Ion-pair binding by mixed N,S-donor 2-ureidopyridine ligands†

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The synthesis of a simple ambidentate ligand 1-(3-methylsulfanyl-phenyl)-3-pyridin-2-yl-urea (**L**) capable of binding metal ions *via* a pyridyl nitrogen atom or thioether sulfur donor is reported. The pyridyl functionality is located adjacent to an anion binding urea group allowing this region of the ligand to bind contact ion-pairs by simultaneous coordination and hydrogen bonding interactions. This intimate ion-pair binding coordination mode is demonstrated by the X-ray crystal structures of [Ag(**L**)]X (X = $CH_3CO_2^-$, **1**; NO_3^-, **2**). The non-coordinating PF_6^- anion is not bound as an ion-pair in [Ag(**L**)](PF_6) (**3**) and the urea NH groups exhibit short contacts to carbonyl oxygen and π-systems. The X-ray crystal structure of [Ag(**L**)$_4$]BF_4 (**4**) is also reported, showing the ligand to be exclusively S-bound. Anion binding by **L** and its silver(I) complex is also explored by solution ^{1}H NMR spectroscopic methods.

Introduction

Metal-based hosts for anions are receiving increasing current interest.[1–32] As well as being convenient counter-ions, metal centres, with their strong coordination geometric tendencies, also represent an excellent platform for the assembly of structurally well-defined anion binding hosts.[1] Recent work on 3-aminopyridine, 3-methylaminopyridine and 3-ureidopyridine type ligands has resulted in a number of separated ion-pair binding compounds in which a series of two to four ligands are organised by a metal centre into a binding pocket for an attendant anion.[8,10,11,18,19] In these systems the anion and cation binding regions are far apart and there is no direct interaction between the charged components. Such a situation is potentially unstable since it involves charge separation and contrasts to macrobicyclic systems prepared by Smith and co-workers in which a neutral macrobicycle binds to an alkali metal halide contact ion-pair.[33–36] Earlier work by Reinhoudt *et al.* has also used a metal centre as a direct anion binding site, supported by remote hydrogen bonding interactions.[37,38] We now report the design of a simple ligand containing an intimately connected hybrid metal–anion binding site complementary to a contact ion-pair.

Results and discussion

Synthesis and structure

The ligand 1-(3-methylsulfanyl-phenyl)-3-pyridin-2-yl-urea (**L**) was designed by analogy with the related 1-(3-methylsulfanyl-phenyl)-3-phenyl-urea,[39] to bind to metal ions such as Ag(I) through both the thioether and pyridyl functionalities. While the thioether is remote from the urea anion binding group, the 2-pyridyl metal binding group and the urea form a connected ion-pair binding site of the type illustrated in Fig. 1. In the presence of binary metal salts of univalent cations (MX) the ligand should thus either form a N,S-bound coordination polymer or a discrete $M_2X_2L_2$ assembly, possibly templated by suitable anions. Depending on the relative strengths of the M–N and M–S bonds, we anticipate that the pyridylurea-bound MX ion-pair could be stable in solution and this fragment might then dimerise or assemble *via* labile metal–sulfur interactions.

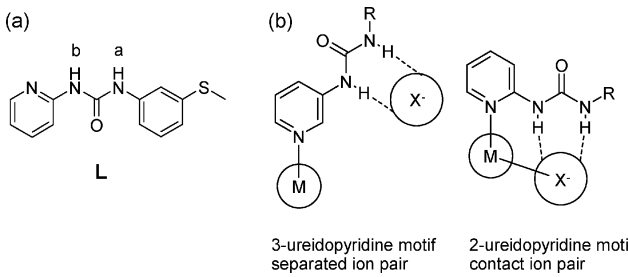

Fig. 1 (a) Structure of ligand **L** and (b) comparison of the proposed ion-pair binding mode of **L** with analogous 3-pyridyl urea complexes.

The conformational preferences of ligand **L** itself were analysed by X-ray crystallography. Remarkably **L** exists in at least four polymorphic modifications and these will be reported separately. The molecular conformation in the four different solid forms is very similar and involves an *anti* conformation for the N,N′-disubstituted urea moiety such as to produce an S(6) intramolecular hydrogen bonded ring[40] from the urea γ-NH to the pyridyl nitrogen atom as is common with 2-pyridylureas.[41] The remaining urea NH and the carbonyl oxygen atom then form an $R_2^2(8)$ intermolecular hydrogen bonded ring, Fig. 2.

The reaction of **L** with silver(I) salts yields compounds of formula [Ag(**L**)]X (X = CH_3CO_2, **1**; NO_3, **2** and PF_6, **3**) all of which have been characterised by X-ray crystallography. The acetate complex **1** exists as two polymorphs (monoclinic and triclinic forms A and B, respectively), Fig. 3, in both of which, as anticipated, the anion is simultaneously bound to both the urea moiety by hydrogen bonding and the metal ion by coordination

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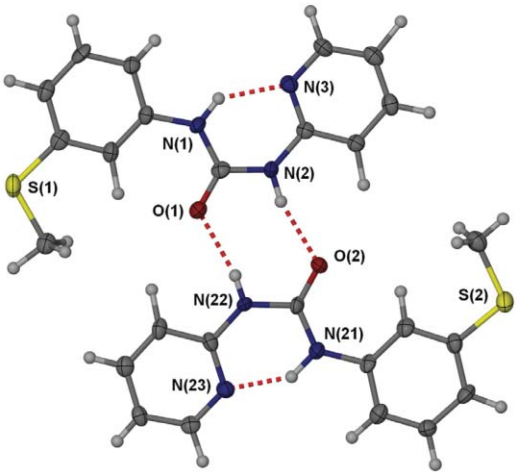

Fig. 2 Conformation and hydrogen bonding of ligand **L** derived from X-ray crystallography.

as shown in Fig. 1(b). In both solid forms the Ag(I) ion adopts an irregular three-coordinate geometry, binding to the pyridyl nitrogen atom, the sulfur atom of an adjacent ligand and one oxygen atom of the acetate counter-ion. However, in form A, the silver ion is additionally weakly coordinated by a sulfur atom (Ag···S 3.191 Å) from an adjacent coordination polymeric strand (see below), while the silver atoms in polymorph B are linked together by Ag···Ag interactions (3.013 Å). One oxygen atom of the acetate anion is coordinated to the silver ion in each form, while the second oxygen atom is hydrogen bonded in a typical $R_2^1(6)$ pattern[20] to the urea moiety. The 1 : 1 ratio between ligand and metal salt means that the complex adopts an extended coordination polymer structure in the solid state in both polymorphs. Both structures are built out of zig-zag shaped 1D polymer strands which form corrugated layers. The two crystal forms differ in the conformation of the polymer at the metal centre, with form A adopting an anti-parallel arrangement of the ligands within the 1D polymer strands, while in form B the arrangement is parallel. Hydrogen bond distances are given in Fig. 3 and are slightly longer in form B than form A. Form B is also less dense than form A (1.78 g cm^{-3} *vs.* 1.81 g cm^{-3}) and hence it may be that form B is a kinetic form and form A is the stable polymorph.

The X-ray crystal structure of the nitrate complex **2** also exhibits a very similar ion-pair binding motif to that found for **1**, consistent with the similar shape of the nitrate and acetate ions. Nitrate is much less basic than acetate, however, and hence the Ag–O_{anion} distances are much longer than in the acetate complex structures. The single short Ag–O_2CCH_3 bond of *ca.* 2.25 Å is replaced by two much longer Ag–ONO_2 contacts each *ca.* 2.5 Å long. The fact that nitrate is able to coordinate on all three edges (*i.e.* to each pair of oxygen atoms) also means that the extended geometry of the structure is rather different. While it is again a coordination polymer, the structure is based on an infinite network of dimeric $\{Ag(NO_3)(L)\}_2$ units linked together by bridging nitrate anions and Ag–S interactions, Fig. 4. The coordination geometry of the Ag(I) centres is thus distorted tetrahedral rather than distorted trigonal, as in **1**.

In contrast to acetate and nitrate, the non-coordinating PF_6^- anion in complex **3** would not be expected to interact with the Ag(I) centre in these kinds of systems and indeed this proves to be the case with the shortest Ag···F distances in excess of 3.4 Å. As a result the silver ions are essentially linear, two-coordinated bound by pyridyl nitrogen and thioether groups to produce a

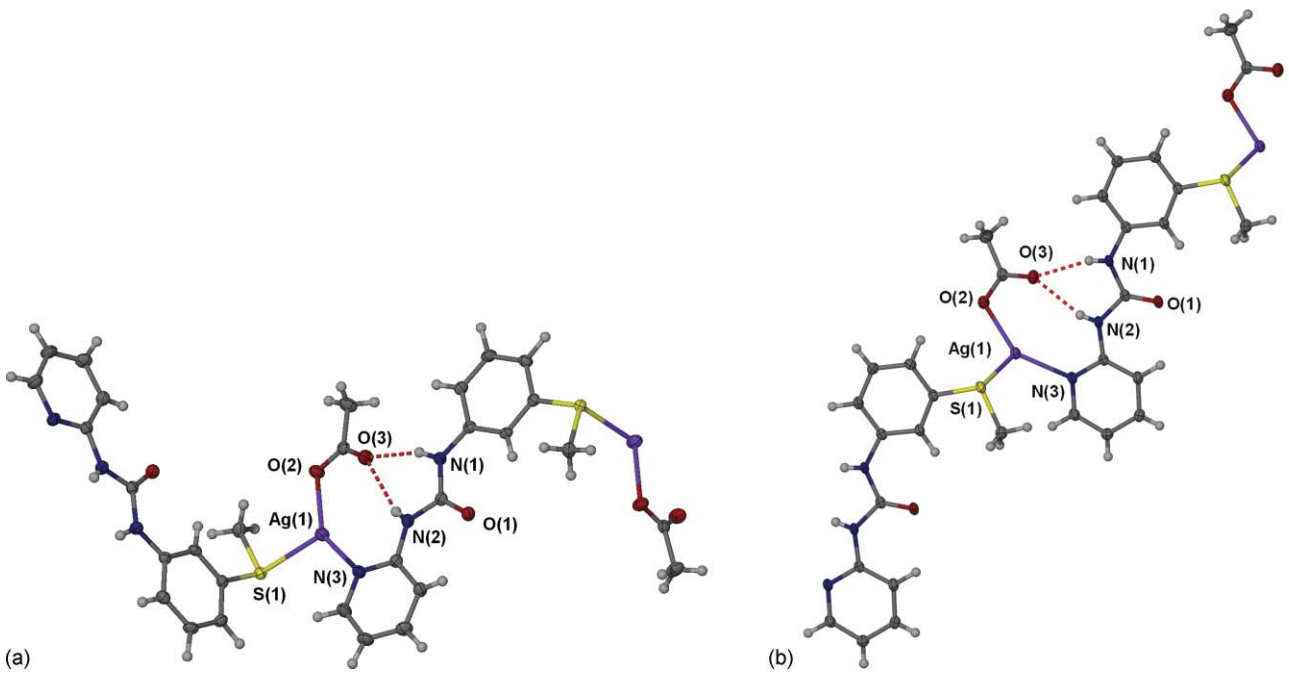

Fig. 3 Silver(I) acetate contact ion-pair binding motif in two polymorphs of [Ag(**L**)](CH_3CO_2) (**1**) (a) monoclinic form A and (b) triclinic form B (ellipsoids at 50% level). Selected bond lengths, form A: Ag(1)–N(3) 2.254(2), Ag(1)–O(2) 2.280(2), Ag(1)–S(1) 2.5905(7) Å; form B Ag(1)–O(2) 2.2357(15), Ag(1)–N(3) 2.2383(15), Ag(1)–S(1) 2.5828(5) Å. Selected hydrogen bond distances, form A: N(1)–O(3) 2.759(3), N(1)–O(3) 2.759(3) Å; form B: N(1)–O(3) 2.819(2), N(2)–O(3) 2.857(2) Å.

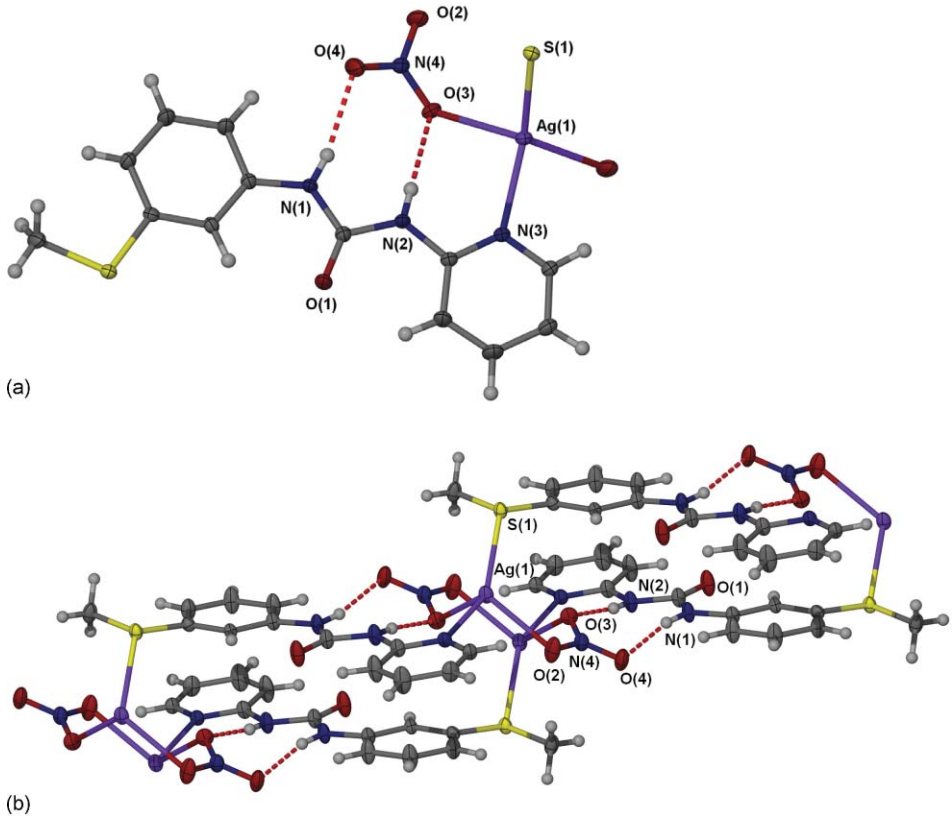

Fig. 4 Silver(I) nitrate contact ion-pair binding motif in [Ag(**L**)](NO_3) (**2**) (a) repeat unit (b) extended structure (ellipsoids at 50% level). Selected bond lengths: Ag(1)–N(3) 2.2636(16), Ag(1)–S(1) 2.4674(5), Ag(1)–O(2) 2.4957(17), Ag(1)–O(3) 2.5789(15) Å. Selected hydrogen bond distances: N(1)–O(4) 2.920(2), N(2)–O(3) 2.946(2) Å.

1D coordination polymer chain, Fig. 5. There is also a long Ag–O interaction from the silver ion to the urea oxygen atom. In the absence of a strong hydrogen bond acceptor anion the urea oxygen atom acts as a hydrogen bond acceptor for a single urea NH···O hydrogen bond, in contrast to the usual $R_2^1(6)$ urea tape motif which involves the carbonyl oxygen atom as a bifurcated acceptor.[42–44] This single interaction allows the formation of the long Ag–O bond, leaving the remaining urea NH group to form short contacts to a single fluorine atom and to the pyridyl aromatic ring.

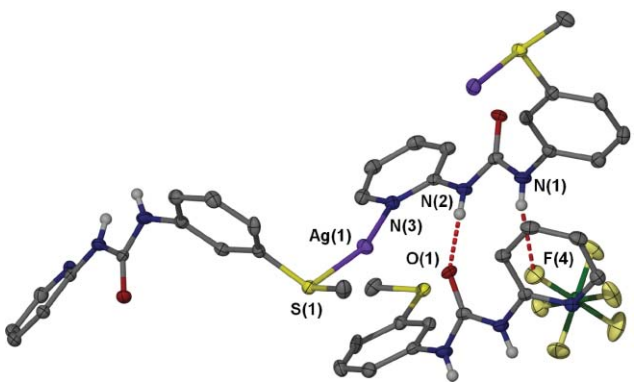

Fig. 5 Silver(I) hexafluorophosphate complex [Ag(**L**)](PF_6) (**3**) (ellipsoids at 50% level). Selected bond lengths: Ag(1)–N(1) 2.206(2), Ag(1)–S(1) 2.4316(6) Å. Selected hydrogen bond distance: N(2)···O(1) 2.885(3), N(1)···F(4) 3.119(3) Å.

Attempts were also made to prepare a 1 : 1 complex with **L** and $AgBF_4$, however, the final isolated product proved to be an interesting 1 : 4 complex [Ag(κ-S-**L**)$_4$](BF_4)·thf (**4**) which was also characterised by X-ray crystallography (Fig. 6). The 1 : 4 ratio may arise from decomposition of some of the silver salt leading to an excess of ligand. The Ag(I) ion is tetrahedrally coordinated solely by the sulfur atoms of four independent ligands with Ag–S distances 2.56–2.60 Å, similar to that found in **1** but rather longer than those in the two-coordinate **3**. The poor hydrogen bond acceptor nature of BF_4^- means that the urea groups do not hydrogen bond to the anion but instead adopt an *anti* conformation exhibiting a very similar combination of intramolecular and intermolecular interactions to those observed in the free ligand structures. The 1 : 4 ratio means that the soft Ag(I) ion is able to satisfy its coordination requirements using only sulfur and hence does not coordinate to the pyridyl nitrogen atoms. As a result the pyridyl groups are free to act as hydrogen bond acceptors. In such case, according to Etter's rules,[44] the intramolecular S(6) motif is dominant forcing the *anti* conformation and hence leaving a single NH group free to form the intermolecular $R_2^2(8)$ motif, as in the free ligand structures.

Solution phase binding

Given the reproducible occurrence of ion-pair binding by **L** in the solid state it is of obvious interest to determine whether there is any evidence for the persistence of these interactions in solution.

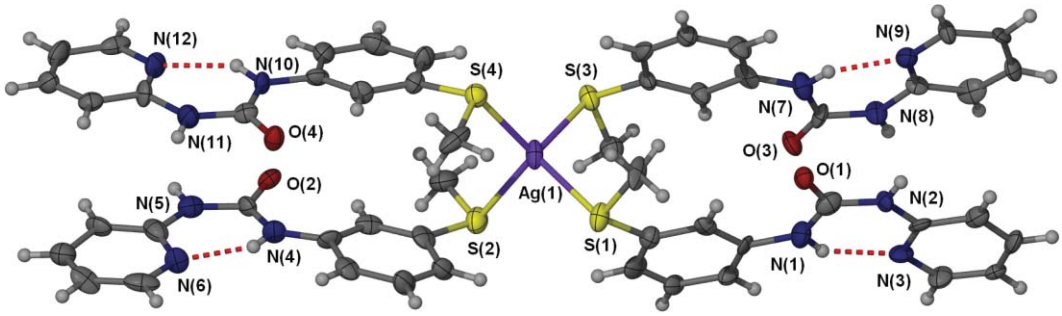

Fig. 6 The cation in the 1 : 4 silver(I) tetrafluoroborate complex $[Ag(\kappa\text{-S-}\mathbf{L})_4](BF_4)\cdot$thf (**4**) (ellipsoids at 50% level).

Unfortunately solution phase binding measurements on **L** and its Ag(I) complexes were complicated by poor solubility. While **L** is soluble in a range of solvents, ^{1}H NMR spectroscopic titrations with metal salts had to be carried out in the highly competitive DMSO-d_6. The solvent titration of free **L** with $NBu_4^+X^-$ (X = NO_3, PF_6^-) did not result in any significant chemical shift changes, suggesting weak binding. However in both acetone-d_6 and DMSO-d_6 solution addition of tetrabutylammonium acetate resulted in the formation of a 1 : 1 complex (confirmed by Job plot analysis, see ESI†). While the DMSO experiment resulted in a conventional binding isotherm behaviour for both NH resonances (NH_a and NH_b, Fig. 1(a)), in acetone the resonance at 8.37 ppm (NH_b) is more dramatically affected than the NH_a signal at 11.53 ppm (Fig. 7). By reference to Fig. 2, we suggest that in acetone the resonance at 11.53 ppm corresponds to the NH proton which is intramolecularly hydrogen bonded to the pyridyl nitrogen atom. Hence in acetone the ligand adopts an *anti* conformation of the urea NH groups as in Fig. 2, while in DMSO it is *syn* as a result of hydrogen bonding to the solvent.

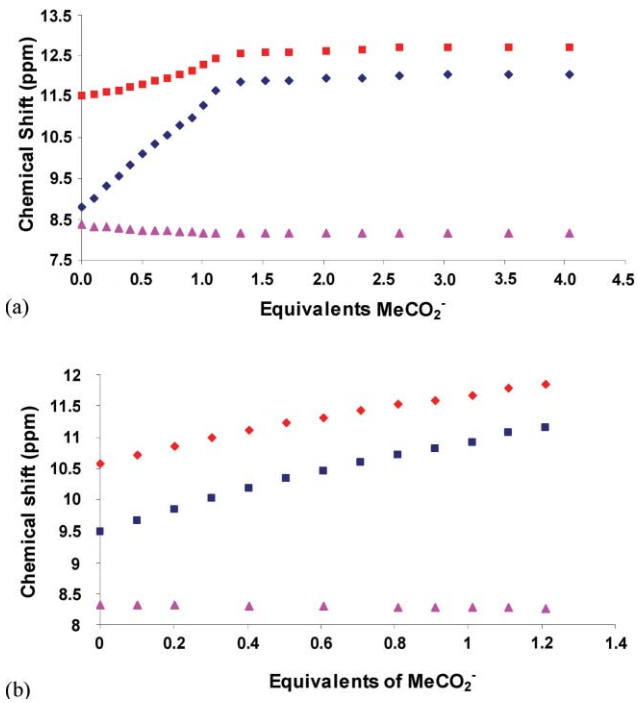

Fig. 7 (a) ^{1}H NMR spectroscopic titration of **L** with $NBu_4^+OAc^-$ (a) in acetone-d_6 and (b) in DMSO-d_6. (■ = sulfanylphenyl NH, ♦ = pyridyl NH, ▲ = CH).

Titration of free **L** with silver(I) trifluoromethanesulfonate (as a control using a non-coordinating anion) resulted in a small change of $\Delta\delta$ *ca.* –0.1 ppm in DMSO suggesting that Ag(I) complexation alone does not result in a significant change in the chemical shift of the urea NH resonances of **L** (see ESI†). ^{1}H NMR spectroscopic titrations were then undertaken of **L** with $NBu_4^+MeCO_2^-$ in the presence of 0.5, 1 and 2 equivalents of $AgCF_3SO_3$, relative to **L** (Fig. 8). In the presence of 0.5 equivalents of Ag(I) (a 2 : 1 **L** : Ag ratio) in contrast to the titration of the free ligand, no change was observed in the chemical shift of NH_a until 0.5 equivalents of anion had been added. However, NH_b exhibits a downfield chemical shift change of *ca.* 0.4 ppm in the same range. In the presence of one equivalent of Ag(I), a similar behaviour is observed except that the chemical shift of NH_a remains unchanged until one equivalent of acetate is added. Interestingly the titration isotherm in the presence of two equivalents of Ag(I) looks very similar to the plot obtained in the presence of one equivalent of silver, *i.e.* the chemical shift of NH_a begins to change after addition of one equivalent of acetate. We interpret this data by postulating anion binding by a 1 : 1 complex of silver(I) and **L**. Thus in the presence of 0.5 equivalents of Ag(I) the first 0.5 equivalents of acetate are bound by the silver complex, affecting NH_b but not NH_a. After this process is complete additional acetate is bound by the excess free ligand (as demonstrated by Fig. 7(b)), and/or by the "Ag**L**$^+$" complex in a different binding mode. In the presence of one equivalent of Ag(I) it requires one equivalent of acetate to bind to the "Ag**L**$^+$" complex. Additional acetate is then bound in a different binding mode to give a "Ag**L**·2$MeCO_2^-$"species. There is precedent for this binding of more than one anion by these kinds of complexes.[18] In the presence of two equivalents of silver(I) half of the silver is in excess and makes no difference to the shape of the isotherm. This latter experiment establishes that acetate is not being bound by Ag(I) in the absence of **L**. The fact that it is NH_b and not NH_a that is most affected by acetate anion binding by "Ag**L**$^+$" is surprising. Examination of the crystal structure data shown in Fig. 3 suggests that both NH resonances should be affected. It is possible that a different binding mode occurs in solution along the lines of that shown in Fig. 9.

Conclusions

We have shown that the 2-ureidopyridine motif is capable of binding anions and cations as contact ion-pairs in the solid state

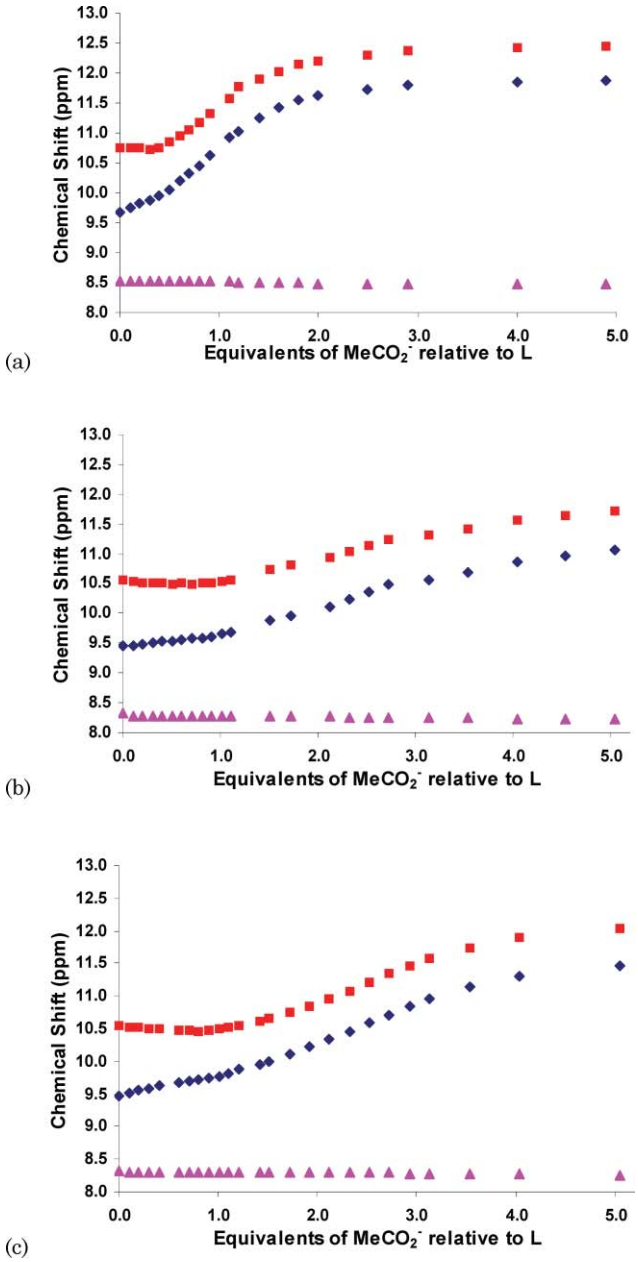

Fig. 8 ^{1}H NMR spectroscopic titration of **L** with $NBu_4^+MeCO_2^-$ in the presence of (a) 0.5, (b) 1.0 and (c) 2.0 equivalents of $AgCF_3SO_3$. (■ = sulfanylphenyl NH, ♦ = pyridyl NH, ▲ = CH).

for Ag(I) salts. Solubility problems prevent an extensive solution phase study on a range of anions, however for the strongly bound acetate the presence of silver(I) cations significantly perturbs the anion binding behaviour of the free ligand and the data suggests the formation of a 1 : 1 Ag : **L** complex that binds to acetate *via* the formation of at least one NH · · · anion hydrogen bond.

Experimental

X-Ray crystallography†

Suitable single crystals were grown by slow evaporation in the dark and mounted using silicon grease on a thin glass fibre. Crystallographic measurements were carried out on a Bruker SMART CCD 6000 (**1A**, **1B**, **2**, **3**) and Rigaku R-AXIS Spider IP (**4**) diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The standard data collection temperature was 120 K, maintained using an open flow N_2 Cryostream (OxfordCryosystems) device. Integration was carried out using the Bruker SAINT and Rigaku FSProcess packages. Data sets were corrected for Lorentz and polarisation effects, and for the effects of absorption. Structures were solved using direct methods and refined by full-matrix least squares on F^2 for all data using SHELXTL[45] software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. Molecular graphics were produced using the programs X-Seed[46,47] and POV-Ray.[48] Crystal data for the structures studied are listed in Table 1.

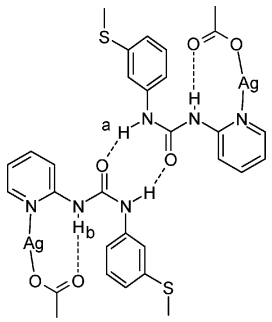

Fig. 9 Speculative acetate binding mode in a 1 : 1 Ag : **L** complex involving a chemical shift change in NH_b but not in NH_a upon acetate binding.

Syntheses

1-(3-Methylsulfanyl-phenyl)-3-pyridin-2-yl-urea (L). 2-Amino pyridine (2.84 g, 30.2 mmol) was reacted with 3-thiomethyl phenyl isocyanate (4.95 g, 30.2 mmol) in 25 ml of chloroform solvent at room temperature resulting in the formation of a white solid. The product was isolated by filtration and washed with a small amount of diethyl ether to give 7.00 g (89%) of the product. ^{1}H NMR (DMSO-d_6): 10.55 (1H, bs, NH), 9.46 (1H, bs, NH), 8.29 (1H, d, $J = 5.2$ Hz, PyH), 7.73 (1H, dt, $J = 1.6$, 7.2 Hz, PyH), 7.51 (2H, m, ArH), 7.24 (2H, m, ArH), 7.01 (1H, dd, $J = 4.8$, 6.4 Hz, PyH), 6.91 (1H, dt, $J = 3.2$, 6.0 Hz, PyH), 2.45 (3H, s, CH_3). IR (ν/cm^{-1}) 1683 s (C=O), 3214 br (NH). Mp 141 °C. Anal. Calcd (%) for $C_{13}H_{13}N_3OS$: C, 60.21; H, 5.05, N, 16.20. Found (%) C, 60.17; H, 5.07; N, 16.03.

[Ag(L)](CH$_3$CO$_2$) 1 (form A). Ligand **L** (30 mg, 0.115 mmol) in THF (2 ml) was mixed with silver acetate (19 mg, 0.115 mmol) in methanol : H_2O (1 : 1 v/v, 2 ml) and the mixture was allowed to evaporate slowly resulting in the formation of colourless single crystals suitable for X-ray diffraction analysis. IR (ν/cm^{-1}) 1200, 1441, 1548, 1576, 1765 s ($\nu_a(CO_2)$), 3323 m (ν(NH)). Mp 185 °C (decomp.). Anal. Calcd (%) for $C_{15}H_{16}N_3O_3SAg$: C, 42.27; H, 3.78; N, 9.86. Found (%) C, 42.02; H, 3.73; N, 9.66.

[Ag(L)](CH$_3$CO$_2$) 1 (form B). The second polymorph of **1** was obtained by dissolving **L** (30 mg, 0.115 mmol) in THF (2 ml) and mixing with silver acetate (19 mg, 0.115 mmol) in methanol : acetonitrile (1 : 1 v/v, 2 ml) and leaving the mixture to evaporate slowly. This resulted in the formation of colourless single crystals suitable for X-ray diffraction analysis. IR (ν/cm^{-1}) 1411, 1467, 1531, 1579, 1612, 1718 s ($\nu_a(CO_2)$), 3199 m (ν(NH)),

Table 1 Crystal data and structure refinement for compounds **1** (forms **A** and **B**), and **2–4**

Compound	**1-A**	**1-B**	**2**	**3**	**4**
Formula	$(C_{13}H_{13}N_3OS)Ag(CH_3CO_2)$		$(C_{13}H_{13}N_3OS)Ag\ (NO_3)$	$(C_{13}H_{13}N_3OS)Ag(PF_6)$	$(C_{13}H_{13}N_3OS)_4Ag(BF_4)(C_4H_8O)$
Formula weight	426.24		429.20	512.16	1304.08
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$Pca2_1$
a/Å	4.3552(1)	7.6567(4)	7.9094(2)	8.7396(2)	11.034(2)
b/Å	19.5739(6)	9.7852(4)	9.6883(3)	12.2836(2)	32.057(6)
c/Å	18.4288(6)	11.5435(5)	10.6752(3)	15.3536(3)	16.422(3)
α/°	90	73.77(1)	89.97(1)	90	90
β/°	95.12(2)	77.40(1)	69.83(1)	90	90
γ/°	90	75.77(1)	75.89(1)	90	90
V/Å^3	1564.75(8)	794.47(6)	741.53(4)	1648.27(6)	5809(2)
Z	4	2	2	4	4
$\rho_{calc.}$/mg m^3	1.809	1.782	1.922	2.064	1.491
μ/mm^{-1}	1.439	1.417	1.526	1.519	0.563
$F(000)$	856	428	428	1008	2688
Reflections collected	14 537	8976	9809	21 967	36 273
Independent reflections, R_{int}	4130, 0.062	4591, 0.018	4302, 0.0182	4817,0.026	11 378, 0.116
No. of parameters	272	272	260	243	684
Final R_1 $[I > 2\sigma(I)]$	0.0359	0.0282	0.0278	0.0255	0.0941
wR_2 (all data)	0.1035	0.0789	0.0758	0.0615	0.2317
GOF on F^2	1.085	1.020	1.018	0.979	1.023

3279 m (ν(NH)). Mp 180 °C (decomp.). Anal. Calcd (%) for $C_{15}H_{16}N_3O_3SAg$: C, 42.27; H, 3.78; N, 9.86. Found (%) C, 42.03; H, 3.75; N, 9.91.

[Ag(L)](NO$_3$) 2. Ligand **L** (30 mg, 0.115 mmol) was dissolved in THF (2 ml) and added to a solution of silver nitrate (20 mg, 0.118 mmol) in H_2O (2 ml). The mixture was left to slowly evaporate for five days resulting in the formation of colourless single crystals. IR (ν/cm^{-1}) 681, 760, 1304, 1387, 1535, 1578, 1608, 1709, 3129, 3278. Mp 180 °C (decomp.). Anal. Calcd (%) for $C_{13}H_{13}N_4O_4SAg$: C, 36.40; H, 3.01; N, 13.10. Found (%) C, 36.30; H, 3.07; N, 13.07.

[Ag(L)](PF$_6$) 3. Ligand **L** (30 mg, 0.115 mmol) was dissolved in THF (2 ml) and added to a solution of silver hexafluorophosphate (20 mg, 0.079 mmol) in H_2O (2 ml). The mixture was left to slowly evaporate for five days resulting in the formation of colourless single crystals. IR (ν/cm^{-1}) 987 br (PF_6), 1649 s (C=O), 3308 br (NH), 3477 br (H_2O). Anal. Calcd (%) for $C_{13}H_{12}N_3OSAgPF_6$: C, 30.42; H, 2.56; N, 8.11. Found (%) C, 30.50; H, 2.56; N, 8.22. Mass 511.16 (M + H).

[Ag(L)$_4$](BF$_4$)·thf 4. Ligand **L** (30 mg, 0.115 mmol) in THF (2 ml) was mixed with a solution of silver tetrafluoroborate (22.5 mg, 115 mmol) in THF : H_2O (1 : 1 v/v, 2 ml) and the mixture was allowed to evaporate resulting in the formation of colourless single crystals. IR (ν/cm^{-1}) 1037 s (BF_4), 1597, 1554, 1657, 3307 m (NH), 3368 (m, NH). Anal. Calcd (%) for $C_{52}H_{52}N_{12}O_4S_4AgBF_4$: C, 52.75; H, 4.43; N, 14.20. Found (%) C, 51.50; H, 4.43; N, 14.10.

Acknowledgements

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