Structural Manipulation of Hydrogen Bond Networks Using Sulfonated Phosphane Ligands and Their Complexes: Competition and Interplay Between Strong and Weak Hydrogen Bonds

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Using the sulfonated phosphane $[PPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$, $\mathbf{L}^-$, we have demonstrated that metal centres can readily be incorporated into guanidinium sulfonate (GS) hydrogen-bonded networks, and that the increase in steric bulk on going from $[C(NH_2)_3][\mathbf{L}]$ (**1**) to $[C(NH_2)_3][AuCl(\mathbf{L})]$ (**2**) leads to a flattening of the GS sheets. The crystal structures of $[C(NH_2)_3][\mathbf{LS}]$ **3** and $[C(NH_2)_3][\mathbf{LSe}]$ **4** ($\mathbf{LS}^- = [SPPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$, $\mathbf{LSe}^- = [SePPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$) reveal disorder in both the sulfonate groups and the guanidinium cations, which is a consequence of *pseudo*-sixfold phenyl embraces between the anions. These interactions, identical to those observed in Ph_3PS and Ph_3PSe, position the sulfonate groups too close together for regular quasihexagonal hydrogen bonding motifs to be formed. The regular GS hydrogen bonding patterns can also be disrupted by using an anion containing two sulfonate groups such as that in $[C(NH_2)_3]_2\{cis\text{-}[PdCl_2(\mathbf{L})_2]\}$ (**5**). In this case the incorporation of two sulfonate groups from each anion into the same hydrogen-bonded sheet also serves to constrain the distance between the sulfur atoms to a value incommensurate with that enabling a guanidinium cation to hydrogen bond to both groups. In this case irregular GS sheets are formed involving fewer N–H···O hydrogen bonds than in **1** and **2**.

Introduction

The use of intermolecular interactions in the design and synthesis of solid-state structures — a process often referred to as crystal engineering — has attracted enormous interest over the past few years.[1] Previously, we have reported the use of multiple hydrogen bonds to control the aggregation of metal complex cations and anions containing complementary hydrogen bonding groups.[2] The incorporation of two hydrogen bond donors (D) on each cation face and two hydrogen bond acceptors (A) on each anion face, giving an overall DD:AA interaction, ensures that secondary interactions are all favourable, thus enhancing the total energy of the interaction.

The guanidinium sulfonate (GS) system is another case in which the cations and anions are linked together by pairs of hydrogen bonds in the DD:AA arrangement, though, since both cations and anions contain three hydrogen bonding faces, the hydrogen bond interactions in this system lead to quasihexagonal arrays and the formation of infinite two-dimensional sheets.[3,4] These GS sheets are particularly robust to changes in the steric and electronic properties of the sulfonate substituents, and bilayer or pillared-brick structures incorporating disulfonates can be used to include many guest molecules.[5] In this paper we show how monosulfonated triphenylphosphane $[PPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$, $\mathbf{L}^-$, a ligand initially prepared for biphasic catalysis,[6] can be incorporated into GS arrays, therefore providing a means of introducing metal centres into hydrogen-bonded networks in which two dimensions are controlled by the hydrogen bonds. A recent communication from Kathó and coworkers[7] using guanidinium to crystallise sulfonated phosphanes has prompted us to report our findings.[8] To this end, the syntheses and crystal structures of $[C(NH_2)_3][\mathbf{L}]$ (**1**), $[C(NH_2)_3][AuCl(\mathbf{L})]$ (**2**), $[C(NH_2)_3][\mathbf{LS}]$ (**3**), $[C(NH_2)_3][\mathbf{LSe}]$ (**4**) and $[C(NH_2)_3]_2\{cis\text{-}[PdCl_2(\mathbf{L})_2]\}$ (**5**) are reported ($\mathbf{LS}^- = [SPPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$, $\mathbf{LSe}^- = [SePPh_2(C_6H_4\text{-}m\text{-}SO_3)]^-$). Analysis of the structures reveals that predetermination of the relative positions of the sulfonate groups, either through interactions between the triphenylphosphane groups or through coordination of two phosphane ligands to a metal centre, can lead either to disruption of the quasihexagonal hydrogen bonding motif or to disorder in the GS sheets.

Results and Discussion

Metathesis of Na[**L**] with guanidinium chloride in methanol gave colourless crystals of $[C(NH_2)_3][\mathbf{L}]$ (**1**) suitable for analysis by X-ray crystallography. The asymmetric unit of

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1 showed the presence of two independent guanidinium cations and two independent triphenylphosphane sulfonate anions. Hydrogen bond interactions between the cations and anions lead to the formation of the anticipated quasihexagonal GS arrays [Figure 1 (top)], despite the steric bulk of the triphenylphosphane group. A single-layer sheet structure is adopted, with PPh$_3$ groups located on both sides of the GS sheets. The sheets are corrugated, with a "hinge" between hydrogen-bonded ribbons [Figure 1 (bottom)], and this is reflected in an inter-ribbon angle of 103°, based on the angle between guanidinium planes in neighbouring ribbons. Similar distortions to GS sheets have been observed previously,[3] and occur as a means of minimising void space within the structure.

The single-layer sheet structure ensures that triphenylphosphane groups from neighbouring sheets project into the inter-sheet space. The major interaction between these groups involves pairs of [**L**]$^-$ anions, based on P(1) and P(2) in neighbouring sheets, which adopt sixfold phenyl embraces (6PEs).[9] Two C−H···O interactions are also evident [C(8)···O(1) 3.548(10), H(8)···O(1) 2.66(1) Å, C(8)−H(8)···O(1) 160.8(5)°; and C(36)···O(6) 3.639(10), H(36)···O(6) 2.75(1) Å, C(36)−H(36)···O(6) 161.0(5)°].

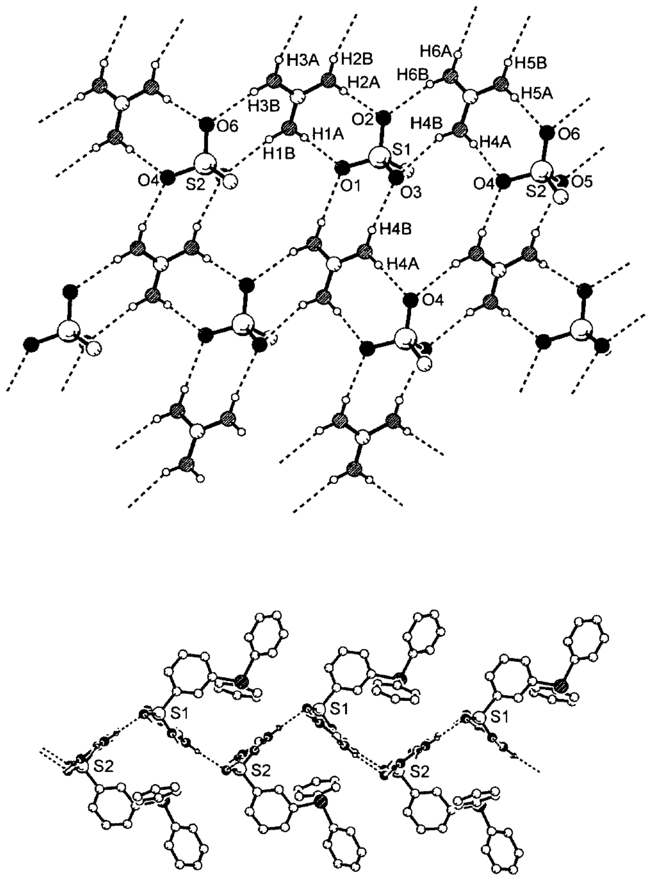

Figure 1. (top) Quasihexagonal hydrogen-bonded GS sheets in the crystal structure of [C(NH$_2$)$_3$][**L**] (**1**); hydrogen bond lengths (Å) and angles (°): N(1)···O(1) 2.974, H(1A)···O(1) 2.12, N(1)−H(1A)···O(1) 176; N(1)···O(5) 3.056, H(1B)···O(5) 2.24, N(1)−H(1B)···O(5) 158; N(2)···O(5) 3.010, H(2A)···O(5) 2.16, N(2)−H(2A)···O(5) 170; N(2)···O(2) 3.008, H(2B)···O(2) 2.15, N(2)−H(2B)···O(2) 176; N(3)···O(4) 3.061, H(3A)···O(4) 2.20, N(3)−H(3A)···O(4) 177; N(3)···O(6) 3.038, H(3B)···O(6) 2.20, N(3)−H(3B)···O(6) 165; N(4)···O(3) 3.050, H(4A)···O(3) 2.21, N(4)−H(4A)···O(3) 167; N(4)···O(4) 3.053, H(4B)···O(4) 2.20, N(4)−H(4B)···O(4) 175; N(5)···O(6) 2.981, H(5A)···O(6) 2.12, N(5)−H(5A)···O(6) 174; N(5)···O(3) 3.046, H(5B)···O(3) 2.20, N(5)−H(5B)···O(3) 166; N(6)···O(2) 3.021, H(6A)···O(2) 2.18, N(6)−H(6A)···O(2) 166; N(6)···O(1) 2.981, H(6B)···O(1) 2.13, N(6)−H(6B)···O(1) 171; (bottom) side-on view of one of the GS sheets in the structure of **1**

The gold complex Na[AuCl(**L**)] was formed from the reaction of [AuCl(SC$_4$H$_8$)] and Na[**L**] in acetone, and recrystallised from methanol. Metathesis of Na[AuCl(**L**)] with guanidinium chloride in methanol gave colourless crystals of [C(NH$_2$)$_3$][AuCl(**L**)] (**2**) which were suitable for X-ray crystallography. The structural analysis of **2** showed the presence of one guanidinium cation and one [AuCl(**L**)]$^-$ anion in the asymmetric unit. As in **1**, the sulfonate groups form quasihexagonal hydrogen-bonded arrays through N−H···O interactions with guanidinium cations, and these lead to the formation of GS sheets [Figure 2 (top)]. Although the interactions within the sheets are similar to those in **1**, there are two main differences. Firstly, the presence of the AuCl group coordinated to each phosphane serves to flatten the sheets, and the inter-ribbon angle in **2** is increased to 161° [Figure 2 (bottom)]. In other GS sheet structures, increase in steric bulk or inclusion of guest molecules can have the effect of reducing the degree of distortion from planarity, hence the AuCl group can be regarded as a "guest" within the [C(NH$_2$)$_3$][**L**] lattice, albeit one with a directional coordination binding site. Secondly, the quasihexagonal sheets are distorted such that the intra-ribbon S···S distance is increased to 8.105 Å, equal to the unit cell parameter *a*. In simple guanidinium sulfonate structures[3,4] closest S···S distances within the GS sheets range from 6.57 to 7.77 Å. The distortion of the GS sheets in **2** is also apparent in the values of the N−H···O angles.

These distortions are related to the interactions between the (triphenylphosphane)gold chloride units. Dance and Scudder have shown[10] the importance of interactions between multiple phenyl groups in the crystal structures of PPh$_3$ complexes. In **2**, *pseudo*-sixfold phenyl embraces serve to link the AuCl(PPh$_3$) units into chains running perpendicular to the direction of the hydrogen-bonded ribbons (Figure 3). In these *pseudo*-sixfold phenyl embraces, the AuCl unit acts in a similar manner to a phenyl group, so that each embrace involves three phenyl rings on one anion and two phenyl rings and the AuCl group on the other. These interactions bring the phosphorus atoms on closest phosphane groups to within 6.49 Å of each other, and position sulfur atoms from the same sheet at 11.29 Å, equal to the unit cell parameter *b*, from each other. *Pseudo*-sixfold phenyl embraces in which gold-containing groups are involved have been shown to be recurrent structural motifs in the crystal structures of gold-PPh$_3$ complexes.[11] Au···Au interactions have previously been exploited as crystal engineering tools in conjunction with hydrogen bond networks.[12] However, in the crystal structure of **2** there are no aurophilic interactions, the shortest Au···Au distance being 7.35 Å.

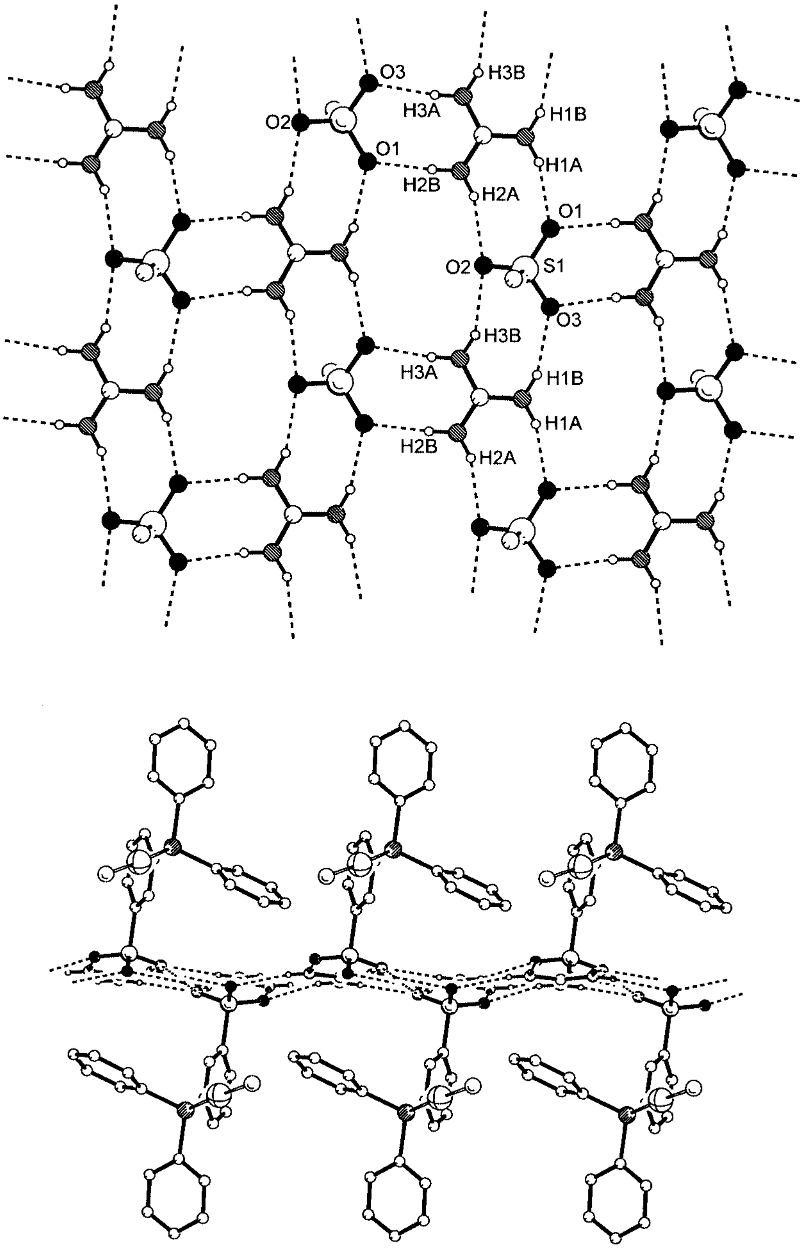

Figure 2. (top) Quasihexagonal hydrogen-bonded GS sheets in the crystal structure of $[C(NH_2)_3][AuCl(\mathbf{L})]$ (**2**); hydrogen bond lengths (Å) and angles (°): N(1)···O(1) 2.988, H(1A)···O(1) 2.16, N(1)−H(1A)···O(1) 157; N(1)···O(3) 3.030, H(1B)···O(3) 2.19, N(1)−H(1B)···O(3) 160; N(2)···O(2) 3.024, H(2A)···O(2) 2.19, N(2)−H(2A)···O(2) 159; N(2)···O(1) 2.907, H(2B)···O(1) 2.03, N(2)−H(2B)···O(1) 175; N(3)···O(3) 2.913, H(3A)···O(3) 2.05, N(3)−H(3A)···O(3) 169; N(3)···O(2) 3.049, H(3B)···O(2) 2.23, N(3)−H(3B)···O(2) 155; (bottom) side-on view of one of the GS sheets in the structure of **2**

The compounds Na[**LS**] and Na[**LSe**] were prepared from the oxidation of Na[**L**] with elemental sulfur or selenium in methanol. Metathesis with $[C(NH_2)_3]Cl$ in methanol gave colourless crystals of $[C(NH_2)_3][\mathbf{LS}]$ (**3**) and $[C(NH_2)_3][\mathbf{LSe}]$ (**4**) respectively. X-ray structural analyses of **3** and **4** showed that both compounds possess one cation and one anion in their asymmetric units, and that they are essentially isostructural. Both **3** and **4** are disordered with regard to the sulfonate oxygen atom positions (1:1 ratio between two sets of positions) and the guanidinium cations (2:1:1 ratio between three positions in **3**, 50:37:13 between similar positions in **4**). Although GS sheets are formed [Figure 4 (top)], the presence of this disorder makes an unambiguous evaluation of the inter-ribbon angle impossible, though estimated values of 150° for **3** and 153° for **4** suggest that, as anticipated, the Group 16 atom is less sterically demanding than the AuCl fragment [Figure 4 (bottom)]. The disorder in these structures can be rationalised by consideration of the interactions between the triphenylphosphane sulfide (or selenide) units.

In a similar manner to the (triphenylphosphane)gold chloride units in **2**, the triphenylphosphane sulfides and selenides form *pseudo*-sixfold phenyl embraces involving three phenyl rings on one anion and two phenyl rings and the

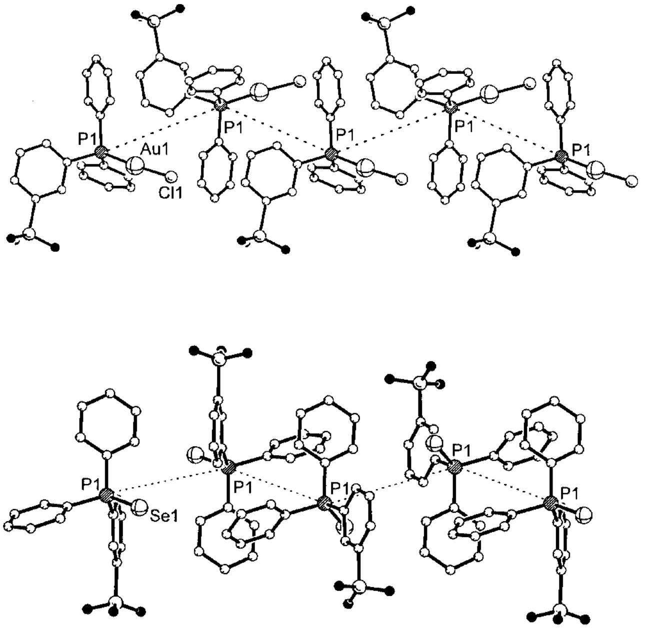

Figure 3. *Pseudo*-sixfold phenyl embraces linking the anions into chains in the crystal structures of $[C(NH_2)_3][AuCl(\mathbf{L})]$ (**2**) and $[C(NH_2)_3][\mathbf{L}Se]$ (**4**)

Group 16 atom on the other. These embraces lead to the formation of chains running in the same direction as the hydrogen-bonded ribbons, which possess closest P···P distances of 6.17 Å for **3** and 6.27 Å for **4** (Figure 3). This chain formation ensures that sulfonate groups within the same sheet are positioned with S···S distances of 9.27 Å for **3** and 9.49 Å for **4**, in both cases equal to the respective unit cell parameter *b*. In addition to these interactions, each triphenylphosphane sulfide or selenide unit forms a second *pseudo*-sixfold phenyl embrace, approximately perpendicular to the first, in this case arising from neighbouring centrosymmetrically related pairs of anions, and involving two phenyl rings and the Group 16 atom. This interaction leads to P···P distances of 5.75 Å and 5.90 Å for **3** and **4**, respectively. Both types of *pseudo*-sixfold phenyl embrace are also observed in the crystal structures of Ph_3PS[13] and Ph_3PSe,[14] and together they serve to dictate the relative positions of the sulfonate groups in **3** and **4**. These groups are too close together for the guanidinium cations to form regular hydrogen bonding patterns, and as a consequence the cations are disordered. In one of the three orientations, N−H groups are directed out of the plane of the GS sheets, and form N−H···S or N−H···Se hydrogen bonds to the sulfide or selenide together with $R_2^1(6)$ rings [N(1B)···S(1) 3.35(1), H(1B2)···S(1) 2.52(1) Å, N(1B)−H(1B2)···S(1) 157(1)° and N(3B)···S(1) 3.41(1), H(3B1)···S(1) 2.61(1) Å, N(3B)−H(3B1)···S(1) 151(1)° for **3**; N(1B)···Se(1) 3.29(2), H(1B1)···Se(1) 2.46(2) Å, N(1B)−H(1B1)···Se(1) 158(1)° and N(3B)···Se(1) 3.44(3), H(3B2)···Se(1) 2.67(2) Å, N(3B)−H(3B2)···Se(1) 148(2)° for **4**].

The complex $Na_2\{cis\text{-}[PdCl_2(\mathbf{L})_2]\}$ was formed from the reaction of [PdCl₂(cod)] with Na[**L**] in acetonitrile/methanol. Metathesis of this sodium salt with guanidinium nitrate in the same solvent mix gave several products including small, yellow crystals of $[C(NH_2)_3]_2\{cis\text{-}[PdCl_2(\mathbf{L})_2]\}$ (**5**) suitable for analysis at the SRS facility. The structural analysis of **5** showed the presence of GS sheets [Figure 5 (top)], with both of the sulfonate groups from each complex anion incorporated into the same sheet. The hydrogen bonding patterns in **5** are less regular than those observed in **1** and **2**. Only two of the six independent guanidinium faces are involved in DD:AA interactions. Of the remaining faces, two form $R_2^1(6)$ rings with sulfonate oxygen atoms whereas another forms bifurcated N−H···O hydrogen bonds. The final guanidinium face is not involved in any N−H···O hydrogen bonding, instead forming N−H···Cl interactions to the metal-bound chlorides.[15] The distortions from the regular pattern observed for **1** and **2** are a consequence of the distance constraint imposed by virtue of the two sulfonate groups arising from the same anion (S···S 9.21 Å) coupled with the triangular shape of the guanidinium cation. It is not possible to orientate the cation to enable it to form two N−H···O hydrogen bonds with both sulfonates as the groups are too far apart.

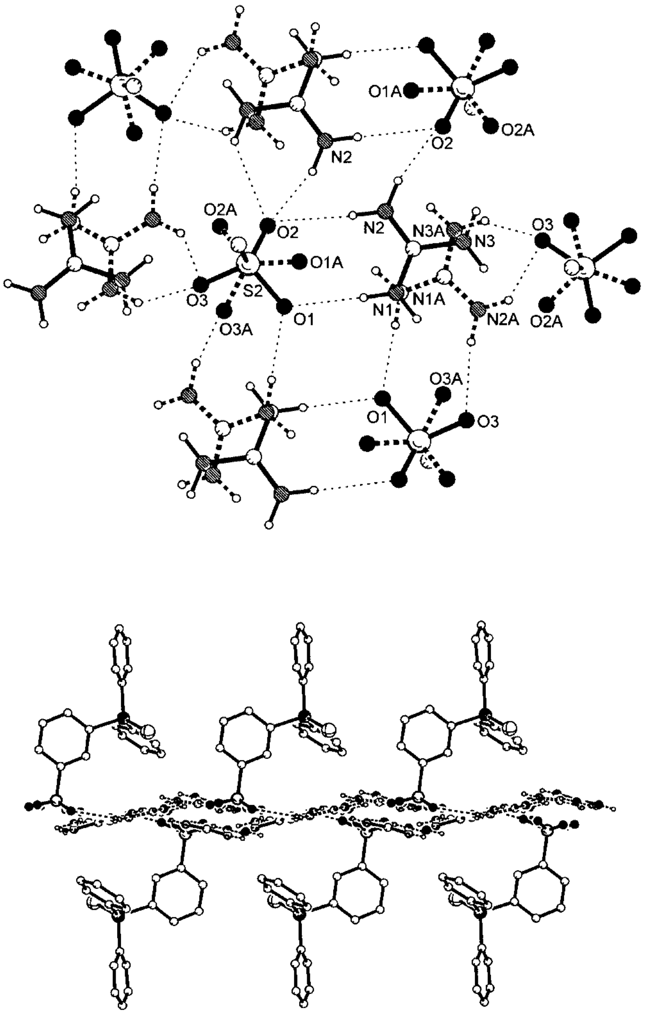

Figure 4. (top) GS sheet formation in $[C(NH_2)_3][\mathbf{L}S]$ (**3**); for the guanidinium cations only two of the three positions are shown for clarity; (bottom) side-on view of one of the GS sheets in the structure of **3**

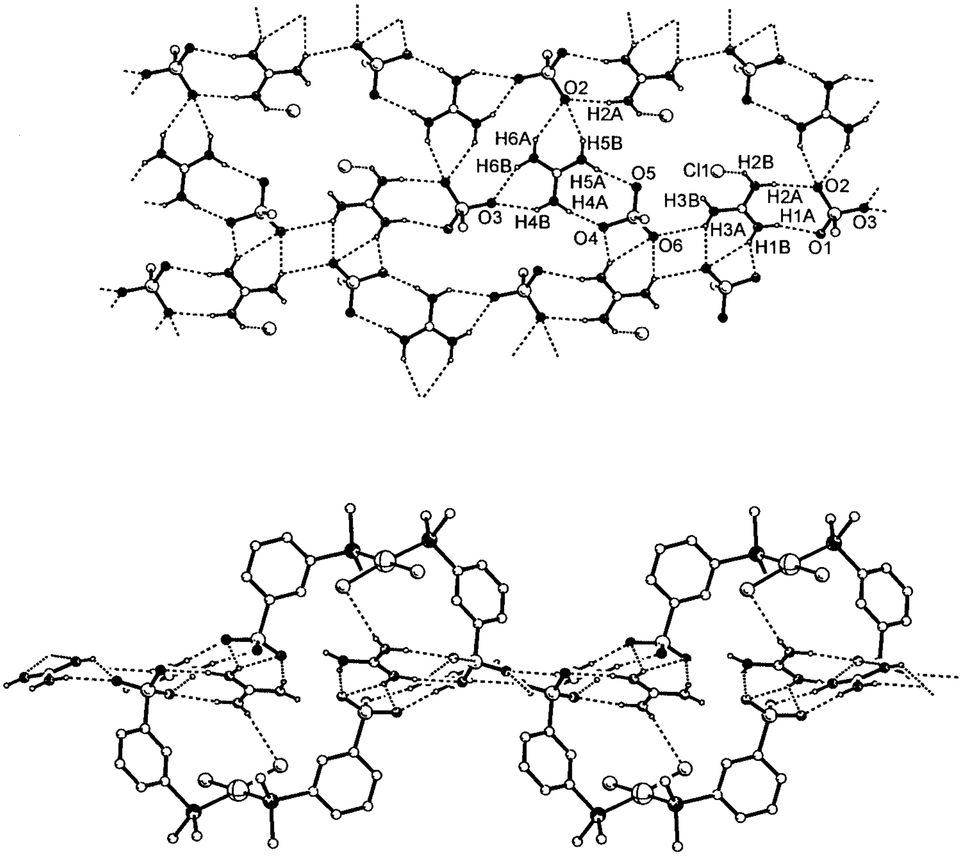

Figure 5. (top) GS sheet formation in $[C(NH_2)_3]_2\{cis\text{-}[PdCl_2(\mathbf{L})_2]$ (**5**); hydrogen bond lengths (Å) and angles (°): N(1)$\cdots$O(1) 2.911, H(1A)$\cdots$O(1) 2.06, N(1)−H(1A)$\cdots$O(1) 162; N(1)$\cdots$O(4) 2.893, H(1B)$\cdots$O(4) 2.12, N(1)−H(1B)$\cdots$O(4) 146; N(1)$\cdots$O(6) 3.219, H(1B)$\cdots$O(6) 2.43, N(1)−H(1B)$\cdots$O(6) 150; N(2)$\cdots$O(2) 2.902, H(2A)$\cdots$O(2) 2.04, N(2)−H(2A)$\cdots$O(2) 168; N(2)$\cdots$Cl(1) 3.253, H(2B)$\cdots$Cl(1) 2.56, N(2)−H(2B)$\cdots$Cl(1) 136; N(3)$\cdots$O(6) 3.140, H(3A)$\cdots$O(6) 2.32, N(3)−H(3A)$\cdots$O(6) 154; N(3)$\cdots$O(6) 3.003, H(3A)$\cdots$O(6) 2.50, N(3)−H(3A)$\cdots$O(6) 117; N(4)$\cdots$O(4) 2.810, H(4A)$\cdots$O(4) 1.94, N(4)−H(4A)$\cdots$O(4) 168; N(4)$\cdots$O(3) 2.855, H(4B)$\cdots$O(3) 2.11, N(4)−H(4B)$\cdots$O(3) 142; N(5)$\cdots$O(5) 2.923, H(5A)$\cdots$O(5) 2.05, N(5)−H(5A)$\cdots$O(5) 171; N(5)$\cdots$O(2) 2.994, H(5B)$\cdots$O(2) 2.19, N(5)−H(5B)$\cdots$O(2) 153; N(6)$\cdots$O(2) 3.079, H(6A)$\cdots$O(2) 2.30, N(6)−H(6A)$\cdots$O(2) 147; N(6)$\cdots$O(3) 2.927, H(6B)$\cdots$O(3) 2.21, N(6)−H(6B)$\cdots$O(3) 139; (bottom) side-on view of one of the GS sheets in the structure of **5**; for clarity only the *ipso* carbon atoms on the unfunctionalised phenyl rings are shown

As with compounds **1−4**, the phosphanes are located on either side of the GS sheets [Figure 5 (bottom)]. Parallel fourfold phenyl embraces (P4PEs) link centrosymmetrically related pairs of phosphanes based on P(1), and pairs of phosphanes based on P(2), and, as in the structures of **2−4**, these interactions serve to constrain the distances between sulfonate groups.

The structures reported in this paper clearly demonstrate that sulfonated phosphane ligands and their metal complexes can be incorporated into hydrogen-bonded networks based on guanidinium sulfonate sheets. This system is sufficiently robust to cope with the increased steric bulk that accompanies inclusion of a coordination centre. The interactions between phosphane groups − involving C−H$\cdots\pi$ interactions and *pseudo*-sixfold phenyl embraces − observed in the crystal structures of molecules such as Ph_3PS and Ph_3PSe can be preserved in their guanidinium sulfonate adducts, and these are important in determining the relative positions of the sulfonate groups. Although the GS motif is flexible to a range of S$\cdots$S distances, if the sulfonates are positioned too closely to each other, guanidinium cations are unable to form regular hydrogen bonding patterns, and disorder in both the cation and the anion sulfonate groups is observed. In contrast, when the S$\cdots$S distance is constrained by having two sulfonate groups from the same complex incorporated into the same sheet, significant distortions from the quasihexagonal array may result.

Taken together, these structural analyses demonstrate that supramolecular interactions that are generally considered weak can compete effectively with strong hydrogen bonds in determining gross structures. Clearly, the disorder and the distortions observed in the GS networks in **3**, **4** and **5** occur with loss of some, but not all, of the stabilisation energy. Non-disordered structures in the cases of **3** and **4** would involve either steric clashes or voids within the structure, both of which are energetically unfavourable. Similarly, non-distorted GS sheets in **5** would result in unfavourable bond lengths and/or angles within the anions, which would also be energetically less favourable than the loss of hydrogen bonding in the distorted GS network.

We are currently exploring the use of bis(phosphane) complexes containing unsaturated metal centres to bridge between GS sheets with a view to exploring the reversible coordination of small molecules.

Experimental Section

Synthesis of metal complexes of [**L**]$^-$ were routinely carried out using Schlenk-line techniques under pure dry dinitrogen using dioxygen-free solvents. Metathesis reactions were carried out with no special precautions to exclude air. Microanalyses (C, H and N) were carried out by Mr. Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet Nexus FT-IR spectrometer as KBr pellets. The compounds Na[**L**][16] and [AuCl(SC$_4$H$_8$)][17] was prepared according to the literature methods.

Synthesis of Na[AuCl(L)]: Na[**L**] (0.182 g, 0.50 mmol), dissolved in acetone (10 cm^3) was added to a solution of [AuCl(SC$_4$H$_8$)] (0.158 g, 0.50 mmol) in acetone (10 cm^3). The resultant solution was stirred for 2 h, filtered, and the solvent removed in vacuo. Recrystallisation from methanol gave a colourless crystalline material. Yield 0.188 g (64%). ^{31}P NMR (CD$_3$OD): $\delta = 46.0$ (s) ppm. IR: ν(SO$_3$) 1670s cm^{-1} (br).

Synthesis of Na[AuCl(LS)]: An excess of elemental sulfur was added to a solution of Na[**L**] (0.200 g, 0.55 mmol) in wet methanol (30 cm^3) and the mixture stirred vigorously for 3 h. Unreacted sulfur was removed by filtration, then the solvent was removed in vacuo and the crude solid recrystallised from methanol. Yield 0.191 g (88%). ^{31}P NMR (CD$_3$OD): $\delta = 46.3$ (s) ppm.

Na[AuCl(**LSe**)] was prepared in an analogous manner using elemental selenium.

Synthesis of Na$_2${*cis*-[PdCl$_2$(L)$_2$]}: A solution of Na[**L**] (0.276 g, 0.70 mmol) in methanol (25 cm^3) was added dropwise with stirring to a solution of [PdCl$_2$(cod)] (0.100 g, 0.35 mmol) in acetonitrile (30 cm^3) giving a slight darkening of colour. Stirring was continued for 45 min, and then the solvent was removed in vacuo and the crude yellow-orange solid recrystallised from methanol. Yield 0.235 g (74%). ^{31}P NMR (CD$_3$OD): $\delta = 25.6$ (s) ppm. IR: ν(SO$_3$) 1641s cm^{-1} (br), 1536s.

Synthesis of [C(NH$_2$)$_3$][L] (1): Na[**L**] (0.100 g, 0.27 mmol) and [C(NH$_2$)$_3$]Cl (0.026 g, 0.27 mmol) were dissolved in methanol (10 cm^3), and the solvent allowed to slowly evaporate. After two weeks colourless crystals were harvested. Yield 0.077 g (70%). C$_{19}$H$_{20}$N$_3$O$_3$PS (401.4): calcd. C 56.9, H 5.02, N 10.5; found C 57.2, H 4.99, N 10.0. IR: ν(NH) 3380s cm^{-1} (br), 3195s (br); ν(SO$_3$)/δ(NH$_2$) 1684s, 1571s, 1431m.

Synthesis of [C(NH$_2$)$_3$][AuCl(L)] (2): Na[AuCl(**L**)] (0.100 g, 0.17 mmol) and [C(NH$_2$)$_3$]Cl (0.016 g, 0.17 mmol) were dissolved in methanol (10 cm^3), and the solvent allowed to slowly evaporate. After one week colourless crystals were harvested. Yield 0.085 g (80%). C$_{19}$H$_{20}$AuClN$_3$O$_3$PS (633.8): calcd. C 36.0, H 3.18, N 6.63; found C 36.0, H 3.16, N 6.44. IR: ν(NH) 3400s cm^{-1} (br), 3273s, 3202s; ν(SO$_3$)/δ(NH$_2$) 1684s, 1569m, 1479m.

Synthesis of [C(NH$_2$)$_3$][LS] (3): Na[**LS**] (0.100 g, 0.25 mmol) and [C(NH$_2$)$_3$]Cl (0.024 g, 0.23 mmol) were dissolved in methanol (10 cm^3), and the solvent allowed to slowly evaporate. After two weeks colourless crystals were harvested. Yield 0.085 g (80%). C$_{19}$H$_{20}$N$_3$O$_3$PS$_2$ (433.5): calcd. C 52.2, H 4.65, N 9.70; found C 52.6, H 4.51, N 9.60. IR: ν(NH) 3388s cm^{-1} (br), 3208s (br); ν(SO$_3$)/δ(NH$_2$) 1664s, 1577s, 1431s.

Crystals of [C(NH$_2$)$_3$][**LSe**] **4** were prepared in a similar manner from Na[**LSe**] and [C(NH$_2$)$_3$]Cl.

Synthesis of [C(NH$_2$)$_3$]$_2${*cis*-[PdCl$_2$(L)$_2$]} (5): Na$_2${*cis*-[PdCl$_2$(**L**)$_2$]} (0.050 g, 0.045 mmol) in methanol (5 cm^3) was added to [C(NH$_2$)$_3$]NO$_3$ (0.013 g, 0.10 mmol) in acetonitrile (5 cm^3). The solvent was allowed to slowly evaporate, and after two weeks small yellow crystals were obtained.

Crystallography

Single crystals of compounds **1**−**5** were prepared by the methods above. Data were collected using a Enraf−Nonius CAD4 automatic four-circle diffractometer for **1** and a Nonius Kappa CCD diffractometer for **2**, **3** and **4**. Crystals of **5** were too small to ana-

Table 1. Crystal data for compounds **1**−**5**

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	C$_{19}$H$_{20}$N$_3$O$_3$PS	C$_{19}$H$_{20}$AuClN$_3$O$_3$PS	C$_{19}$H$_{20}$N$_3$O$_3$PS$_2$	C$_{19}$H$_{20}$N$_3$O$_3$PSSe	C$_{38}$H$_{40}$Cl$_2$N$_6$O$_6$P$_2$PdS$_2$
M	401.41	633.83	433.47	480.37	980.12
Temperature/K	296(2)	170(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$Pca2_1$	$P2_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	19.4240(10)	8.1050(4)	14.3160(4)	14.4130(2)	10.145(2)
b (Å)	7.969(5)	11.2910(5)	9.2710(3)	9.49200(10)	12.763(3)
c (Å)	25.621(4)	12.1120(6)	16.1200(7)	16.0910(2)	17.019(4)
α (°)					85.125(9)
β (°)		98.475(3)	108.1670(10)	107.9850(10)	84.163(9)
γ (°)					79.192(9)
V (Å^3)	3966(3)	1096.31(9)	2032.85(12)	2093.81(4)	2148.4(9)
Z	8	2	4	4	2
μ(Mo-K_α) (mm^{-1})	0.268	7.025	0.366	1.994	0.780
Reflections collected	3733	13383	29789	19837	11184
Independent reflections	3571	4567	3543	3698	7062
R(int)	0.0089	0.0495	0.0931	0.0782	0.0322
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0541, 0.1357	0.0345, 0.0762	0.0482, 0.1071	0.0410, 0.0898	0.0578, 0.1294
R indices (all data)	0.0788, 0.1486	0.0374, 0.0773	0.0809, 0.1230	0.0787, 0.1056	0.0706, 0.1352

lyse at Bath so data were collected at Station 9.8 of the SRS, Daresbury. Corrections for Lorentz and polarisation were implemented in all cases, with extinction corrections being merited for **2** and **3**. All atoms were refined anisotropically. Absorption corrections were also applied to data for **2** and **4**. In **2**, the largest residual peak and hole are proximate to C(11) (1.54 Å) and Au(1) (0.84 Å) respectively. These are artifacts of the data and are not chemically significant. Details of the data collections and structure solutions are given in Table 1.

As mentioned above, the structures of **3** and **4** were subject to considerable disorder. In **3**, there was 1:1 disorder of sulfonate oxygens between O(1)−O(3) and O(1A)−O(3A). Threefold disorder was also observed in the guanidinium moiety (ratio 2:1:1) between atoms labelled therein without suffix, atoms with suffix "A" and atoms with suffix "B" respectively. These fragments were refined subject to being flat, and atomic displacement parameters therein were also constrained. Compound **4**, which is isostructural with **3**, was treated similarly during refinement, with the exception of the occupancies assigned to the disordered guanidinium fragments. All structures were solved using SHELXS-97 and refined using SHELXL-97.[18] Hydrogen atoms were readily located in the penultimate difference Fourier maps for the non-disordered structures **1**, **2** and **5** but in the final least-squares cycles they were included at calculated positions throughout.

CCDC-191297 (**1**), -191298 (**2**), -191299 (**3**), -191300 (**4**) and -191301 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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