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Ditopic azathioether macrocycles as hosts for transition metal salts†

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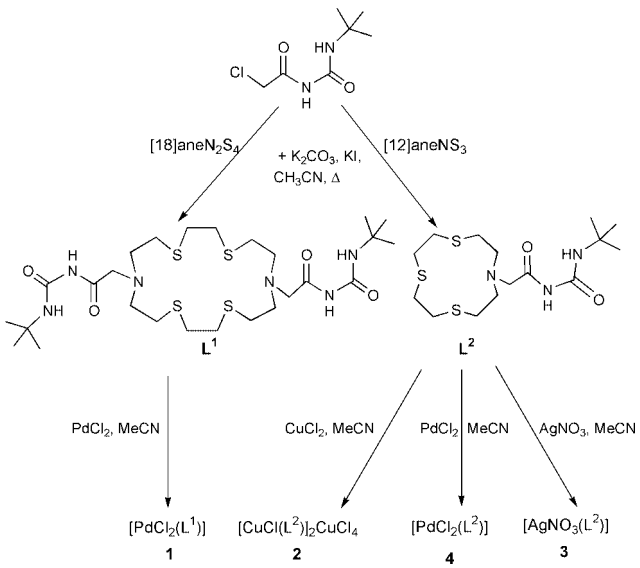
The synthesis and complexation of two heteroditopic lariat azathioether macrocycles L^1 and L^2 incorporating acylurea functionalised pendant arms are described; L^1 and L^2 are capable of simultaneously binding both the cationic and anionic moieties of a metal salt as confirmed by the structures of $[PdCl_2(L^1)]$, $[CuCl(L^2)]_2CuCl_4$ and $[Ag(NO_3)(L^2)]$ and by ^1H NMR studies in solution on $[Ag(NO_3)(L^2)]$.

Interest in the design and synthesis of heteroditopic receptors that can simultaneously bind both cationic and anionic moieties of a metal salt stems from the anticipation that such compounds may act as potent ionophores for the selective extraction and transport of base, toxic and/or precious metal salts from process streams.[1–3] A common approach has been to combine cation complexing agents such as crown O-ethers and calixarenes with proven anion receptors,[1–6] facilitating the tandem complexation of Group 1 halides, pseudo-halides and hydrogen phosphates. However, this choice of cation receptor precludes the *simultaneous* complexation of softer transition metal salts. Indeed, general ditopic receptors for transiton metal salts are exceedingly rare,[7,8] Thioether crowns represent powerful ligands for binding transition metal cations, even under low pH conditions where aza ligands are simply protonated and are no longer able to function as cation receptors.[9] We report herein definitive structural evidence for three systems that show simultaneous cation and anion binding.

Reaction of $PdCl_2$ with the new lariat azathiocrown L^1 in boiling MeCN results in the formation of **1** as a yellow powder (Scheme 1).†‡ Binding of Cl^- in solution by NMR methods could not be probed since **1** is soluble only in protic solvents where H-exchange occurs. The structure of **1**§ confirms the Pd(II) centre ligated in a square-planar geometry to the four S-donors resulting in an overall 'chair' conformation of the ligand. A Pd···Cl contact of 3.364(2) Å is observed at both axial sites of the Pd(II) ion and is indicative of weak electrostatic interactions between these centres. However, when viewing the extended molecular structure of **1**, it becomes apparent that the inner urea N atom N(2) is involved in H-bonding to the Cl^- anion of a second, approximately perpendicular molecule [N(2)···Cl(AA) 3.332(5) Å] (Fig. 1). The outer urea N atom N(3) is found to be H-bonding to the acyl oxygen O(1) of the same arm [N(3)···O(1) 2.689(7) Å] so constricting the librational freedom of the anion host. As expected, the symmetry-related equivalent N(2A) is H-bonded to the Cl^- ClD of a third $[PdCl_2(L^1)]$ molecule [N(2A)···ClD 3.331(5) Å] resulting in supramolecular aggregation *via* a zigzag chain. It is therefore apparent that ligand L^1 is capable of binding not only the Pd^{II} cation within the macrocyclic sulfur array, but also the associated Cl^- anions by concerted intermolecular H-bonding and metal–anion electrostatic interactions with the pendant arm.

The reaction between $CuCl_2$ and L^2 in MeOH (Scheme 1) affords dark green **2**.†‡ The molecular structure of **2** (Fig. 2)§ confirms that the asymmetric unit comprises two $[CuCl(L^2)]^+$ cations and a $[CuCl_4]^{2-}$ dianion. In each cation, the Cu(II) centre is coordinated octahedrally with the inner acyl oxygen of the pendant arm occupying an equatorial site.[10] The cations are organized such that the pendant arms assume a 'parallel' arrangement to each other; this position is presumably dictated by the presence of the $[CuCl_4]^{2-}$ anion, which is H-bonded to the inner urea N–H of each arm [N(2)···Cl(6) 3.29(2), N(5)···Cl(5) 3.27(2) Å]. The observed distorted tetrahedral geometry of $[CuCl_4]^{2-}$ is typical for this dianion.[11] As with L^1, the monobrachial azathioether L^2 is therefore able to simultaneously bind cationic and anionic halo-metal fragments; this system formally represents a methodology for the extraction and transport of $CuCl_2$.



Scheme 1 Synthesis and complexation reactions of the heteroditopic ligands L^1 and L^2.

† Electronic supplementary information (ESI) available: full experimental details. See http://www.rsc.org/suppdata/cc/b1/b109486f/

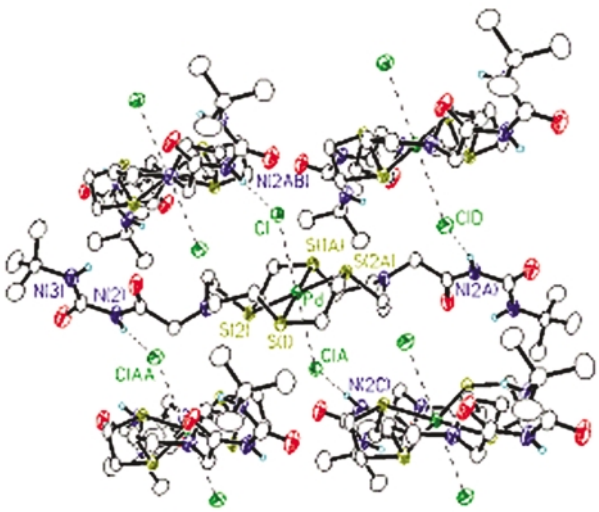


Fig. 1 View of structure of $[PdCl_2(L^1)]$.

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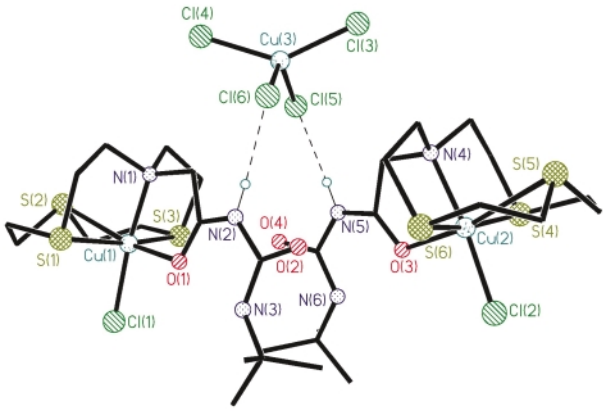


Fig. 2 View of structure of $[CuCl(L^2)]_2CuCl_4$.

Neither **1** or **2** allow for NMR studies on solution complexation. However, the reaction between $AgNO_3$ and L^2 yields $[Ag(NO)_3(L^2)]$, **3**,†‡ which is soluble in CD_3CN. The solid state structure of **3**§ confirms that the Ag(I) cation is complexed by the azathiocrown with the anion receptor arm extending radially (Fig. 3). Inspection of the extended structure reveals a bond between Ag(I) and a S-donor of a second cation [Ag–S(4A) 2.496(2) Å], so completing a five-coordinate, square pyramidal geometry at Ag(I) and affording an overall two-dimensional step-polymeric motif. Although displaying two-fold rotational disorder, the NO_3^- anion is clearly H-bonded to the pendant arm *via* the urea N(15), interacting in varying degrees with O(2), O(2′) and O(1) [N(15)–O(2) 3.27(3), N(15)–O(2′) 2.50(2), N(15)–O(1) 3.43(3) Å].

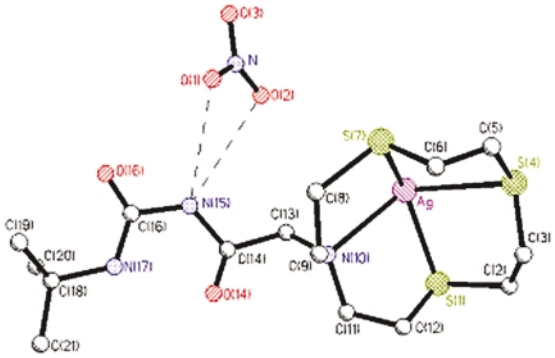
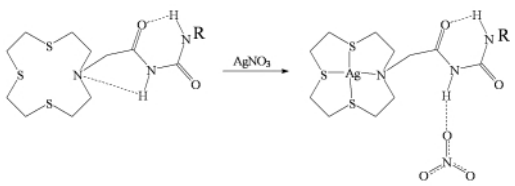


Fig. 3 View of structure of $[Ag(NO_3)(L^2)]$.

Addition of $AgNO_3$ to a solution of L^2 in MeCN leads initially to an upfield shift for the N(15)–H proton from δ_H 9.01 in L^2 to 8.65 on addition of 0.4 equivalents of $AgNO_3$. This upfield shift reflects the breaking of the internal H-bonding in free L^2 (confirmed by structural studies) on complexation to Ag(I) (Scheme 2). On further addition of $AgNO_3$, this resonance shows the expected downfield shift to δ_H 8.85 for **3** reflecting H-bonding of the acylurea arm to the nitrate anion as confirmed by the crystal structure of **3**. Addition of $[^nBu_4N][NO_3]$ to **3** leads



Scheme 2 Cleavage of internal H-bonding in L^2 on binding to $AgNO_3$.

to further downfield shifts for the N(15)–H resonance (to δ_H 9.39, 9.55 and 9.65 on addition of 1, 2 and 3 equivalents of $^nBu_4NNO_3$, respectively) consistent with anion binding in solution. Significantly, addition of $[^nBu_4N][NO_3]$ to L^2 does not shift the N(15)–H resonance; therefore, anion binding to L^2 can only occur once cation binding within the macrocyclic cavity and concomitant cleavage of the internal H-bonding takes place, thus affording an element of cooperativity to this system. Compound **4** has also been prepared and characterised.†‡

In conclusion, we have confirmed that the combination of thioether macrocycles with functionalised acylurea lariat arms affords heteroditopic receptors that have a wide applicability for the complexation of transition metal salts. These results have important implications for the extraction and transport of transition metal salts, especially at low pH where thioether crowns can still function as avid metal cation receptors.

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Notes and references

‡ For **1**: Anal. Found: C, 38.70; H, 5.77; N, 9.92. $C_{26}H_{50}Cl_2N_6O_4PdS_4$ requires: C, 38.30; H, 6.25; N, 10.32%; ^{1}H NMR (CD_3OD): δ_H 8.40 (br s, 1H, NH), 3.9–3.0 (br m's, 28H, macrocycle H/ CH_2), 1.37 (s, 18H, Bu^t); MS (FAB, +ve NBA matrix): *m/z* 744 ($M^+ - 2Cl$ 100%). For **2**: Anal. Found: C, 30.74; H, 4.95; N, 7.58. $C_{30}H_{58}Cl_6Cu_3N_6O_4S_6$ requires: C, 30.99; H, 5.03; N, 7.23%; MS (FAB, +ve NBA matrix): *m/z* 477 {$[CuCl(L^2)]^+$ 45}, 442 {$[Cu(L^2)]^+$ 50%}. For **3**: Anal. Found: C, 33.17; H, 5.39; N, 10.64. $C_{15}H_{29}AgN_4O_5S_3$ requires: C, 32.79; H, 5.32; N, 10.20%; ^{1}H NMR (CD_3CN): δ_H 8.85 (brs, 1H, NH), 8.08 (br s, 1H, NH), 3.40 (s, 2H, CH_2), 2.85 (br m's, 16H, macrocyclic CH_2's), 1.35 (s, 9H, CMe_3); MS (FAB, +ve NBA matrix): *m/z* 488 ($M^+ - NO_3$, 100%); IR (KBr disc): ν/cm^{-1} 3449 (vbr, m), 3299 (br, m), 1712 (s), 1348 (vs). For **4**: Anal. Found: C, 32.71; H, 4.97; N, 8.00. $C_{15}H_{29}Cl_2N_3O_2PdS_3$ requires: C, 32.35; H, 5.25; N, 7.54%. ^{1}H NMR (CD_3OD): δ_H 4.2–3.2 (br m's, 18H, macrocycle H/ CH_2), 1.38 (s, 9H, Bu^t). ^{1}H NMR (CD_3CN): δ_H 8.30 (br s, 1H, NH), 8.15 (br s, 1H, NH), 3.70–2.80 (m's, 18H, macrocyclic H), 1.36 (s, 9H, Bu^t). MS (FAB, +ve NBA matrix): *m/z* 522 ($M^+ - Cl$, 65), 484 ($M^+ - 2Cl$, 70%).

§ CCDC reference numbers 134350–134352. See http://www.rsc.org/suppdata/cc/b1/b109486f/ for crystallographic data in CIF or other electronic format.

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