Red solution (C)	Red solution (C)	3.0–6.0
CoCl ₂ ·6H ₂ O	Red solution (C)	Pink precipitate	3.0–6.0
Co(NO ₃) ₂ ·6H ₂ O	Red solution (C)	Red solution (C)	3.0–6.0
MnCl ₂ ·4H ₂ O	Clear solution	Clear solution	3.0–6.0
MnSO ₄ ·H ₂ O	Clear solution	Crystalline material	3.0–6.0
Mn(NO ₃) ₂ ·4H ₂ O	Clear solution	Clear solution	3.0–6.0

C = Clear, O = Opaque & T = Transparent, ^a Gelation experiments were performed at 9:1 DMF/water (v/v) and ^b Gelation experiments were performed at 8:2 DMF/water (v/v)

Addition of varying ratios of copper(II) salts and **4PNA** in 1:1 DMF/water mixture (v/v) established that a ratio of 1:2 metal:ligand resulted in optimal gel formation.

Figure 2: Reaction of copper(II) acetate with **4PNA** (1:2 ratio) (a) crystals and gel 3wt% of the gelator and (b) opaque gel formed at higher gelator concentration (9wt%) in 1:1 DMF/water (v/v) respectively.

In the case of copper(II) acetate, mixing an aqueous solution of metal salt and DMF solution of ligand (1:2 metal:ligand ratio) resulted in a clear solution from 2 wt% to 6 wt% which formed transparent blue gels on standing overnight. These gels subsequently yielded crystals over 24 – 48 h depending on concentration (2 – 6 wt%), whereas the higher concentration (above 7 wt%) resulted in an opaque gel (Figure 2). However, with a 1:1 metal:ligand ratio gelation was observed above 4 wt%. We repeated these gelation experiments with copper(II) chloride in 1:1 DMF/water mixture (v/v) and similar results were obtained. An opaque green solution was obtained by mixing an aqueous solution of metal salt and DMF solution of ligand (1:2 metal:ligand ratio), which formed opaque green gels on standing overnight at various concentrations (from 2.6 wt% to 10 wt%). Gels were also observed with 1:1 metal:ligand ratio at 3.3 wt%. The copper (II) nitrate complex of **4PNA** formed a gel in 1:2 metal:ligand ratio at 3 wt% concentration. Gelation were also observed by changing the anion to more hydrogen bonding anions namely perchlorate and sulphate. In case of perchlorate, gels were observed at higher concentration of DMF (9:1 DMF/water mixture, v/v) at 4 wt% gelator concentration

whereas for sulphate anion gelation occurred at 3.5 wt% in 8:2 DMF/water mixture (v/v). Increasing the proportion of DMF led to increased solubility and no gelation were observed for copper(II) acetate and copper(II) nitrate. In case of copper(II) perchlorate, copper(II) chloride and copper(II) sulphate gelation observed at higher DMF concentrations.

Similar results were observed in DMSO/water mixture for all copper(II) complexes. These results indicate that copper(II) coordination selectively enhances the gelation ability of **4PNA**, particularly in the case of copper(II) acetate and copper(II) chloride to a much lesser degree in the other analogues. The selective effect of copper(II) is also noteworthy. The selectivity of metal salts in gelation process have been reported. The perchlorate and nitrate salts of Ag(I) selectively formed metallogels indicating the importance of metal salts in gelation⁵⁰. The selectivity of copper(II) chloride salts over other copper(II) salts in metallogel formation have been reported⁵¹. Recently, the selectivity of copper(II) chloride and bromide over perchlorate, nitrate, sulphate, and acetate anions was reported⁵². These studies reveal the importance of metal salts specifically copper(II) salts in metallogel formation. In the present study, a series of copper(II) salts enhance the gelation property of the ligand (**4PNA**) over other metal salts. This is presumably due to the versatile nature of the copper(II) geometry such as Jahn-Teller distorted nature, which weakens water binding in all copper(II) salts.

Gelation experiments for complexes of all copper(II) salts were also performed in pure water. Addition of copper(II) acetate and copper(II) chloride to **4PNA** (1:2 metal:ligand ratio) in pure water gave gels above 1.5 wt% and 3 wt% respectively whereas reaction of other copper(II) salts with **4PNA** in water gave immediate precipitate in every case. These results indicate that DMF is acting as a solubilising medium while water acts as an antisolvent. This delicate balance between hydrophobic effects and other intermolecular interactions is required to achieve the gel three-dimensional elastic self-assembled networks. These results clearly indicate that 1:2 metal:ligand ratio is optimal.

Gel thermal stability

Formation of supramolecular gels at room temperature is relatively unusual, implying slow coordination or slow nucleation of the gel fibres. Slow cooling is a more common way to bring about the necessary supersaturated solution from which gel fibre growth can occur. The thermal stability of the room temperature copper(II) metallogels of **4PNA** was evaluated by analysing the temperature at which the gel was converted into a liquid phase (T_{gel}). Copper(II) acetate gels displayed T_{gel} of 58°C and 61°C for 2 wt% and 4 wt% respectively. The T_{gel} for copper(II) chloride was 64°C for 3wt% and for copper(II) nitrate gels at 6.4 wt% was 53°C. In comparison, the T_{gel} for the analogous copper(II) perchlorate and sulphate gels at 4 wt% and 5 wt% were 55°C and 65°C respectively. These results indicate that the thermal stability depends on the hydrogen bonding ability of the anions. The

copper(II) acetate and copper(II) chloride gels are thermoreversible at minimum gel concentrations whereas copper(II) nitrate and copper(II) sulphate gels were thermoreversible at higher concentrations (5-6 wt%). However, prolonged heating at elevated temperature (<90°C) resulted in the decomposition of these complexes.

Figure 3: SEM images of 1:2 copper acetate gels of **4PNA** (a) in DMF/water and (b) in only water displaying fibrous network

Scanning electron microscopy

The morphologies of the copper(II) gels of **4PNA** were studied by SEM analysis. The gels prepared from water and DMF/water (1:1, v/v) were filtered and dried under high vacuum. A small portion of the dried gel was placed on the pin mount with graphite planchets on top and gold coated. The SEM of copper(II) acetate complex of **4PNA** (4 wt%) images revealed that both xerogels display fibrous network, although some crystalline material is also evident in the xerogels obtained from DMF/water (Figure 3a). This may arise from the drying process given the relative volatility of water compared to DMF, which may well result in partial dissolution and reprecipitation. The width of the gel fibrils varies from 13 nm to 40 nm irrespective of the anion and solvent in which the gel is prepared (Figure S3, ESI†).

Crystal Structures

Complexes obtained from the reaction of **4PNA** with metal salts such as copper(II) acetate, cadmium(II) acetate, zinc (II) nitrate and cadmium nitrate were characterised by single crystal X-ray crystallography. Crystals were isolated by the slow evaporation of EtOH/water mixture of **4PNA** and metal salts. Crystallographic details (Table S14) and hydrogen bonding parameters (Table S15) are given in the ESI†.

Crystalline structure of [Cu(4PNA)₂(OAc)₂]

X-ray quality crystals were obtained by the slow evaporation of ethanol-water mixture of copper(II) acetate and **4PNA** to give a mononuclear 1:2 complex of formula [Cu(4PNA)₂(OAc)₂] (**1**), with a stoichiometry consistent with the optimal ratio required for gel formation.

Figure 4: (a) Molecular structure of **1** and (b) the 1-D hydrogen bonded chain observed in the solid state.

The copper(II) metal centre lies on an inversion centre and displays a Jahn-Teller distorted octahedral geometry with the oxygen atoms of the acetate anion adopting an asymmetric chelate coordination mode in the equatorial position. The axial positions are occupied by the pyridyl nitrogen atoms of the **4PNA** ligands which coordinate via the 4-aminopyridine-derived end of the molecule. The nicotinoyl-derived pyridyl group is uncoordinated in the structure and does not take part in strong intermolecular interactions. The nitrogen atom of the amide moiety of **4PNA** is hydrogen bonded to oxygen atom of the metal coordinated acetate anion resulting in a 1-D hydrogen bonded chain (N...O = 2.8188(19)Å, ∠N-H...O = 164.0(17)°). This type of structure could give rise to hydrogen bonded 1D fibre formation and hence gelation⁵³ (Figure 4b).

Crystalline structure of [Cd(4PNA)₂(OAc)₂(H₂O)].2H₂O

Slow evaporation of a solution of cadmium(II) acetate and **4PNA** in EtOH/water at a 1:2 metal:ligand ratio resulted in a complex of formula [Cd(4PNA)₂(OAc)₂(H₂O)].2H₂O (**2**) over a period of one week. Although, the coordination mode of acetate and **4PNA** are similar to **1**, the water coordination results in a distorted pentagonal bipyramidal Cd(II) metal centre (Figure 5a). The nitrogen atom of the amide moiety of **4PNA** display hydrogen bonding to the metal coordinated acetate anion resulting via N-H...O interactions (N...O = 2.856(2) – 2.950(2) Å, ∠N-H...O = 166(3)-172(2)°). The uncoordinated water molecules are hydrogen bonded to the oxygen atoms of the metal-bound acetate anions. One of these water molecules is further hydrogen bonded to the nitrogen atom of nicotinoyl-derived pyridyl group resulting in a 2D hydrogen bonded network (Figure 5b). The cross-linking provided by the hydrogen bonding to the additional water molecules may explain why this material forms a crystalline solid rather than a gel.

Figure 5: (a) Molecular structure of **2**, uncoordinated water molecules are not shown and (b) the 2-D hydrogen bonded chain observed in the solid state (uncoordinated water molecules are shown in purple).

Crystalline structure of [Zn(4PNA)₂(NO₃)₂(H₂O)₂]

Single crystals of formula [Zn(4PNA)₂(NO₃)₂(H₂O)₂] (**3**) suitable for X-ray analysis were obtained by the slow evaporation of EtOH/water mixture of zinc(II) nitrate and **4PNA** (1:2 metal:ligand ratio) over a period of one week. The Zn(II) atom lies on an inversion centre and the structure of **3** is very similar to **1** except that the poorer ligating properties of the

nitrate anion and smaller size of zinc(II) result in monodentate coordination and the completion of the coordination sphere by two adventitious water molecules. The nitrogen of the amide moiety form hydrogen bonds to the oxygen atom of the nitrate anion ($N\cdots O = 2.920(2)$ Å, $\angle N-H\cdots O = 161(2)^\circ$) and the oxygen atoms are hydrogen bonded to the metal coordinated water molecules. These hydrogen bonding interactions result in a 2-D hydrogen bonded network (Figure 6b).

Crystalline structure of $[Cd(4PNA)_2(NO_3)_2(H_2O)_2]$

Crystallization of 4PNA from a solution of cadmium(II) nitrate in EtOH/water in a 1:2 metal:ligand ratio gives a complex of formula $[Cd(4PNA)_2(NO_3)_2(H_2O)_2]$ (**4**) with cadmium(II) atom lies on an inversion centre, which is isomorphous with **3**. Although, the metal-ligands bond distances are slightly longer than the zinc analogue, the hydrogen bonding patterns are similar (for example amide moiety and oxygen atom of the nitrate anion; $N\cdots O = 2.959(4)$ Å, $\angle N-H\cdots O = 164.0^\circ$) resulting in a 2-D hydrogen bonded network (Figure S4, ESI†).

Figure 6: (a) Molecular structure of **3** and (b) the 2-D hydrogen bonded chain observed in the solid state.

It is quite interesting to note that in all these structures the $N-H\cdots O$ synthon is observed where the nitrogen atom of the amide moiety of 4PNA is hydrogen bonded to oxygen atom of the metal coordinated anion. Comparison of the hydrogen bonding distance clearly indicates that compound **1** is having strong hydrogen bond ($N\cdots O = 2.8188(19)$ Å). These strong interactions may be attributed to the lack of water molecules resulting in more electron density around the donor atom, thereby forming rigid 1-D network which could account for its gelation ability.

X-ray powder diffraction (XRPD)

It is interesting to note that the hydrogen bonding pattern in compound **1** is 1-D whereas the solid state structures of non-gelators **2**, **3** and **4** are 2-D hydrogen bonded networks. In order to determine whether these single crystal structures are of relevance to the 1:2 stoichiometry gels formed by the copper(II) complexes we compared the XRPD pattern calculated from the single crystal data with the experimental pattern of the xerogel obtained from DMF/water and the bulk precipitate from EtOH/water (Figure 7). This data showed that the structure of the aqueous DMF derived copper acetate xerogel is similar to that of the single crystal despite the fact that the sample crystallized from a different solvent. The precipitate obtained from aqueous ethanol is also the same solid form. Given the

simple nature of the complex in **1**, its 1:2 stoichiometry which matches the ratio needed for optimal gelation and the persistence of this solid form in all three samples we believe that this complex is the gelator and the formation of a 1D hydrogen bonded tape due to the lack of coordinated water is a key factor in the gelation behaviour.

Figure 7: XRPD data for the copper(II) acetate/4PNA xerogel, precipitated product and simulated pattern from the single crystal X-ray data.

While the structural information of copper(II) chloride complex was not available due to the lack of single crystals, we have performed a Cambridge Structural Database (CSD)⁵⁴ analysis and found that 91% of copper(II) chloride structures do not have coordinated water molecules (ESI†). This might be the reason that copper(II) chloride complex of 4PNA shows excellent gelation properties. Although, the structure of the copper(II) nitrate complex of 4PNA has not been determined, the closely related *N*-phenyl-4-pyridinecarboxamine (4PPC) complex $[Cu(4PPC)_2(NO_3)_2(H_2O)_2]$ contains two aqua ligands,⁵⁵ suggesting that the relatively inefficient gelation behaviour of the copper(II) nitrate complex of 4PNA may also arise from additional water hydrogen bonding. The perchlorate and sulphate salts of copper(II) are known to have coordinated water molecules. The fact that these copper(II) complexes does form weak gels at high weight percent, as opposed to crystalline complexes expected for the other hydrated metals complexes, may arise from the Jahn-Teller distorted nature of copper(II) meaning that the water is relatively weakly bound in comparison to the zinc(II) analogue. Further evidence for the hydrated nature of the copper(II) ~~nitrate~~ complexes of 4PNA comes from the IR spectrum of the material. We compared the IR spectra of the complexes (as synthesised) with the xerogels. The IR spectrum of the xerogels of copper(II) acetate and crystals were similar. The other complexes displayed a slight broad $\nu(OH)$ band compared to the bulk solid (as synthesised), which supports the effect of metal bound water in gelation process (Figure S8-S12 ESI†).

Conclusions

The gelation ability of 4PNA was analysed in the presence of various metal ions such as manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) salts. Interestingly, gelation of 4PNA metal complexes was observed only in the case of copper(II) salts. The selective gelation of all the copper(II) salts compared to the other metal salts may be attributed to Jahn-Teller distorted nature of copper(II), which weakens water binding in all copper(II) salts. Specifically, the

copper(II) acetate complex of 4PNA is a good gelator of polar solvents while the analogous zinc and cadmium nitrate and acetate complexes do not form metallogels. We suggest that this selective gelation ability of the copper(II) acetate salt has a structural origin and is correlated with the lack of coordination to water in the complex gelators, preventing 2D hydrogen bonded network formation and favouring the formation of 1D hydrogen bonded fibrils. An interesting feature of the gelators is the availability of non-coordinated pyridyl nitrogen atoms for further modification³⁴ and work directed to the incorporation of metallic nanoparticles using these anchor points is currently in progress.

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Notes and references

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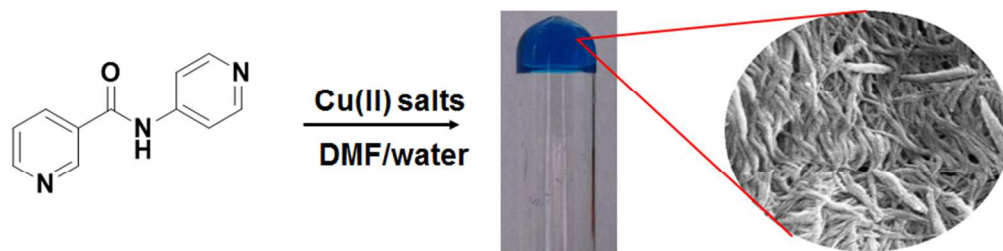
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† Electronic Supplementary Information (ESI) available: Crystallographic information in CIF format for the structure of **1**, **2**, **3** & **4**. Details of gelation experiments, PXRD comparison, SEM of copper(II) nitrate gel and T_{gel} measurement. See DOI: 10.1039/b000000x/

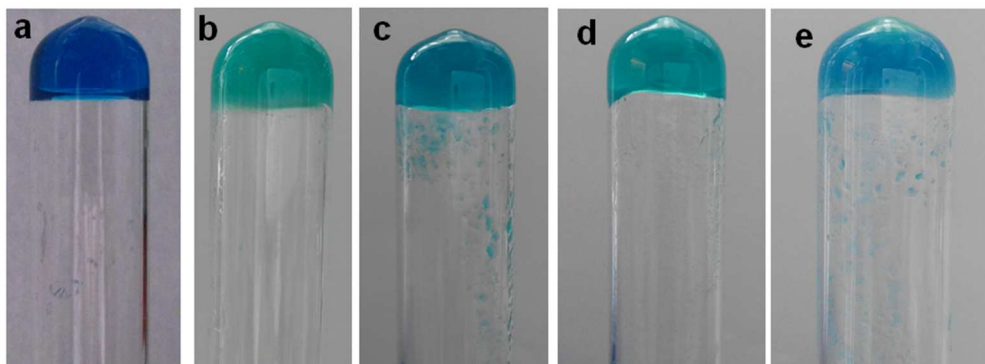
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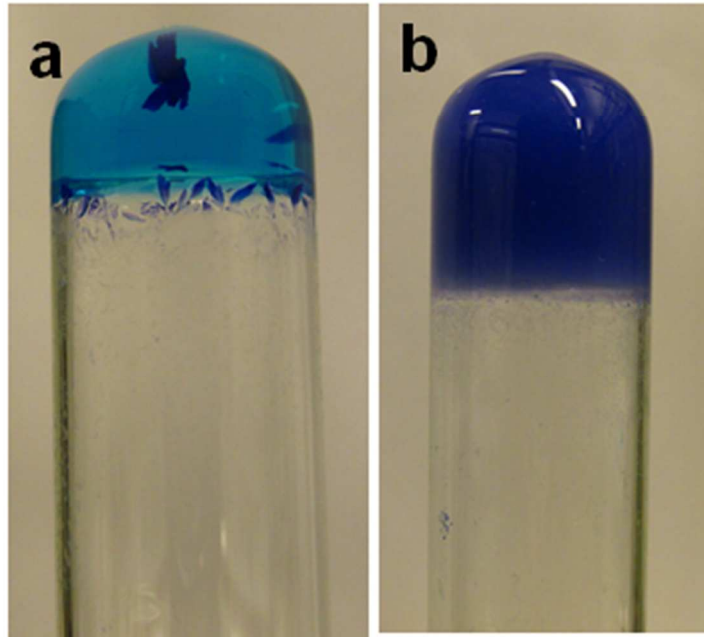
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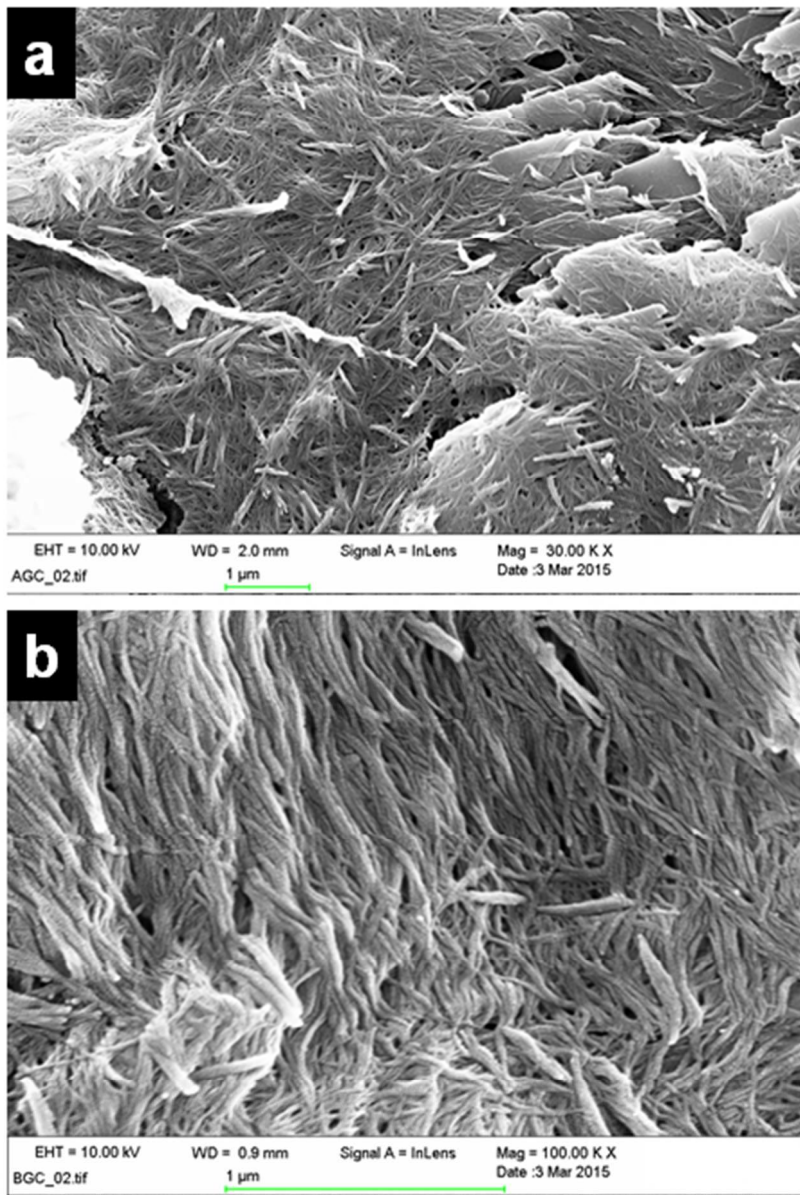
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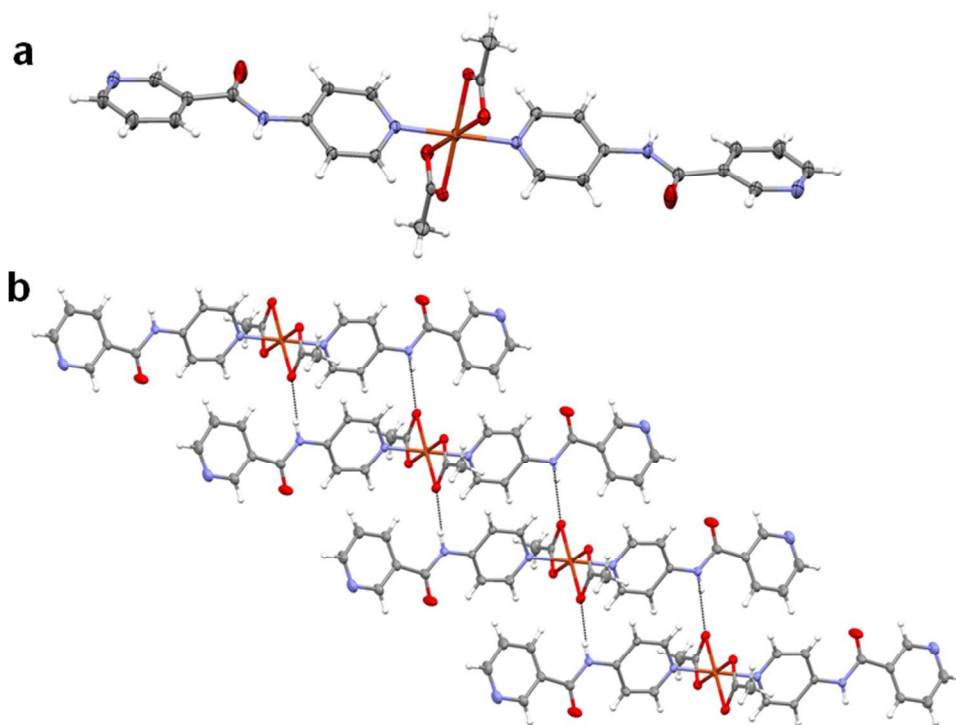
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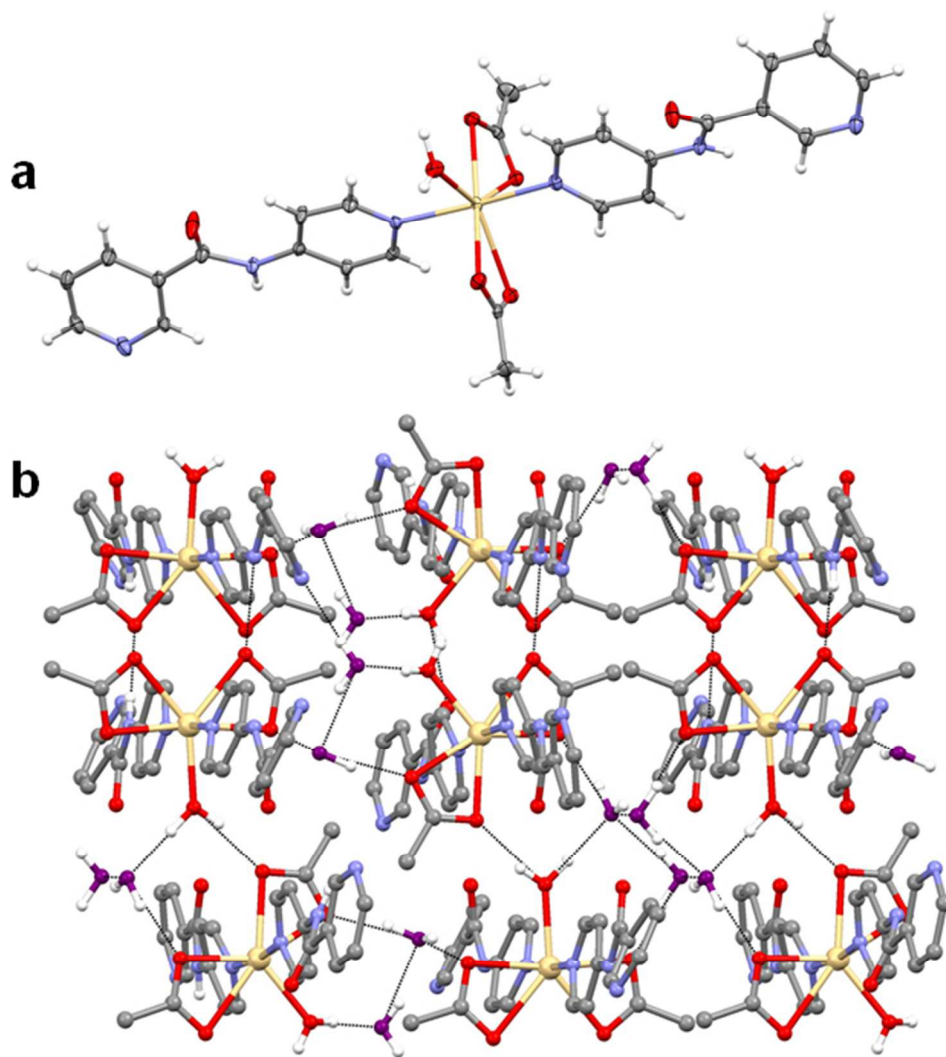
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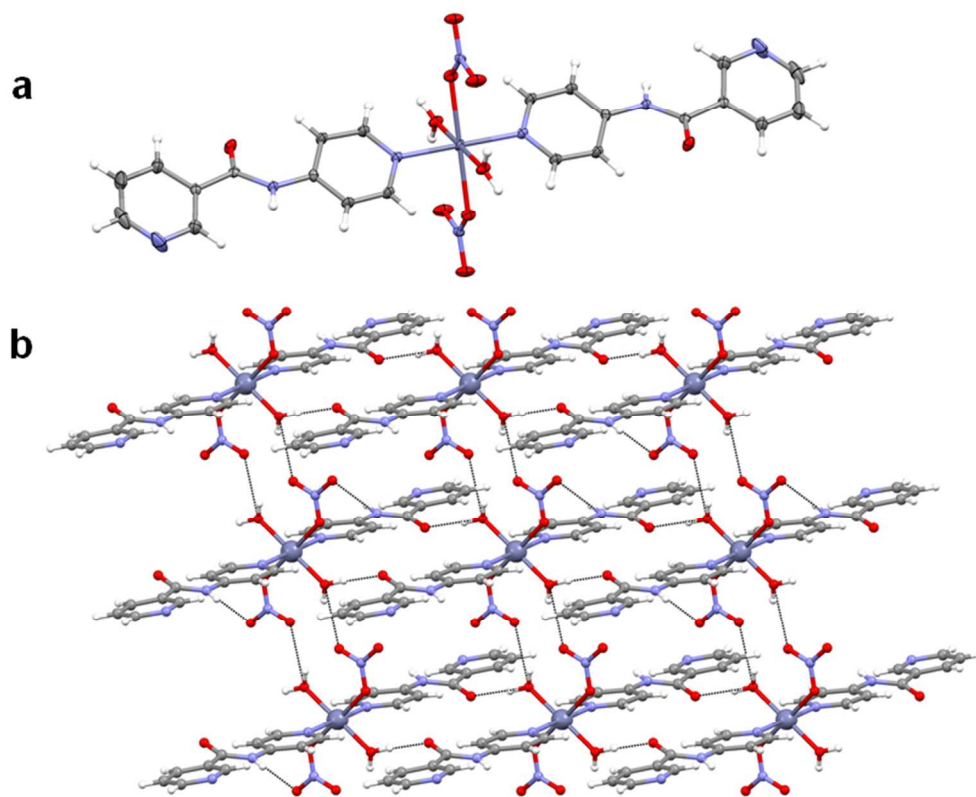
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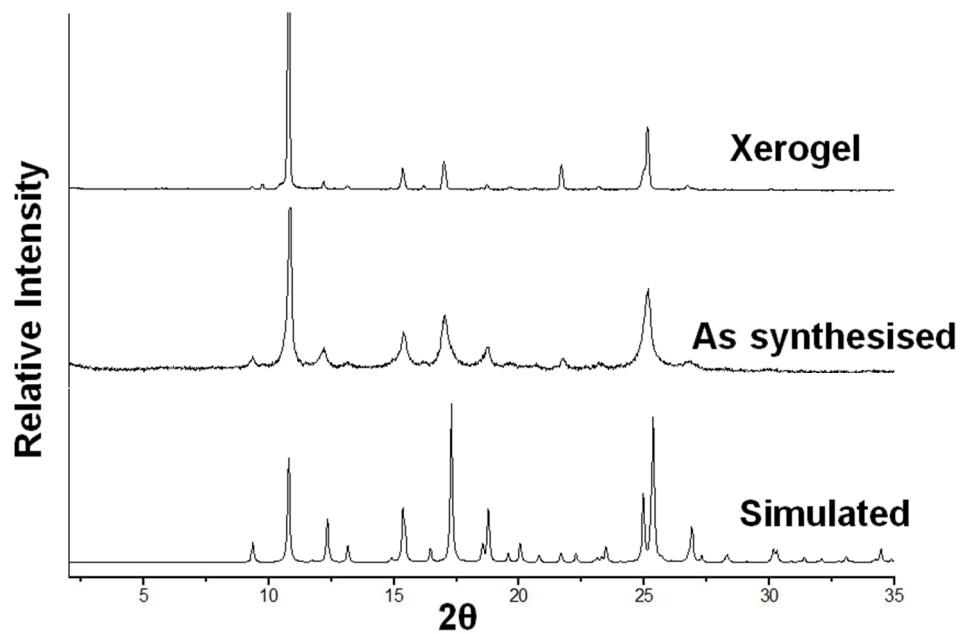
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