# Dalton Transactions

# PAPER

# **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Dalton Trans., 2013, 42, 5818

Received 13th November 2012, Accepted 5th February 2013

www.rsc.org/dalton

DOI: 10.1039/c3dt32710h

# Introduction

The design of efficient sulphate selective receptors is important due to their biological and environmental significance.<sup>1–3</sup> Researchers have developed various neutral receptors with amide/urea/pyrrole functionalities for the recognition of sulphate.<sup>4–13</sup> Cationic receptors such as triazolium, imidazolium, protonated Schiff base macrocycles *etc.* are also popular for recognition of sulphate.<sup>14–16</sup> However, the efficient binding and separation of sulphate from aqueous medium is still challenging because of its larger size, diffusive nature, existence of different charge states (SO<sub>4</sub><sup>2–</sup> and HSO<sub>4</sub><sup>–</sup>) in physiological pH and high hydration energy ( $\Delta G_h = -1080$  kJ mol<sup>–1</sup>).<sup>17,18</sup> One of

# Selective recognition of sulphate in a Cu(II) assisted 1D polymer of a simple pentafluorophenyl substituted pyridyl-urea *via* second sphere coordination†

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A pentafluorophenyl ( $-C_6F_5$ ) substituted 3-pyridyl urea, L<sup>1</sup>, is explored extensively to demonstrate  $SO_4^{2-}$ binding exclusively via second sphere coordination in the cavity of a 1D polymeric self-assembly of L<sup>1</sup>, selectively assisted by Cu<sup>2+</sup>. A single crystal X-ray diffraction study depicts  $SO_4^{2-}$  encapsulation in the  $C_2$ symmetric cleft via nine hydrogen bonding interactions contributed by eight urea protons of four L<sup>1</sup> moieties in  $[CuL_4^1(DMF)_2]SO_4$  (1). To revalidate the importance of  $Cu^{2+}$  selective anion coordination via exclusive second sphere coordination, a complex of  $L^1$  and  $Cu(NO_3)_2$ , *i.e.*  $[CuL_4^1(H_2O)_2](NO_3)_2$  (2), is also isolated and characterized by a single crystal X-ray diffraction study. When  $SO_4^{2-}$  salts of different metal ions such as  $Co^{2+}/Ni^{2+}$  are employed, the first sphere coordination of  $SO_4^{2-}$  is observed in cases of complexes [CoL<sup>1</sup><sub>3</sub>(DMF)<sub>2</sub>SO<sub>4</sub>] (3) and [NiL<sup>1</sup><sub>3</sub>(DMF)<sub>2</sub>SO<sub>4</sub>] (4) respectively. These results clearly suggest the importance of Cu<sup>2+</sup> towards anion recognition via purely second sphere coordination in the case of complexes 1 and 2. To understand the importance of  $(-C_6F_5)$  substitution in the design of L<sup>1</sup> towards such recognition of  $SO_4^{2-}$  in 1, the phenyl (– $C_6H_5$ ) analogue of L<sup>1</sup>, *i.e.* L<sup>2</sup>, is allowed to complex with the  $SO_4^{2-}$ salt of Cu<sup>2+</sup>. Interestingly,  $L^2$  shows first sphere SO<sub>4</sub><sup>2-</sup> coordination in the complex [CuL<sup>2</sup><sub>2</sub>(DMF)- $(H_2O)_2SO_4$ ] (5). Solution state UV-Vis experiments of L<sup>1</sup> with various copper salts such as Cu(ClO<sub>4</sub>)<sub>2</sub>, CuSO<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub> and CuBr<sub>2</sub> in DMF show the formation of a binary complex corresponding to 1. Further,  $Cu^{2+}$  selective second sphere coordination of  $SO_4^{2-}$  in solution is also demonstrated by UV-Vis studies of complexes isolated from the mixtures of various  $Cu^{2+}$  salts and/or  $SO_4^{2-}$  salts of different metal ions.

> the successful strategies to overcome some of the above difficulties is the recognition of sulphate by metal ion templated self assemblies that can completely encapsulate the anionic guest from the solvent sphere.19,20 For instance, Lehn,<sup>21</sup> Loeb,<sup>22,23</sup> Custelcean,<sup>24,25</sup> Dastidar,<sup>26–29</sup> and others<sup>30-37</sup> have demonstrated the selective binding of SO<sub>4</sub><sup>2-</sup> in the cavity of respective metal ion assisted self-assemblies using various monomeric units such as linear tris-bipyridyl, n-butyl urea functionalised isoquinoline, tren based tripodal pyridyl urea and linear bis-pyridyl urea/amide. Very recently, Custelcean et al. have shown the selective binding of tetrahedral oxyanions in an M<sub>4</sub>L<sub>6</sub> cage.<sup>38,39</sup> Further, Wu et al. have shown SO<sub>4</sub><sup>2-</sup> encapsulation in the cavity of the Cu<sup>2+</sup> assisted assembly of naphthyl substituted monopyridyl urea.<sup>40</sup> But the phenomenon of selective SO4<sup>2-</sup> separation via metal ion templated self-assembly from the aqueous mixtures of different inorganic salts has not been explored much. Herein, we demonstrate the effect of pentafluorophenyl vs. phenyl substitutions in simple 3-pyridyl urea based monomeric units  $(L^1 \text{ and } L^2)$  towards the second sphere recognition of SO<sub>4</sub><sup>2-</sup> via the  $Cu^{2+}$  assisted self-assembly of  $L^1 \nu s$ . first sphere coordination

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<sup>†</sup>Electronic supplementary information (ESI) available: NMR, ESI-MS, FT-IR, PXRD, UV/Vis experiment results, and X-ray crystallographic details. CCDC 889000, 889001, 889002, 889003, 889004 and 889005. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32710h

of SO<sub>4</sub><sup>2-</sup> to the metal centre in the case of L<sup>2</sup>. Further, we show the selectivity of SO<sub>4</sub><sup>2-</sup> over other anions (NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>) and Cu<sup>2+</sup> over other metal ions (Co<sup>2+</sup>/Ni<sup>2+</sup>/Zn<sup>2+</sup>) towards selective SO<sub>4</sub><sup>2-</sup> recognition *via* the formation of a 1D polymeric structure. To the best of our knowledge this represents the first example of Cu<sup>2+</sup> assisted self-assembly of L<sup>1</sup> towards the formation of a SO<sub>4</sub><sup>2-</sup> encapsulated 1D polymer from a mixture of multiple components (Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>).

# **Results and discussion**

#### Synthesis

In the case of metal ion templated self-assembly towards recognition of anions, ligands should consist of a metal binding site and anion binding functionalities, either separated by a spacer or integrated into one unit. The designing principle of  $L^1$  and  $L^2$  is as follows: (i) pyridine is a mono-dentate ligand and can coordinate to the metal centre with appropriate functionality and orientation; (ii) pentafluorophenyl substituted urea can act as a strong H-bond donor towards anions especially tetrahedral oxyanions;<sup>8,41</sup> (iii) to understand the importance of the electron withdrawing pentafluorophenyl substituent, the phenyl substituted analogue of  $L^1$ , *i.e.*  $L^2$ , is also synthesized. The syntheses of  $L^1$  and  $L^2$  are accomplished by a simple one step reaction with 3-amino pyridine and pentafluorophenylisocyanate or phenylisocyanate respectively, in dry DCM, in good yield (Scheme 1).

#### Single crystal X-ray study

Second sphere  $SO_4^{2-}$  coordination by  $L^1$  and  $Cu^{2+}$  assembly. Single crystals of  $L^1$ , suitable for X-ray diffraction studies, were obtained upon slow evaporation from a DMF solution of  $L^1$  at RT (Fig. 1S, ESI<sup>†</sup>). Further complexation studies were carried out using single crystals of  $L^1$ . Our choice of metal ion is  $Cu^{2+}$ because it can be easily coordinated with the pyridyl centre of the ligand to form an assembly that can favour anion recognition via second sphere coordination with the urea moieties. We attempted to isolate the single crystals of different Cu<sup>2+</sup> salts such as CuSO<sub>4</sub>, Cu(ClO<sub>4</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub> and CuBr<sub>2</sub> suitable for X-ray diffraction studies. However, we were only able to isolate the single crystals of complexes of L1 with  $CuSO_4$  and  $Cu(NO_3)_2$  as  $[CuL_4^1(DMF)_2]SO_4$ , 1 and  $[CuL_{4}^{1}(H_{2}O)_{2}](NO_{3})_{2}$ , 2 respectively. Single crystals of 1 suitable for X-ray analysis were obtained upon slow evaporation of a DMF-H<sub>2</sub>O (4:1) solution of  $L^1$  and CuSO<sub>4</sub> at RT. The crystal structure of 1 shows that the  $Cu^{2+}$  is coordinated by four L<sup>1</sup> and two DMF molecules trans to each other in a distorted octahedral arrangement, thus forming two oppositely located inversion-related C2-symmetric clefts. Two molecules of the  $Cu^{2+}$  complex are aligned along the C<sub>2</sub>-axis to create a cavity that encapsulates a  $SO_4^{2-}$  ion in its centre (Fig. 1a). The bond distance of Cu<sup>2+</sup> to all four coordinated pyridine N atoms of L<sup>1</sup> is 2.05 Å, whereas the Cu<sup>2+</sup>...O bond distance (Cu<sup>2+</sup> and DMF coordination) is 2.50 Å (Table 4S, ESI<sup>+</sup>). The fluorine substitution on the phenyl ring of L<sup>1</sup> enhances the electron withdrawing capability, thus urea N-H can act as a better H-bond donor towards anions. All the four urea arms within a capsule participate in hydrogen bonding interactions with the encapsulated  $SO_4^{2-}$ . Thus there are a total of nine hydrogen bonding interactions between eight NH groups of the four L<sup>1</sup> moieties and four O atoms of one  $SO_4^{2-}$  ion (Fig. 1b). Two oxygen atoms, O1 and O3, accept three hydrogen bonds each, whereas the other oxygen atoms, O2 and O4, accept two and one hydrogen bond from the urea proton of  $L^1$  respectively (Table 3S, ESI<sup>+</sup>). A correlation of N-H···O angles vs. H···O distances (Fig. 2) shows that all the nine contacts fall within the strong hydrogen bonding region (*i.e.*,  $d_{H\dots O} < 2.5$  Å and  $d_{N\dots O} < 3.2$  Å). Out of nine contacts only one contact, N7-H7...O1, has an N–H…O angle <140°, *i.e.* 128°, with a  $d_{N...O}$  value of 2.97 Å. Interestingly, this SO<sub>4</sub><sup>2-</sup> encapsulated capsular assembly further extends into an infinite 1D chain (Fig. 1a) assisted by two weak



**Scheme 1** Schematic representation of synthesis of pentafluorophenyl substituted 3-pyridyl urea (**L**<sup>1</sup>) and phenyl substituted 3-pyridyl urea (**L**<sup>2</sup>).



**Fig. 1** (a) Second sphere recognition of  $SO_4^{2-}$  in a  $Cu^{2+}$  assisted 1D polymer  $[CuL_4^1(DMF)_2] SO_4$ , **1**. (b) Close view of  $SO_4^{2-}$  coordination by four urea groups in the assembly in **1**.



Fig. 2 The scatter plot of N–H···O angle vs. H···O distance for the hydrogen bonds in complex 1.



Fig. 3 Comparison of the PXRD pattern of complex 1: (a) simulated and (b) experimental.

C-F···H-C interactions (C53-F19···H44A-C44 and C33-F14···H2-C2) (Fig. 2S, ESI<sup>+</sup>).

It is important to mention here that Wu et al. have demonstrated the encapsulation of  $SO_4^{2-}$  in the  $C_3$  symmetric cavity of the Cu2+ assisted assembly of six naphthyl substituted monopyridyl urea ligands,<sup>40</sup> whereas Steed et al. have demonstrated the cleft binding of  $SO_4^{2-}$  with *p*-methylphenyl substituted 3-pyridyl urea by the metal ion template self-assembly.42 Again, the FT-IR study of the isolated mass, obtained upon the reaction of L<sup>1</sup> and CuSO<sub>4</sub> in a DMF-H<sub>2</sub>O binary solvent system, exhibits a strong peak at 1109 cm<sup>-1</sup> (symmetric stretching frequencies of  $SO_4^{2-}$ ). Thus, the FT-IR study of the isolated mass clearly indicates the formation of 1 (Fig. 25S, ESI<sup>+</sup>). Further, in order to check the bulk purity of the isolated mass, we have undertaken the PXRD experiments. The simulated powder X-ray pattern of 1 obtained from single crystal X-ray data and the experimental powder X-ray of isolated mass show similar patterns that suggests the bulk purity of the isolated mass of 1 (Fig. 3).

Second sphere NO<sub>3</sub><sup>-</sup> coordination by L<sup>1</sup> and Cu<sup>2+</sup> assembly. Crystals of  $[CuL_4^1(H_2O)_2](NO_3)_2$ , 2 suitable for single crystal X-ray analysis were obtained from L<sup>1</sup> and Cu(NO<sub>3</sub>)<sub>2</sub> following similar conditions as in 1. The crystal structure of 2 shows that the Cu<sup>2+</sup> is coordinated by four L<sup>1</sup> molecules and two H<sub>2</sub>O



**Fig. 4** (a) Single crystal X-ray structures of complex  $[CuL_4^1(H_2O)_2](NO_3)_2$ , **2** showing cleft binding of  $NO_3^-$  via second sphere coordination. (b) Close view of  $NO_3^-$  coordination in the assembly of **2**.

molecules *trans* to each other in a  $C_4$  symmetric four bladed propeller shaped distorted octahedral arrangement (Fig. 4a). The Cu<sup>2+</sup> centre is coordinated to the pyridine N atom of four  $L^1$  with the bond distance of 2.05 Å, whereas the  $Cu^{2+}\cdots O$ bond distances (Cu<sup>2+</sup> and H<sub>2</sub>O coordination) are 2.28 and 2.42 Å (Table 7S, ESI<sup>+</sup>). Each NO<sub>3</sub><sup>-</sup> ion is in five hydrogen bonding interactions in the cleft of the metal organic coordination polymer: four from urea N-H of two  $L^1$  of two  $Cu^{2+}$ assemblies and one from the lattice water molecule. Two oxygen atoms, O6 and O7, accept two hydrogen bonds each, whereas the other oxygen atom, O5, accepts one hydrogen bond (Fig. 4b). A correlation of N-H-O angles vs. H-O distances (Fig. 3S, ESI<sup>†</sup>) shows that all the contacts fall within the strong hydrogen bonding region (*i.e.*,  $d_{H...O} < 2.5$  Å and  $d_{N...O} <$ 3.2 Å). Out of five contacts only one contact, N1-H1...O6, has an N-H···O angle <140°, *i.e.* 128°, with a  $d_{\text{N···O}}$  value of 3.02 Å. Though the second sphere recognition of NO<sub>3</sub><sup>-</sup> is observed, no such anion encapsulated 1D polymeric self assembly is observed as in the case of 1. These results show the importance of  $SO_4^{2-}$  for such an assembly in complex 1. Thus, the 1D-polymeric assembly in 1 could be attributed to the tetrahedral shape, different size and basicity of  $SO_4^{2-}$  compared to  $NO_3^{-}$ .

First sphere  $SO_4^{2-}$  coordination in L<sup>1</sup> and  $Co^{2+}/Ni^{2+}$  assemblies. To understand the coordination of  $L^1$  with the SO<sub>4</sub><sup>2-</sup> salts of other metal ions such as Co<sup>2+</sup>/Ni<sup>2+</sup>, we have isolated single crystals [CoL<sup>1</sup><sub>3</sub>(DMF)<sub>2</sub>SO<sub>4</sub>], 3 and [NiL<sup>1</sup><sub>3</sub>(DMF)<sub>2</sub>SO<sub>4</sub>], 4 suitable for X-ray diffraction studies by reacting L<sup>1</sup> with CoSO<sub>4</sub> and NiSO<sub>4</sub>. The crystal structures analyses of 3 and 4 show that the metal centre is coordinated by three L<sup>1</sup> moieties, one O-atom of SO<sub>4</sub><sup>2-</sup> and two DMF molecules *trans* to each other in a distorted octahedral arrangement in each case (Fig. 5a and 5b). In both these complexes  $SO_4^{2-}$  is directly coordinated to the metal centres (i.e. first sphere coordination). Further, each  $SO_4^{2-}$  ion is in seven hydrogen bonding interactions: six from the N–H protons of three L<sup>1</sup> units contributed from three different Co<sup>2+</sup>/Ni<sup>2+</sup> assemblies and the remaining one from the lattice water molecule (Fig. 5c and 5d). The metal ion-ligand (Table 1)/sulphate-ligand bond distances (Tables 9S and 11S, ESI<sup>†</sup>) of both the complexes are quite similar, which suggests the isostructural nature of these two complexes. The phenomenon of one-dimensionally developed complex formation in



**Fig. 5** Single crystal X-ray structures of complex  $[CoL_{3}^{1}(DMF)_{2}SO_{4}]$ , **3** (a), and  $[NiL_{3}^{1}(DMF)_{2}SO_{4}]$ , **4** (b) showing first sphere coordination of  $SO_{4}^{2-}$ . Close view of  $SO_{4}^{2-}$  coordination in the assembly in **3** (c) and in **4** (d).

Table 1 Metal ligand bond distances in complexes 3 and 4

Atoms	Distance (Å)	Atoms	Distance (Å)
Ni1…O5 (DMF)	2.07	Co1…O4 (DMF)	2.09
Ni1…O6 (DMF)	2.06	Co1…O5 (DMF)	2.10
Ni1…O1 (SO <sub>4</sub> )	2.09	$Co1 \cdots O6 (SO_4)$	2.10
$Ni1 \cdots N1 (L^1)$	2.13	$Co1 \cdots N4 (L^1)$	2.18
Ni1 $\cdots$ N2 $(L^1)$	2.14	$Co1 \cdots N5 (L^1)$	2.18
Ni1 $\cdots$ N3 $(L^1)$	2.13	$Co1 \cdots N6 (L^1)$	2.19

the case of  $L^1$  and  $CuSO_4$  (1) is not observed in the Co and Ni systems (3 and 4). Thus, the first sphere coordination of  $SO_4^{2-}$ in both complexes 3 and 4 further justifies the importance of  $Cu^{2+}$  for such an assembly in complex **1**. This can be attributed to the more susceptible Jahn-Teller distortion effect of Cu<sup>2+</sup> compared to Co<sup>2+</sup> and Ni<sup>2+</sup> ions. Again, the FT-IR study of the isolated masses, obtained upon the reaction of L<sup>1</sup> and CoSO<sub>4</sub>/ NiSO4 in a DMF-H2O binary solvent system, indicates strong peaks at 1113 cm<sup>-1</sup> and 1117 cm<sup>-1</sup> (symmetric stretching frequencies of SO<sub>4</sub><sup>2-</sup>) respectively. Thus, the FT-IR study of both the isolated masses clearly indicates the formation of 3 and 4 respectively (Fig. 17S and 18S, ESI<sup>+</sup>). Further, in order to check the bulk purity of the isolated masses, we have undertaken the PXRD experiments for comparison with the simulated pattern obtained from the corresponding single crystal X-ray data (Fig. 4S and 5S, ESI<sup>+</sup>).

First sphere  $SO_4^{2-}$  coordination in  $L^2$  and  $Cu^{2+}$  assembly. On the other hand, the phenyl analogue of  $L^1$ , *i.e.*  $L^2$ , was synthesised in order to understand the importance of fluorine substituted phenyl towards the formation of organized self-assembly structure. Single crystals of  $[CuL^2_2(DMF)(H_2O)_2SO_4]$ , 5 suitable for X-ray analysis were obtained following the same procedure as in complex 1. The crystal structure of 5 also shows that  $SO_4^{2-}$  is directly coordinated with the  $Cu^{2+}$  centre along with the two pyridyl units of two  $L^2$  molecules, two water molecules and one DMF molecule in a distorted octahedral fashion (Fig. 6a). The coordinated  $SO_4^{2-}$  is also hydrogen bonded with the urea N-H groups of other  $L^2$  molecies in a chaotic fashion (Fig. 6b). Each  $SO_4^{2-}$  ion is in six hydrogen



**Fig. 6** (a) Single crystal X-ray structures of complex  $[CuL^2_2(DMF)(H_2O)_2SO_4]$ , **5** showing first sphere coordination of  $SO_4^{2-}$ . (b) Close view of  $SO_4^{2-}$  coordination in the assembly of **5**.

bonding interactions: four from the N-H protons of two L<sup>2</sup> units are contributed from two different Cu2+ assemblies and the remaining two are from water molecules coordinated to the other Cu<sup>2+</sup> assembly. Thus, in this case, first sphere coordination of SO4<sup>2-</sup> with the Cu<sup>2+</sup> is observed instead of second sphere  $SO_4^{2-}$  recognition as in the case of 1. The  $Cu^{2+}$  and  $SO_4^{2-}$  assisted self-assembly phenomenon in the case of L<sup>1</sup> could be attributed to the electron withdrawing nature of the pentafluorophenyl group that enhances the acidic nature of urea N-H protons as well as facilitates the intermolecular C-F···H-C interactions. Of course, there could be pivotal roles of both  $Cu^{2+}$  and  $SO_4^{2-}$  for such organized assembly. Again, the FT-IR study of the isolated mass, obtained upon the reaction of L<sup>2</sup> and CuSO<sub>4</sub> in a DMF-H<sub>2</sub>O binary solvent system, exhibits a strong peak at 1097 cm<sup>-1</sup> (symmetric stretching frequencies of SO<sub>4</sub><sup>2-</sup>). Thus, the FT-IR study of the isolated mass clearly indicates the formation of 5 (Fig. 19S, ESI<sup>†</sup>). Further, in order to check the bulk purity of the isolated mass, we have undertaken the PXRD experiments. The simulated powder X-ray pattern of 5 obtained from single crystal X-ray data and the experimental powder X-ray of the isolated mass show similar patterns (Fig. 6S, ESI<sup>+</sup>).

#### Selectivity studies

Solution state selectivity towards Cu<sup>2+</sup> assisted SO<sub>4</sub><sup>2-</sup> recognition. Solution state UV-Vis experiments were carried out with  $L^1$  and various copper salts such as  $Cu(ClO_4)_2$ ,  $CuSO_4$ ,  $Cu(NO_3)_2$ ,  $CuCl_2$  and  $CuBr_2$  upon addition of a 3:1(v/v) equimolar  $(10^{-3} \text{ M})$  solution of  $L^1$  and the respective salts of  $Cu^{2+}$ in DMF in order to follow the formation of the selective binary complex (Fig. 7). UV/Vis spectra show broad absorption bands  $(\lambda_{\text{max}})$  at 774, 753, 764, 868 and 890 nm respectively for L<sup>1</sup> with the above various Cu2+ salts corresponding to the d-d transitions. In  $SO_4^{2-}$  and  $NO_3^{-}$  complexes blue shifted absorption spectra whereas in Cl<sup>-</sup> and Br<sup>-</sup> complexes red shifted absorption spectra compared to the absorption band at 774 nm for L<sup>1</sup> and Cu(ClO<sub>4</sub>)<sub>2</sub> under the same experimental conditions are observed. The mixture of L<sup>1</sup> and all these Cu<sup>2+</sup> salts also shows an absorption band  $(\lambda_{max})$  at 753 nm as observed in the case of  $L^1$  only with CuSO<sub>4</sub> which suggests the selectivity towards SO<sub>4</sub><sup>2-</sup> in the solution state in the presence of other anions.

Again, solution state UV-Vis experiments with  $L^1$  and the sulphate salts of different transition metal ions such as CuSO<sub>4</sub>,



**Fig. 7** UV/Vis spectra upon addition of  $L^1$  (1 × 10<sup>-3</sup> M) and different Cu<sup>2+</sup> salts solution (1 × 10<sup>-3</sup> M) at 3 : 1(v/v) in DMF at 298 K. The double headed arrow shows the  $\lambda_{max}$  positions.



**Fig. 8** UV/Vis spectra upon addition of  $L^1$  ( $1 \times 10^{-3}$  M) and  $SO_4^{2-}$  salts of different metal ions solution ( $1 \times 10^{-3}$  M) at 3 : 1(v/v) in DMF at 298 K. The inset figure shows the close view of UV-Vis spectra in cases of  $L^1$  and CoSO<sub>4</sub>/NiSO<sub>4</sub>. The double headed arrow shows the  $\lambda_{max}$  positions.

CoSO<sub>4</sub> and NiSO<sub>4</sub> were also carried out upon addition of a 3 : 1 (v/v) equimolar (10<sup>-3</sup> M) solution of L<sup>1</sup> and the respective salts of SO<sub>4</sub><sup>2-</sup> in DMF. Although a sharp absorption peak at 753 nm is observed in the case of L<sup>1</sup> and CuSO<sub>4</sub>, low intensity absorption peaks at 531 nm for CoSO<sub>4</sub> and 403 nm and 675 nm peaks for NiSO<sub>4</sub> are observed (Fig. 8). Here it is important to mention that the absorption peaks of the isolated complexes of **1**, 3 and 4 are similar as we observed in the case of *in situ* complexation of L<sup>1</sup> and CuSO<sub>4</sub>/CoSO<sub>4</sub>/NiSO<sub>4</sub> as mentioned above. When the UV-Vis experiment is carried out in the case of L<sup>1</sup> with the mixtures of CuSO<sub>4</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub> and ZnSO<sub>4</sub>, an absorption band ( $\lambda_{max}$ ) at 753 nm is observed. This result suggests the selectivity of Cu<sup>2+</sup> towards the formation of complex **1** in the solution in the presence of other metal ions such as Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>.

Selectivity studies by isolating solid masses from different mixtures. The selective formation of a binary complex 1 in the presence of other anions was also established by isolating the product of 1' from the reaction of  $L^1$  with different anionic salts of  $Cu^{2+}$  in an aqueous DMF binary solvent system



**Scheme 2** Selective formation of complex **1** from (a) different anionic salts of  $Cu^{2+}$ , (b) different metal salts of  $SO_4^{2-}$  in aqueous medium and (c) all the salts used in paths a and b together.



Fig. 9 Comparison of the PXRD pattern of complex 1 (simulated, blue) with the experimental PXRD of 1' (wine), 1'' (green) and 1''' (purple).

following path a (Scheme 2). Further the selectivity experiment was also carried out following path b (Scheme 2) where complex 1" was isolated in the presence of various metal sulphate salts (CuSO<sub>4</sub>, NiSO<sub>4</sub>, CoSO<sub>4</sub> and ZnSO<sub>4</sub>) in aqueous medium. We also isolated complex 1" from the mixtures of all the salts used in paths a and b together following path c. The blue single crystal isolated 1', 1" and 1" from the above three approaches are characterised by single crystal XRD, powder XRD and UV/Vis spectroscopic studies. Single crystals of the isolated masses suitable for X-ray diffraction analysis are obtained upon slow evaporation of the DMF solution of the isolated masses. The crystal structure parameters of the crystals obtained from 1', 1" and 1" are exactly the same as 1. Thus, the X-ray structure confirms the selective formation of  $Cu^{2+}$  assisted  $SO_4^{2-}$  encapsulated 1D polymer 1. In order to check the bulk purity of the isolated masses (1', 1'' and 1'''), we have undertaken the PXRD experiments. The results show that the simulated powder X-ray patterns of 1 and the experimental powder X-ray patterns of the isolated complexes (1', 1" and 1"") are similar in nature (Fig. 9). Thus, these suggest the bulk



Fig. 10 UV/Vis spectra of 1 and isolated complexes (1', 1" and 1"") each at  ${\sim}10^{-3}$  M in DMF at 298 K.

purity of the isolated complexes obtained from various mixtures. Again the solution state UV-Vis spectroscopic studies of **1**, **1'**, **1''** and **1'''** show absorption maxima  $\lambda_{max}$  at 752 ± 3 nm with comparable  $\varepsilon$  values (235.08, 219.50, 221.54 and 225.90 M<sup>-1</sup> cm<sup>-1</sup> respectively) (Fig. 10). Thus, these studies clearly demonstrate the selective formation of Cu<sup>2+</sup> assisted SO<sub>4</sub><sup>2-</sup> encapsulation *via* a 1D polymer of L<sup>1</sup>.

## Conclusion

In summary, we have demonstrated  $\text{Cu}^{2+}$  templated  $\text{SO}_4^{2-}$  recognition in a 1D polymer by self-assembly of a new pentafluorophenyl substituted pyridyl urea ligand, whereas the phenyl analogue of a similar monopyridyl urea failed to do so. Selective formation of a  $\text{SO}_4^{2-}$  encapsulated 1D polymer has immense potential utility in the field of  $\text{SO}_4^{2-}$  separation in water purification and nuclear waste treatment. Further, this approach of selective formation of a  $\text{Cu}^{2+}$  assisted  $\text{SO}_4^{2-}$  encapsulated 1D complex from a mixture of several subcomponents in aqueous medium could be extended in the case of selective recognition of other anions of environmental concern.

#### Experimental

#### Materials

NMR solvents (DMSO- $d_6$ ), 3-aminopyridine, pentafluorophenylisocyanate, and phenylisocyanate were purchased from Sigma-Aldrich, USA and were used without further purification. CuSO<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub> and ZnSO<sub>4</sub> were purchased from Merck. Chloroform, methanol, dimethylsulfoxide (DMSO), and dimethylformamide (DMF) were purchased from Spectrochem, Ltd, India.

#### Instrumentation

Electron-spray ionisation mass spectroscopy (ESI-MS) experiments were carried out on Water's Q to F Model YA 263 spectrometer in positive ion ESI mode. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker DPX 500 FT-NMR spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C-NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). FT-IR was recorded on a SHIMADZU FTIR-8400S infrared spectrophotometer with KBr pellets. X-ray powder patterns were collected on a Bruker D8 SWAX X-ray diffractometer (CuK $\alpha$  = 1.5418 Å) with a scan rate of 0.3 min per degree in the 5° < 2 $\theta$  < 55° range with a step size of 0.05°. The absorption spectra were recorded with a Perkin Elmer Lambda 950 UV-VIS-NIR scanning spectrophotometer at 298 K.

#### X-ray crystallographic refinement details

Crystals suitable for single crystal X-ray diffraction studies were selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystal of L<sup>1</sup> and complexes 1–4 were collected using MoK $\alpha$  ( $\lambda$  = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with a CCD area detector at 100 K. The data integration and reduction were processed with SAINT43 software provided with the software package of SMART APEX II. An empirical absorption correction was applied to the collected reflections with SADABS.44 The structures were solved by direct methods using SHELXT<sup>45</sup> and were refined on  $F^2$  by the full-matrix least-squares technique using the SHELXL-9746 program package. The nonhydrogen atoms were refined anisotropically till convergence. The hydrogen atoms were geometrically fixed at idealized positions whereas the hydrogen atoms attached to the nitrogen atoms were located from the difference Fourier map and refined isotropically till convergence was attained. Graphics were generated using PLATON<sup>47</sup> and MERCURY 2.3.<sup>48</sup> In the case of complex 1, even though the data were collected at 150 K several times, we were unable to assign electron density for solvent molecules in the unit cell. The routine SQUEEZE was applied to intensities data of complex 1 to take into account the disordered solvent molecules.49 The number of electrons found in the solvent accessible void is close to that expected for one DMF molecule in the unit cell. Since we could not assign a proper disorder model of the pentafluorophenyl ring composed of C43, C50-C54 of complex 1, we isotropically refined disordered carbon atoms C51, C52, C53, and associated fluorine atoms F17, F18 and F19. Similarly, in the case of complex 4, the C47 associated with the lattice solvent molecule is also refined isotropically. The C41, C43 and O16 atoms are disordered at two sites and the occupancy factors are refined using the FVAR command of the SHELXTL program and isotropically refined.

Synthesis of compound  $L^1$ . In a 100 ml round bottomed flask, 3-aminopyridine (470 mg, 5 mmol) was dissolved in 40 ml of dry dichloromethane. The mixture was stirred at 0 °C temperature under a nitrogen atmosphere for 15 min. 0.68 ml (5.2 mmol) of pentafluorophenyl isocyanate was dissolved in another 30 ml of dry DCM and taken in a 50 ml pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring at 0 °C temperature. After the addition, the reaction mixture was stirred at room temperature under a nitrogen atmosphere for another 12 h. The white precipitate was filtered, and washed three times with DCM. Then the precipitate was dried in vacuum to yield the desired product as a white solid (1.4 g, 92%). ESI-MS (+ESI): *m/z* calcd for  $C_{12}H_6F_5N_3O$  [M]<sup>+</sup>, 303.0431, found 303.9330. <sup>1</sup>H-NMR (500 MHz, DMSO-d\_6):  $\delta$  9.29 (s, 1H, -NH), 8.67 (s, 1H, -NH), 8.62 (s, 1H, Ar-H), 8.25 (d, 1H, Ar-H, *J* = 3.5 Hz), 7.92 (d, 1H, Ar-H, *J* = 4.5 & 8.5 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d\_6):  $\delta$  152.66 (-*C*=O), 144.54 (Ar-*C*), 143.86 (Ar-*C*), 142.52 (Ar-*C*), 140.79 (Ar-*C*), 138.67 (Ar-*C*), 136.49 (Ar-*C*), 125.98 (Ar-*C*), 124.05 (Ar-*C*), 114.28 (Ar-*C*).

Synthesis of compound L<sup>2</sup>. In a 100 ml round bottomed flask, 3-aminopyridine (470 mg, 5 mmol) was dissolved in 40 ml of dry dichloromethane. The mixture was stirred at 0 °C temperature under a nitrogen atmosphere for 15 min. 0.558 ml (5.2 mmol) of pentafluorophenyl isocyanate was dissolved in another 30 ml of dry DCM and taken in a 50 ml pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring at 0 °C temperature. After the addition, the reaction mixture was stirred at room temperature under a nitrogen atmosphere for another 12 h. The white precipitate was filtered, and washed three times with DCM. Then the precipitate was dried in vacuum to yield the desired product as a white solid (0.95 g, 89%). ESI-MS (+ESI): m/z calcd for  $C_{12}H_{11}N_3O$  [M]<sup>+</sup>, 213.0902, found 214.1315. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>): δ 8.84 (s, 1H, -NH), 8.79 (s, 1H, -NH), 8.61 (s, 1H, Ar-H), 8.19 (d, 1H, Ar-H, J = 4.5 Hz), 7.95 (d, 1H, Ar-H, J = 8.5 Hz), 7.47 (d, 2H, Ar-H, J = 8.0 Hz), 7.30 (m, 3H, Ar-H), 6.98 (t, 1H, Ar-H, J = 7.5 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>): δ 152.61 (-C=O), 142.87 (Ar-C), 140.10 (Ar-C), 139.44 (Ar-C), 136.46 (Ar-C), 128.83 (Ar-C), 125.21 (Ar-C), 123.62 (Ar-C), 122.14 (Ar-C), 118.45 (Ar-C).

Synthesis of complex 1.  $L^1$  (100 mg, 0.33 mmol) was dissolved in 16 ml of DMF; CuSO<sub>4</sub> (25 mg, 0.1 mmol) solution in 4 ml of H<sub>2</sub>O was added to the stirring solution. The reaction mixture was stirred for another 4 h. The resulting solution was filtered and kept for slow evaporation. Blue crystals suitable for single crystal X-ray diffraction studies were formed after 4–5 days. They were filtered and collected after repeated washing with methanol and characterized by single crystal X-ray diffraction, FT-IR and PXRD (yield: 105 mg, 84%).

Synthesis of complex 2. Complex 2 was synthesised in the same way as described in the case of complex 1 by taking  $L^1$  (100 mg, 0.33 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub> (24 mg, 0.1 mmol) and characterized by single crystal X-ray diffraction, FT-IR and PXRD (yield: 65 mg, 45%).

Synthesis of complex 3. Complex 3 was synthesised in the same way as described in the case of complex 1 by taking  $L^1$  (100 mg, 0.33 mmol) and CoSO<sub>4</sub> (28 mg, 0.1 mmol) and characterized by single crystal X-ray diffraction, FT-IR and PXRD (yield: 93 mg, 62%).

Synthesis of complex 4. Complex 4 was synthesised in the same way as described in the case of complex 1 by taking  $L^1$  (100 mg, 0.33 mmol) and NiSO<sub>4</sub> (26 mg, 0.1 mmol) and characterized by single crystal X-ray diffraction, FT-IR and PXRD (yield: 63 mg, 42%).

Synthesis of complex 5. Complex 5 was synthesised in the same way as described in the case of complex 1 by taking  $L^2$  (70 mg, 0.33 mmol) and CuSO<sub>4</sub> (25 mg, 0.1 mmol) and characterized by single crystal X-ray diffraction, FT-IR and PXRD (yield: 44 mg, 55%).

**Complexation by path a.**  $L^1$  (100 mg, 0.33 mmol) was dissolved in 16 ml of DMF; a mixture of Cu<sup>2+</sup> salts (CuSO<sub>4</sub>, Cu-(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub> and CuBr<sub>2</sub> each of 0.1 mmol) in 4 ml H<sub>2</sub>O was added to the solution. Then the reaction mixture was stirred for another 4 h. The resulting solution was filtered and kept for slow evaporation. Blue crystalline solids (1') were formed after 4–5 days. They were filtered and collected after repeated washing with methanol and characterized by UV-Vis, FT-IR and PXRD (yield: 96 mg, 77%).

**Complexation by path b.**  $L^1$  (100 mg, 0.33 mmol) was dissolved in 16 ml of DMF; a mixture of  $SO_4^{2-}$  salts (CuSO<sub>4</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub> and ZnSO<sub>4</sub> each of 0.1 mmol) in 4 ml H<sub>2</sub>O was added to the solution. Then the reaction mixture was stirred for another 4 h. The resulting solution was filtered and kept for slow evaporation. Blue crystalline solids (1") were formed after 4–5 days. They were filtered and collected after repeated washing with methanol and characterized by UV/Vis, FT-IR and PXRD (yield: 89 mg, 71%).

**Complexation by path c.**  $L^1$  (100 mg, 0.33 mmol) was dissolved in 16 ml of DMF; a mixture of all the salts used in paths a and b (CuSO<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub> and ZnSO<sub>4</sub> each of 0.1 mmol) in 4 ml H<sub>2</sub>O was added to the solution. Then the reaction mixture was stirred for another 4 h. The resulting solution was filtered and kept for slow evaporation. Blue crystalline solids (1"') were formed after 4–5 days. They were filtered and collected after repeated washing with methanol and characterized by UV/Vis, FT-IR and PXRD (yield: 93 mg, 75%).

## Acknowledgements

BA acknowledges CSIR for an SRF. PG gratefully thanks DST, India for financial support through a Swarnajayanti Fellowship. X-ray diffraction of complexes was performed in the DST funded National Single Crystal X-ray Facility at the Department of Inorganic Chemistry, IACS.

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