

Simultaneous anion and cation binding by a simple polymer-bound ureidopyridyl ligand

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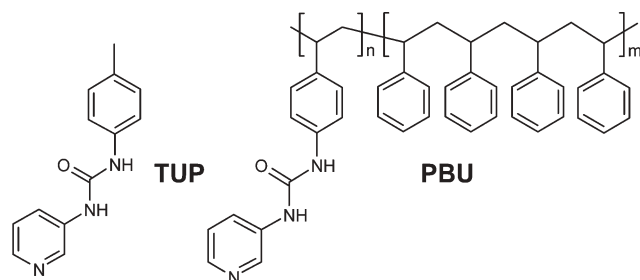
Received (in Columbia, MO, USA) 28th September 2005, Accepted 20th October 2005

First published as an Advance Article on the web 25th November 2005

DOI: 10.1039/b513820e

A polymer-supported ligand capable of simultaneous anion and cation binding is reported along with X-ray crystallographic data showing potential binding modes.

The use of ion-selective resins in ion exchange applications is commonplace,^{1,2} for example in water softening. In applications where the objective is not ion exchange but ion sequestration, however, the process does not involve exchange of one anion or cation for another but the long term binding of a target ion such as a heavy metal ion pollutant to the resin. Under these circumstances charge neutrality considerations necessitate simultaneous binding of an associated counter-anion for a neutral resin. Such neutral (non-ionisable) resins have the potential advantage that no exchange ion is released, allowing applications where rigorous purification is required. In order to be truly selective such a resin must therefore consider the binding and sequestration of an overall neutral *ion pair* rather than the individual target cation or anion. The potential selectivity of neutral ion receptors was highlighted by Reinhoudt *et al.*^{3,4} who have carried out a large body of work on neutral urea-based molecular organic receptors.⁵ Very recently Loeb *et al.*^{6–8} and ourselves^{9–12} have reported a range of anion-binding coordination complexes in which a transition metal cation and conjugate anion, complex with ureido ligands such as **TUP**, which is capable of hydrogen bonding to the anion and coordinating to the metal. The concept mirrors the discrete molecular salt-binding hosts reported by Smith *et al.*^{13,14} Solid state studies of closely related ureidopyridyl complexes have also been reported,¹⁵ and we have shown using neutron diffraction that such ligands can be used to host a remarkable water square.¹⁶ We now report preliminary results of our work on the preparation and salt-binding behaviour of a polymer-bound **TUP** analogue, potentially suitable for heterogeneous salt extraction applications, together with results of model studies using **TUP** itself.



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The orange, polymer-bound ureidopyridine (**PBU**) was prepared from yellow commercial isocyanate “amine scavenger” resin (Aldrich Chemical Co. polystyrene cross-linked with 2% DVB 200–400 mesh, *ca.* 2.0 mmol NCO per gram of resin) by heterogeneous reaction with 3-aminopyridine in dichloromethane suspension in a fashion analogous to the preparation of **TUP**.¹⁰ Complete reaction was verified by ¹³C CP-MAS NMR spectroscopy and solid state IR spectroscopy. The IR spectrum of the **PBU** showed the complete disappearance of the characteristic NCO stretch at 2262 cm⁻¹ and appearance of NH bands analogous to those observed for **TUP**. Elemental analysis indicated a ratio of *ca.* 4.3 : 1, styrene : **TUP** units (*i.e.* number of units $n \approx m$, in formula), approximately consistent with the ratio of 3.6 : 1 obtained from analysis of the starting isocyanate polymer. The **PBU** was exposed to increasing concentrations of copper(II) chloride, copper(II) nitrate, cobalt(II) nitrate and chromium(III) nitrate under conditions of short and prolonged stirring in methanol suspension and under reflux for 24 h. In each case metal salt uptake was observed with the **PBU** taking on the characteristic colour of the metal ion (green for Cu(II), pink for Co(II) and yellowish brown for Cr(III)). The polymer products were recovered by filtration, dried in a vacuum desiccator and subjected to elemental analysis. Metal salt uptake was apparent from the consistent decrease in the %C and %N for CuCl₂ and then increase in %N for the nitrate salts. In all cases the uptake was most pronounced upon prolonged reflux with the maximum uptake in the presence of *ca.* 20 molar excess of metal salt to **TUP** units. The maximum uptake corresponded to a ratio of 0.5 metal ions to pyridyl units (*i.e.* an ML₂ type complex) for Cu(NO₃)₂ and 0.65 for CuCl₂. Uptake of the inert Cr(III) proved the least efficient with a maximum of 0.27 : 1 while uptake of Co(II) nitrate reached *ca.* 0.3 : 1. Thus the results suggest formation of ML₄ type complexes for Cr(III) and Co(II) and ML₂ species for Cu(II). In all cases, however, uptake is slow presumably due to the relatively low surface area of the polymer. IR spectra of the complexed resin showed little change compared to the free ligand. Similar results were obtained for **TUP** model compounds (*vide infra*).

In order to obtain insight into the possible mode of complexation of metal nitrates with the **PBU** ligand a series of model complexes were prepared by reaction of metal salts with **TUP** in methanol solution in 1 : 1 and 1 : 2 ratios. This resulted in the isolation and characterisation by X-ray crystallography of three complexes [Co(**TUP**)₄(H₂O)₂](NO₃)₂·2MeOH (**1**), [Ni(**TUP**)₄(H₂O)₂](NO₃)₂·2MeOH (**2**) and [Cu(**TUP**)₄(H₂O)₂](NO₃)₂ (**3**) in each case exhibiting a 1 : 4 metal : ligand ratio.† Complexes **1** and **2** are isostructural and in each case the ligands

occur in *cis*-related pairs two above the plane of the metal–nitrogen plane and two below (Fig. 1). The nitrate anions are held by hydrogen bonding between pairs of ligands from *adjacent complexes* and thus each ligand in a particular complex interacts with a different nitrate anion. Hydrogen bonding to nitrate is complex and involves both coordinated water and solvent methanol. Tracing out the motifs there is an unusual $R_2^3(8)$ pattern involving interaction of the urea N(2) to nitrate and N(3) to methanol with the ring completed by the methanol O(7)H to nitrate O(6) interaction. The methanol O(7)H is in fact part of a bifurcated interaction with nitrate O(5). The other side of the nitrate interacts with a ligand on an adjacent complex forming the more conventional $R_2^2(8)$ pattern. The nitrate oxygen atom O(4) also accepts a hydrogen bond from a metal-coordinated water molecule O(3). This interaction is apparently key in determining the structure (*vide infra*). The Co–OH₂ bond length of 2.0929(11) Å is typical and is essentially the same in the nickel homologue.

The structure of the copper(II) analogue, complex **3**, represents a fascinating contrast to **1** and **2** while retaining a similar gross structure (Fig. 2). As a d^9 metal ion copper(II) complexes generally exhibit ground state Jahn–Teller distortions¹⁷ and this effect is manifest in **3** by significant elongation of the Cu–OH₂ bond lengths (2.4522(14) and 2.6039(14) Å) compared to **1** and **2**. This longer, weaker interaction to the aquo ligand allows the water to take the place of the methanol in **1** and **2**. The nitrate anions sit in clefts formed by *intramolecular* pairs of TUP ligands which chelate the anions in a pair of $R_2^2(8)$ motifs giving a discrete “ML₄(NO₃)₂” entity, although N(5)···O(4) at 3.27 Å is long. This double chelation of nitrate is closely reminiscent of a doubled version of

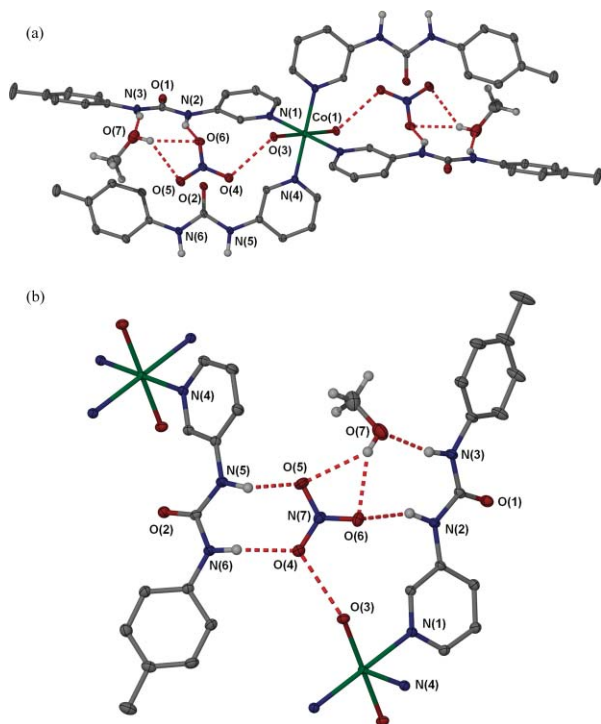


Fig. 1 (a) Thermal ellipsoid plot of [Co(TUP)₄(H₂O)₂](NO₃)₂·2MeOH (**1**) showing intramolecular hydrogen bonding (water H atoms not located). (b) Intermolecular hydrogen bonding *via* nitrate. The remaining water H atom interaction is with a carbonyl oxygen atom on an adjacent molecule.

the chelation of nitrate by Ag(TUP)₂^{9,11} but with the additional involvement of water due to the 90° angle between the ligands.

In order to assess solution phase binding behaviour the diamagnetic zinc(II) complex [Zn(TUP)(H₂O)](CF₃SO₃)₂ (**4**) was prepared by reaction of zinc(II) triflate with TUP in refluxing methanol. Unfortunately **4** did not form X-ray quality crystals, however the complex is likely to contain *trans* diaxial aquo ligands by analogy with **1–3** and the sulfate analogue.^{16,18} ¹H NMR titration of **4** with tetrabutylammonium nitrate in acetone-*d*₆ proved difficult because of significant precipitation after 2.5 equivalents of anion. Clean data were obtained up to 2.5 equivalents but surprisingly little change is noted in the chemical shift of the urea NH protons particularly during the addition of the first equivalent of anion, in contrast to the AgL₂⁺ complex.⁹ The chemical shift of the pyridyl CH protons also changes relatively little until more than one equivalent is added, which the changing gradient of the titration plots suggests more than one binding process. It is likely that some displacement of the pyridyl ligands by the anion is occurring. Representative spectra in the aromatic region are shown in Fig. 3.

In conclusion, a polymer-bound ligand capable of simultaneous coordination to anions and cations has been prepared and exhibits

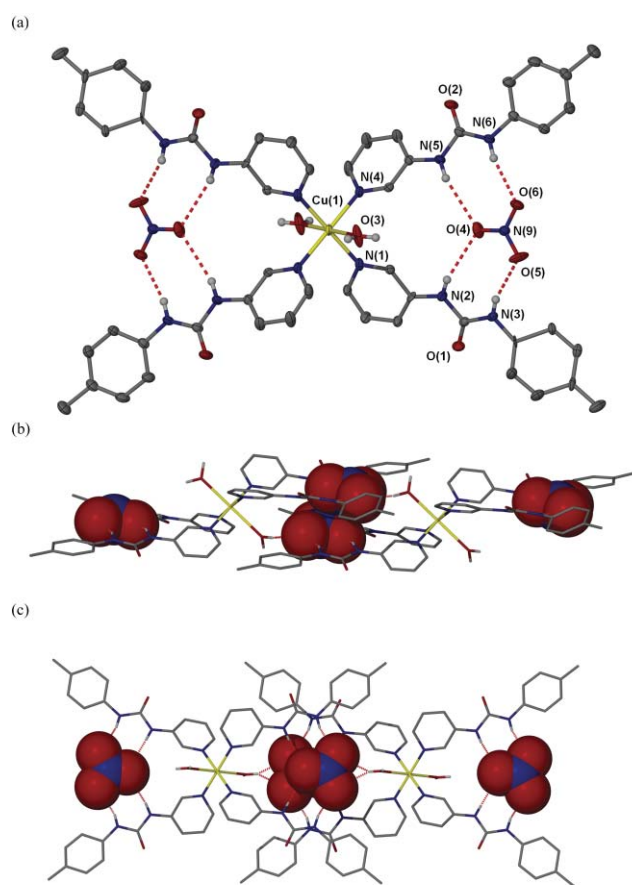


Fig. 2 (a) Thermal ellipsoid plot of [Cu(TUP)₄(H₂O)₂](NO₃)₂ (**3**) showing intramolecular hydrogen bonding. (b and c) Intermolecular hydrogen bonding to form hydrogen bonded dimers *via* coordinated water. The remaining water H atom interaction is with a carbonyl oxygen atom on an adjacent molecule. Nitrate anions shown as van der Waals spheres for clarity.

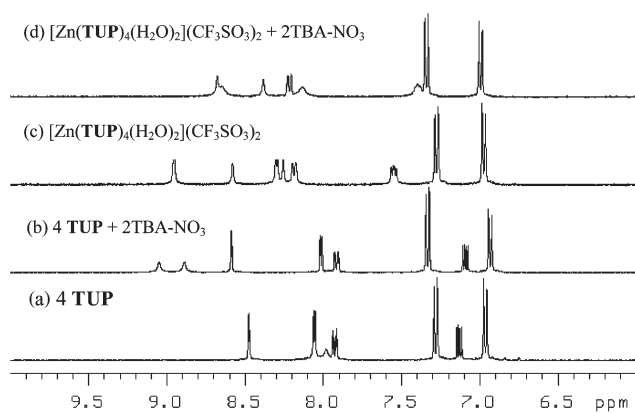


Fig. 3 ^1H NMR spectra of **TUP**: (a) free ligand, (b) in the presence of half an equivalent of tetrabutylammonium nitrate, (c) $[\text{Zn}(\text{TUP})_4(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ and (d) $[\text{Zn}(\text{TUP})_4(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ in the presence of 2 equivalents (0.5 equivalents per **TUP** ligand) of tetrabutylammonium nitrate.

modest selectivity for $\text{Cu}(\text{NO}_3)_2$. Structural evidence suggests that the Jahn–Teller distortion at $\text{Cu}(\text{II})$ enables optimum chelation of nitrate in a remarkable contrast to closely related but non-Jahn–Teller distorted metal ions. The environment within the polymer will be less well defined than the discrete model compounds, and coordination modes will depend on the spacing of **TUP** groups along the polymer chain.

Notes and references

† Crystal data for **1**: $\text{C}_{54}\text{H}_{64}\text{Co}_1\text{N}_{14}\text{O}_{14}$, $M = 1192.12$, $0.22 \times 0.16 \times 0.08 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (Nno. 2), $a = 8.9158(6)$, $b = 12.7512(9)$, $c = 13.6583(9) \text{ \AA}$, $\alpha = 71.6580(10)$, $\beta = 75.9930(10)$, $\gamma = 73.7080(10)^\circ$, $V = 1394.41(16) \text{ \AA}^3$, $Z = 1$, $D_c = 1.419 \text{ g cm}^{-3}$, $F_{000} = 625$, Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 120 \text{ K}$, $2\theta_{\text{max}} = 60.0^\circ$, 18675 reflections collected, 8048 unique ($R_{\text{int}} = 0.03$), Final GooF = 0.8714, $R1 = 0.0360$, $wR2 = 0.0909$, R indices based on 6069 reflections with $I > 3.00\sigma(I)$ (refinement on F^2), 377 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.387 \text{ mm}^{-1}$. Compound **2**: $\text{C}_{54}\text{H}_{64}\text{Ni}_{14}\text{O}_{14}$, $M = 1191.88$, $0.20 \times 0.20 \times 0.14 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.8731(12)$, $b = 12.7159(18)$, $c = 13.7082(19) \text{ \AA}$, $\alpha = 71.814(3)$, $\beta = 76.228(3)$, $\gamma = 74.062(3)^\circ$, $V = 1393.2(3) \text{ \AA}^3$, $Z = 1$, $D_c = 1.420 \text{ g cm}^{-3}$, $F_{000} = 626$, Mo $K\alpha$ radiation,

$\lambda = 0.71073 \text{ \AA}$, $T = 120 \text{ K}$, $2\theta_{\text{max}} = 56.6^\circ$, 15884 reflections collected, 6870 unique ($R_{\text{int}} = 0.07$), Final GooF = 0.9412, $R1 = 0.0795$, $wR2 = 0.1516$, R indices based on 2593 reflections with $I > 1.50\sigma(I)$ (refinement on F^2), 376 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.428 \text{ mm}^{-1}$. Compound **3**: $\text{C}_{52}\text{H}_{56}\text{CuN}_{14}\text{O}_{12}$, $M = 1132.65$, blue irregular, $0.32 \times 0.14 \times 0.10 \text{ mm}^3$, monoclinic, space group $C2/c$ (no. 15), $a = 25.131(3)$, $b = 12.5908(13)$, $c = 16.6161(18) \text{ \AA}$, $\beta = 91.327(2)^\circ$, $V = 5256.2(10) \text{ \AA}^3$, $Z = 4$, $D_c = 1.431 \text{ g cm}^{-3}$, $F_{000} = 2364$, Bruker SMART Apex CCD, Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 120(2) \text{ K}$, $2\theta_{\text{max}} = 60.0^\circ$, 34263 reflections collected, 7657 unique ($R_{\text{int}} = 0.0334$), Final GooF = 0.968, $R1 = 0.0349$, $wR2 = 0.0916$, R indices based on 5941 reflections with $I > 2\sigma(I)$ (refinement on F^2), 467 parameters, 12 restraints. Lp and absorption corrections applied, $\mu = 0.493 \text{ mm}^{-1}$. CCDC 285684–285686. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513820e

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