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Anion coordination and molecular assembly in C2-substituted thiamine–anion systems: effects of the anion and molecular conformation

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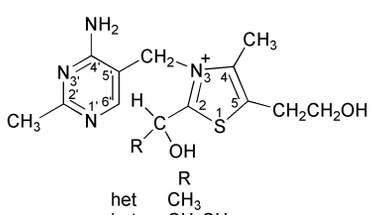
The compounds (het)($PtCl_6$)·$2H_2O$ **1**, (het)(HgI_4)·H_2O **2** (het = 2-(α-hydroxyethyl)thiamine) and (hpt)(Hg_2Br_6) **3** (hpt = 2-(α-hydroxypropyl)thiamine) have been prepared and structurally characterized by X-ray crystallography in order to study the influence of the anion and molecular conformation on the formation of supramolecular architectures that adsorb anionic species. Both het and hpt molecules adopt the usual *S* conformation for C2-substituted thiamine but differ from the *F* conformation for C2-free thiamine derivatives. Two types of characteristic ligand–anion complexation are observed, being of the forms C(6′)–H ··· anion ··· thiazolium-ring (in **1** and **2**) and N(4′1)–H ··· anion ··· thiazolium-ring (in **3**). The reaction of het with $PtCl_6^{2-}$ or HgI_4^{2-} gives a 1-D double-chain in **1**, consisting of two hydrogen-bonded het chains, which are cross-linked by anions through hydrogen bonding and anion ··· aromatic-ring interactions, or a cationic 3-D framework in **2** formed by the stacking of hydrogen-bonded sheets with anion-and-water-filled channels. In the case of **3**, hydrogen-bonded hpt dimers and $HgBr_6^{2-}$ anions form alternate cation–anion columns. A comparison with the cases of C2-free thiamine–anion complexes indicates that the change in molecular conformation results in novel supramolecular assemblies in **1** and **2** and an analogous architecture in **3**, which also depends on the nature of the anions.

Introduction

Anion coordination chemistry is of great current interest involving the design of anion receptors and anion-directed molecular assembly.[1] The supramolecular architectures that adsorb anionic or neutral species can be constructed through metal coordination,[2] which results in extended frameworks comprised of metal ions and ligands linked *via* coordination bonds, or through non-covalent forces[3] such as hydrogen bonds and π–π interactions, by which networks are assembled from building blocks with functional groups, or through a combination of both routes.[4] A large number of different selective intermolecular connections have been developed to generate a variety of multi-dimensional molecular arrays.[5] However, the control of self-assembled arrays with predictable structures is still a great challenge in crystal engineering.

Thiamine (vitamin B_1), in its pyrophosphate form, is a coenzyme for a number of metabolic enzymes.[6] We have demonstrated that thiamine, as a naturally occurring cationic host, is capable of not only binding anions through a combination of hydrogen bonding and anion ··· aromatic-ring interactions but, as a building block, self-assembling into highly ordered supramolecular structures.[7] There are three types of characteristic anion-bridging interactions between thiamine and any anion guest: C(2)–H ··· anion ··· pyrimidine-ring, N(4′1)–H ··· anion ··· thiazolium-ring and C(6′)–H ··· anion ··· thiazolium-ring, which have been defined as 'anion-bridges I, II and III', respectively.[8] Structural studies have revealed that the anion coordination is closely related to the molecular conformation of thiamine, the relative orientation of the thiazolium and pyrimidine rings arising from the rotations around the two single bonds of the methylene group. The 'anion-bridge I' is peculiar to the molecule adopting the *F* conformation and the 'anion-bridges II and III' may occur for both the *F* and *S* conformations (torsion angle φ_T = C(5′)–C(35′)–N(3)–C(2) is approximately 0° and φ_P = N(3)–C(35′)–C(5′)–C(4′) approximately ±90° for the *F* conformation and φ_T is approximately ±100° and φ_P approximately ±150° for the *S* conformation[9]). The supramolecular architectures in thiamine–anion systems proved to be dependent on, at least in part, the nature of the anions. For example, anions I^-,[10a] ClO_4^-, PF_6^- [10b] and BF_4^- [10c,d] facilitate the formation of a helical chain with thiamine molecules hydrogen-bonded in a 'head-to-tail' fashion ('head' refers to the pyrimidine ring and 'tail' to the hydroxyethyl side chain) while a molecular column made up of alternating thiamine dimers and anions is common in the cases of platinate anions $PtCl_4^{2-}$,[11] $PtCl_6^{2-}$ [7a] and $Pt(NO_2)_4^{2-}$.[7b] However, the observation that thiamine adopts the *F* conformation in all of the above structures prompted such considerations as what architectures form and how the anions influence the molecular assembly if thiamine is in the *S* conformation.

C2-substituted thiamine pyrophosphate is a reaction intermediate of thiamine catalysis.[12] It is known that the C2-substituted thiamine derivatives assume the *S* conformation due to the steric hindrance between the substituent and the pyrimidine ring.[13] We have shown that in the structures of 2-(α-hydroxybenzyl)thiamine (hbt) complexes, the crystal packing is mainly dominated by π–π interactions between the pyrimidine ring and the substituted benzyl ring.[14] We now introduce methyl or ethyl groups in place of the benzyl ring (Scheme 1) in an attempt to examine the effects of the substitution and the molecular conformation on anion coordination and molecular assembly in the C2-substituted thiamine–anion systems. The structural



R
het CH_3
hpt CH_2CH_3
hbt C_6H_5

Scheme 1

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Table 1 Selected torsion angles (°) of het and hpt molecules in **1**, **2** and **3**

	1	**2**	**3**
φ_T = C(5′)–C(35′)–N(3)–C(2)	−106.2(7)	−102.3(9)	−96.2(12)
φ_P = N(3)–C(35′)–C(5′)–C(4′)	−167.2(5)	176.1(7)	−173.8(9)

studies of (het)($PtCl_6$)·$2H_2O$ **1**, (het)(HgI_4)·H_2O **2** and (hpt)-(Hg_2Br_6) **3** (het = 2-(α-hydroxyethyl)thiamine and hpt = 2-(α-hydroxypropyl)thiamine) present architectures constructed from het or hpt building blocks with different topologies, which depend on the nature of the anions and the molecular conformation.

Results and discussion

Structures of (het)($PtCl_6$)·$2H_2O$ 1, (het)(HgI_4)·H_2O 2 and (hpt)(Hg_2Br_6) 3

In complexes **1**, **2** and **3**, the het and hpt molecules bear two positive charges because of the quaternary N(3) of the thiazolium ring and the protonation at N(1′) of the pyrimidine ring. As expected, both het and hpt molecules adopt the *S* conformation in terms of the torsion angles given in Table 1. The *S* conformation makes the C(6′)–H bond point over the thiazolium ring while the *F* conformation is characterized by the C(2)–H bond pointing over the pyrimidine ring.

Fig. 1 shows the molecular structure of **1**. As observed

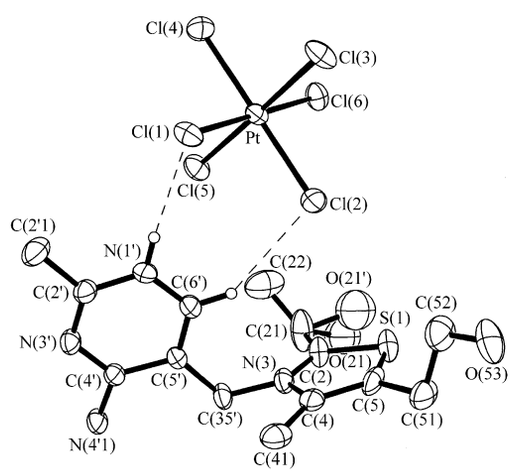

Fig. 1 Molecular structure of **1**, together with the atomic numbering scheme adopted in **1**, **2** and **3**, showing that the het molecule interacts with the $PtCl_6^{2-}$ anion through a C(6′)–H ··· Cl(2) ··· thiazolium interaction ('anion-bridge III'), and an N(1′)–H ··· Cl(1) hydrogen bond. Displacement ellipsoids are drawn at the 30% probability level. Broken lines denote hydrogen bonds (similarly hereinafter). O(21) is disordered over two positions. Water molecules and hydrogen atoms, except those involved in hydrogen bonds, are not shown.

in previous studies[8c,14] the anions may bind to the thiamine derivative in the *S*-form by forming 'anion-bridges II and/or III', the octahedral $PtCl_6^{2-}$ anion in **1** forms the 'anion-bridge III' by accepting a hydrogen bond from C(6′)–H (Table 2), and locating over the thiazolium ring (the closest distance Cl(2) ··· S(1), Table 2). This anion also participates in the formation of an N(1′)–H ··· Cl(1) hydrogen bond with the same het molecule. Fig. 2 shows that the het molecules each with a $PtCl_6^{2-}$ anion attached are self-associated into a 1-D molecular chain through hydrogen bonds between the amino group of one molecule and the hydroxyethyl O(53) of another in a 'head-to-tail' fashion. The two anti-parallel molecular chains are further associated by the electrostatic interactions between the attached $PtCl_6^{2-}$ anion and the pyrimidinium ring from the paring chain (the shortest contact Cl(3) ··· C(2′),

Table 2 Selected hydrogen bonds and close contacts in **1**

Hydrogen bonds			
D(–H) ··· A	D ··· A/Å	H ··· A/Å	D–H ··· A/°
N(1′) ··· Cl(1)	3.231(5)	2.38	171
C(6′) ··· Cl(2)	3.557(6)	2.73	149
N(4′1) ··· O(53)^{i}	2.819(7)	1.96	174
N(4′1) ··· O(W1)	2.997(7)	2.17	161

Close contacts	Distance/Å		Distance/Å
Cl(1) ··· N(1′)^{ii}	3.604(5)	Cl(3) ··· C(2′)^{ii}	3.335(6)
Cl(1) ··· C(6′)^{ii}	3.561(6)	Cl(4) ··· C(2)^{iii}	3.503(8)
Cl(2) ··· S(1)	3.911(3)	Cl(4) ··· N(3)^{iii}	3.307(5)
Cl(3) ··· C(4)^{iii}	3.592(6)	Cl(5) ··· N(1′)	3.475(5)
Cl(3) ··· N(1′)^{ii}	3.458(5)	Cl(6) ··· S(1)^{iv}	3.474(2)

Symmetry code: i $x-0.5, y+0.5, z$. ii $0.5-x, 1.5-y, -z$. iii $x, 1-y, z-0.5$. iv $0.5-x, 0.5-y, -z$.

Table 3 Selected hydrogen bonds and close contacts in **2**

Hydrogen bonds			
D(–H) ··· A	D ··· A/Å	H ··· A/Å	D–H ··· A/°
N(1′) ··· O(W)	2.774(12)	1.92	176
C(6′) ··· I(2)	3.985(8)	3.22	141
N(4′1) ··· N(3′)^{i}	3.016(9)	2.17	166
N(4′1) ··· O(53)^{ii}	2.994(10)	2.22	150
O(53) ··· I(4)^{iii}	3.648(7)	2.68	176
O(21) ··· I(1)	3.528(10)	2.63	152

Close contacts	Distance/Å		Distance/Å
I(1) ··· C(4′)^{iv}	3.669(8)	I(3) ··· N(3)^{v}	3.879(6)
I(1) ··· C(5′)^{iv}	3.952(7)	I(3) ··· C(2′)^{vi}	3.821(8)
I(2) ··· C(5)	4.023(10)	I(3) ··· N(3′)^{vi}	3.842(6)

Symmetry code: i $3-x, -y, 1-z$. ii $0.5+x, 0.5-y, z-0.5$. iii $1.5-x, 0.5+y, 1.5-z$. iv $2-x, -y, 1-z$. v $x-0.5, 0.5-y, 0.5+z$. vi $x-1, y, z$.

Table 2) to create a double-chain structure, which is distinct from the helical chain in thiamine structures.[10] The adjacent double-chains are connected by hydrogen bonds involving water molecules. The disordered hydroxy group of the C(2) substituent is directed to the outside of the double-chain and hydrogen-bonded to the disordered water molecules (not shown in Fig. 2).

Like **1**, the tetrahedral HgI_4^{2-} ion in **2** binds to het through an 'anion-bridge III', which involves a C(6′)–H ··· I(2) hydrogen bond and a somewhat weak electrostatic contact between I(2) and the thiazolium ring (the closest distance I(2) ··· C(5), Table 3). In contrast to the case of **1**, I(1) of the anion forms a hydrogen bond with the substituent O(21) instead of the pyrimidine N(1′), because of the large I ··· I distance in the tetrahedral geometry. As a consequence, nevertheless, a common feature for both **1** and **2** is that the anion is held between the pyrimidinium and thiazolium rings to form the host–guest-like complexation.

The combination of het and HgI_4^{2-} gives an entirely different supramolecular architecture from that of **1**. As shown in Fig. 3, the building block is the base-pairing dimer of het formed by a pair of complementary N(4′1)–H ··· N(3′) hydrogen bonds. The dimer is linked to the other four molecules by N(4′1)–H ··· O(53) hydrogen bonds involving the remaining H atoms of the amino groups, thus producing a 2-D network that exhibits a (4,4) topology.[5b] Each node of the net represents a collection of four hydrogen bonds in the present case, comparable to the case of metal coordination networks in which the nodes are coordinated metal centers, for example, the hydrogen-bond-linked Pt^{II} centers in the isonicotinic acid–platinum(II) complex[4a] and the π–π-interaction-linked Ni^{II} centers in the 4,4′-bpy–nickel(II) complex,[2b] both of which show a (4,4) topological net. Each cavity within the sheet encloses two anions

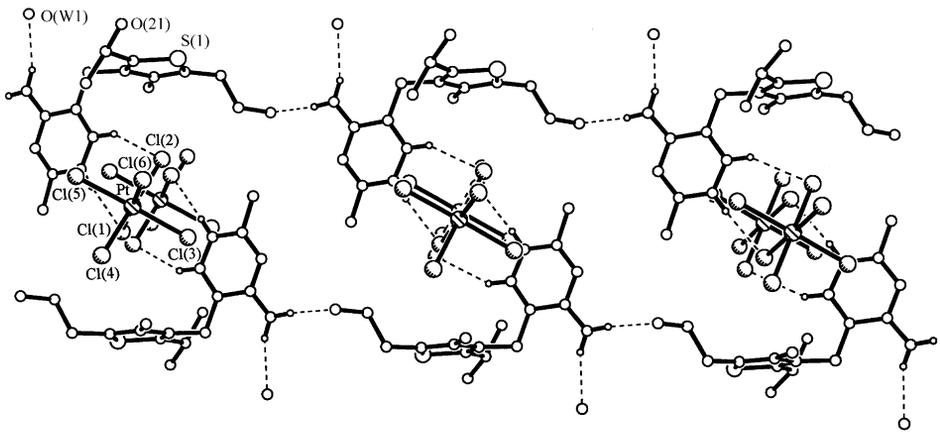

Fig. 2 View of a segment of the double-chain structure in **1**. The two hydrogen-bonded het chains are linked by $PtCl_6^{2-}$ anions through hydrogen bonds and anion ··· aromatic-ring interactions.

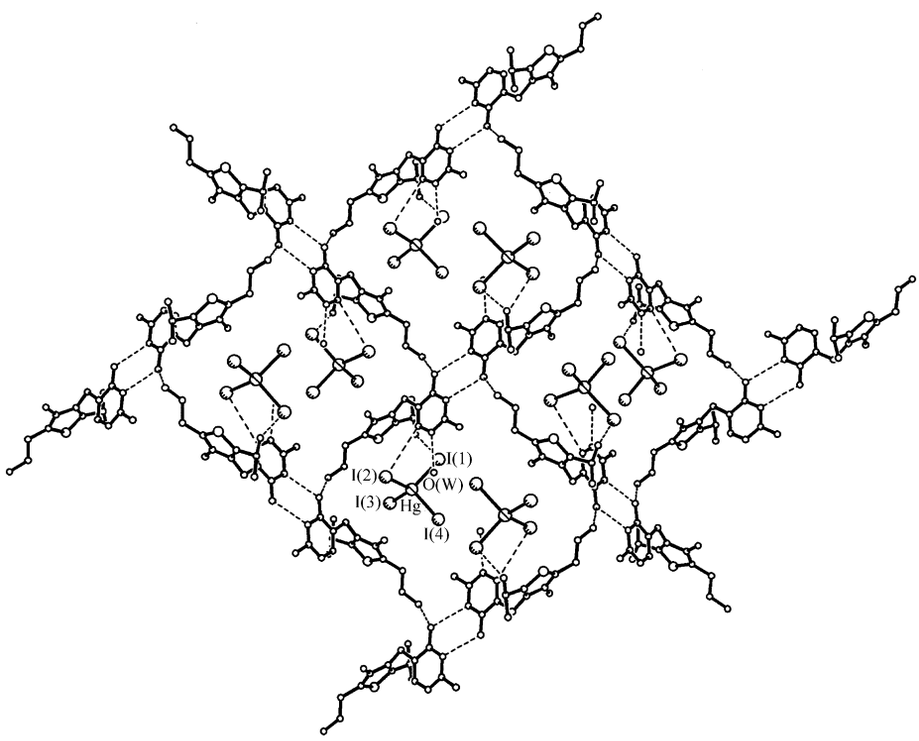

Fig. 3 Top view of a 2-D hydrogen-bonded network in **2**, illustrating the intermolecular connections and the square cavities occupied by anions and water molecules.

and two water molecules related to each other by an inversion center. It is interesting to note that the stacking of the undulated sheets gives a novel cationic framework with extended channels running along the *a* axis (Fig. 4), which are occupied by anion and water guests, although the sheets are staggered in the direction of the average plane. The HgI_4^{2-} anion is adsorbed in the channel mainly by hydrogen bonds from O(21), O(53) and C(6′) and electrostatic forces involving close contacts with thiazolium and pyrimidinium rings in the same sheet and the neighboring sheets.

The anion in **3** occurs as a binuclear $Hg_2Br_6^{2-}$ unit consisting of two edge-sharing tetrahedral Hg^{II} centers. The structure contains two crystallographically independent anions (*A* and *B*), each residing on a center of symmetry. The presence of the binuclear anions results in a distinct supramolecular structure. As shown in Fig. 5a, two hpt molecules self-assemble into a cyclic dimer in a 'head-to-tail' fashion through N(1′)–H ··· O(53) hydrogen bonds, and an anion *B* is sandwiched between the two dimers by O(21)–H ··· Br(5) hydrogen bonds and S(1) ··· Br(6) close contacts (Table 4). This arrangement is extended along the *c* axis to give a 1-D molecular column,

Table 4 Selected hydrogen bonds and close contacts in **3**

Hydrogen bonds			
D(–H) ··· A	D ··· A/Å	H ··· A/Å	D–H ··· A/°
N(1′) ··· O(53)^{i}	2.789(12)	1.94	170
N(4′1) ··· N(3′)^{ii}	3.056(13)	2.20	173
N(4′1) ··· Br(1)	3.478(10)	2.68	155
O(53) ··· Br(2)^{iii}	3.273(9)	2.52	153
O(21) ··· Br(5)	3.209(11)	2.44	156

Close contacts	Distance/Å		Distance/Å
Br(2) ··· N(3)	3.339(8)	Br(4) ··· N(1′)^{i}	3.441(10)
Br(2) ··· C(4)	3.466(10)	Br(4) ··· C(6′)^{i}	3.413(11)
Br(3) ··· N(1′)^{iv}	3.570(10)	Br(5) ··· C(6′)	3.563(11)
Br(3) ··· C(2′)^{iv}	3.473(13)	S(1) ··· Br(6)^{v}	3.506(3)

Symmetry code: i $1-x, 1-y, 1-z$. ii $1-x, 2-y, 2-z$. iii $-x, 1-y, 1-z$. iv $x-1, y, z$. v $1-x, 1-y, -z$.

[–D–A–D–A–], with alternating hpt dimers (D) and anions (A). Although analogous molecular columns have been found in the thiamine–platinate anion complexes[7,11] where thiamine adopts

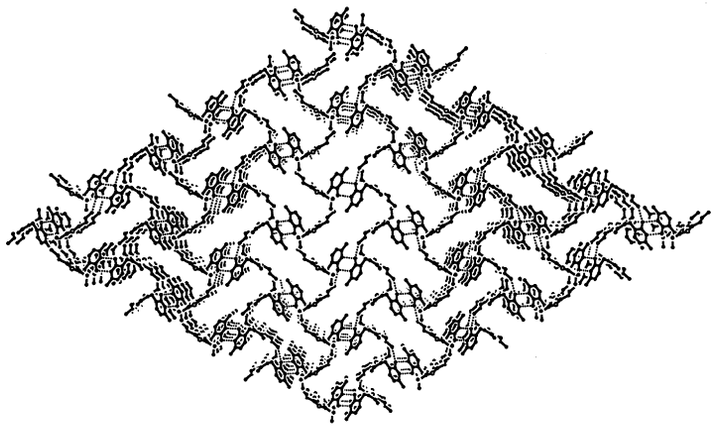

Fig. 4 A view of the 3-D cationic framework formed in **2** down the *a* axis showing the channels. Anion and water guests are omitted for clarity.

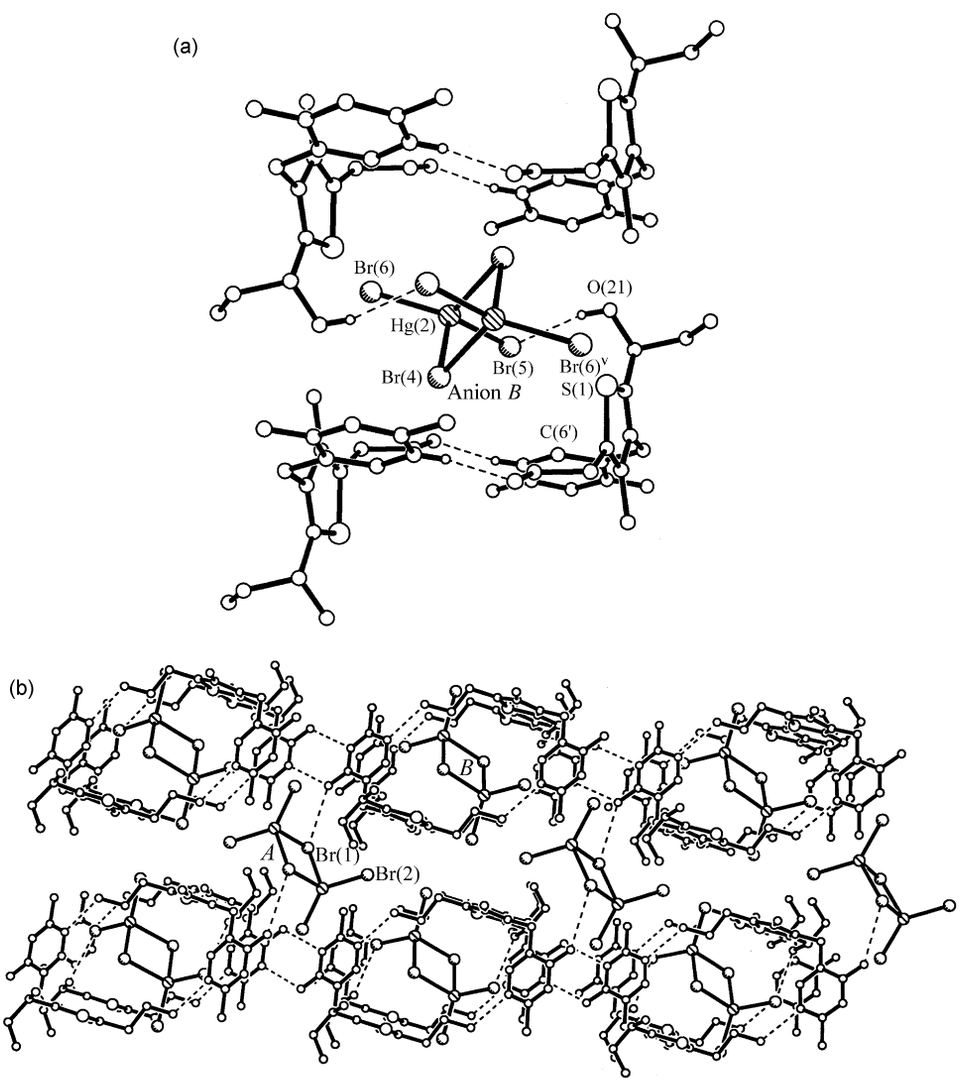

Fig. 5 (a) Side view of a molecular column unit in **3** showing how an anion *B* is sandwiched by two hpt dimers through O(21)–H ··· Br(5) hydrogen bonds and Br(6) ··· S(1) close contacts. (b) Top view of the molecular columns in **3** showing the connections between the columns.

the usual *F* conformation, this is the first observation of the thiamine derivative in the *S*-form. These molecular columns are connected to each other through base-pairing hydrogen bonds N(4′1)–H ··· N(3′) creating a 2-D layer. The anions *A* act as spacers and lie between the layers and cement them together through an 'anion-bridge II', that is, an N(4′1)–H ··· Br(1)–Hg(1)–Br(2) ··· thiazolium interaction, as illustrated in Fig. 5b. Neither anion *A* nor *B* is involved in the formation of an 'anion-bridge III' probably because of the large size of the binuclear coordination anion that precludes the anion from inserting between the pyrimidine and thiazolium rings.

Anion-induced assembly

We have noticed that thiamine as a multifunctional cationic ligand forms host–guest-like complexes with a wide range of anions and a variety of supramolecular structures could be

formed depending on the nature of the anions. It has been shown that the shape and size of the anions are important factors affecting the supramolecular structures of thiamine complexes.[8] For example, the 1-D columnar structure, [–D–A–D–A–], is commonly formed for the moderate-sized centrosymmetric $PtCl_4^{2-}$,[11] $PtCl_6^{2-}$ [7a] and $[Pt(NO_2)_4]^{2-}$ [7b] anions, which match the centrosymmetric cyclic dimer of thiamine, but is not formed for the large $[Pt(SCN)_4]^{2-}$ and $[Pt(SCN)_6]^{2-}$ anions [8a] and non-centrosymmetric $CuCl_4^{2-}$, and $CdCl_4^{2-}$ anions.[15] The formation of the columnar structure in **3** is in agreement with this observation in respect of the existence of the centrosymmetric $Hg_2Br_6^{2-}$ anion, despite its large size which may be a requirement of the *S* conformation (*vide infra*). The lack of a cyclic dimer structure for het in **1**, containing the centrosymmetric $PtCl_6^{2-}$ anion, may be due to the difference in anion coordination modes between **1** and the previously reported thiamine–$PtCl_6^{2-}$ complexes;[7a] that is, the $PtCl_6^{2-}$ anion is coordinated to het through an 'anion-bridge III' interaction in the former while it is joined to thiamine through an 'anion-bridge I' interaction in the latter. Moreover, the $PtCl_6^{2-}$ anion in **1** might not be as suitable in size as $Hg_2Br_6^{2-}$ in **3** for assisting the formation of the cyclic dimer of het in the *S*-form.

The present study also shows that the ability and the extent of the anion to act as a hydrogen-bonding acceptor could influence the molecular assembly. In the structure of (het)Cl_2,[13a] all the hydrogen-bonding donors of het donate their protons to Cl^- ions and thus no direct connections exist between the het molecules. In **1**, the het molecules are self-associated exclusively through N(4′1)–H ··· O(53) hydrogen bonds since the $PtCl_6^{2-}$ anions and water molecules compete for the other hydrogen-bonding sites on het. In contrast, when the more weakly electronegative I^- or Br^- ligands are present in **2** or **3**, two hydrogen bonds [N(4′1)–H ··· N(3′) and N(4′1)–H ··· O(53) in **2** or N(4′1)–H ··· N(3′) and N(1′)–H ··· O(53) in **3**] participate in the molecular self-assembly, leading to multi-dimensional structures.

It has been demonstrated that crystal packing in the hbt complexes[9,14] is controlled by intra- and inter-molecular π–π interactions between the benzyl and pyrimidine rings, resulting in similar packing modes in these complexes, while the methyl and ethyl substituents seem to have less effect on the molecular assembly, thus producing different crystal architectures in **1**–**3**.

Effects of the molecular conformations

It is worth noting the effects of the molecular conformations, *S* and *F*, on the molecular assembly process. In **1**, the steric constrains arising from the anion coordination through an 'anion-bridge III' probably preclude the formation of the cyclic dimer since the dimer in the *S*-form does not provide enough space to accommodate the anion which would lie inside the dimeric macrocycle, in marked contrast to the cases of the thiamine–$PtCl_6^{2-}$ complexes,[7a] where the cyclic dimer in the *F*-form is favored by the $PtCl_6^{2-}$ anion forming an 'anion-bridge I' outside the macrocycle. The large $Hg_2Br_6^{2-}$ anion in **3** forming hydrogen bonds with O(21)–H rather than forming an 'anion-bridge III' allows the formation of the cyclic dimer. On the other hand, it is evident from Fig. 6 that the molecular conformations cause different base-pairing dimers of thiamine, which are also common building blocks in thiamine structures. When thiamine assumes the *F* conformation the thiazolium rings can be *cis* (U-form) or *trans* (Z-form,) with respect to the base-pair plane. The U-form having C_2 symmetry has been observed in (Hthiamine)(thiamine)$(Hg_2I_7)\cdot 2CH_3OH\cdot H_2O$ [16a] and (tmp)$NO_3\cdot 2H_2O$ [8c] (tmp = thiamine monophosphate) and the Z-form having C_i symmetry occurs with higher frequency, for example, in (Hthiamine)(thiamine)$(Hg_2I_7)\cdot 2H_2O$,[16a] (Hthiamine)$[Pt(SCN)_4]\cdot 3H_2O$, (Hthiamine)$[Pt(SCN)_6]\cdot H_2O$,[8a] (tmp)$ClO_4\cdot H_2O$,[8c] (tmp)$(Hg_2Br_5)\cdot 0.5H_2O$ and (tmp)(Hg_3I_8).[16b]

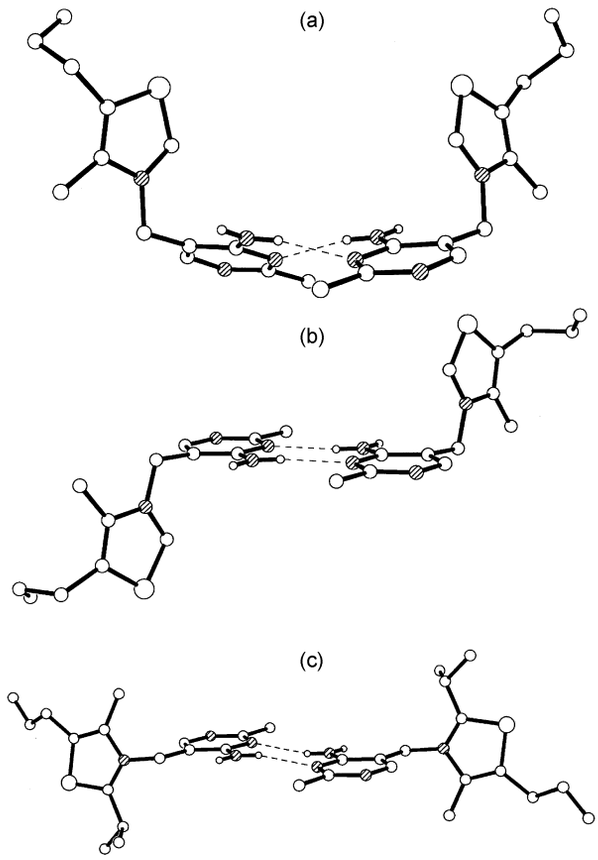

Fig. 6 Base-pairing dimers of thiamine derivatives in different forms indicating the effects of the molecular conformation; (a) the U-form for the thiamine dimer in the *F* conformation, (b) the Z-form for the thiamine dimer in the *F* conformation and (c) the hpt dimer in the *S* conformation (nitrogen, right hatch; others, circle).

When thiamine assumes the *S* conformation, a relatively extended dimer like that in **2** and **3** can be formed (Fig. 6c).

Thermal stability

Thermogravimetric analysis (TGA) was performed under a flow of nitrogen gas. A TGA study on **1** shows a weight loss of 5.3% at 42–97 °C corresponding to the loss of lattice water (calc. 4.8%). The next weight loss 41.2% at 210–424 °C agrees well with the calculated value of 41.2% arising from the release of one het per formula unit. After a total loss of 74.4% of the weight (calc. 74.1%) as the temperature approaches 457 °C, metallic Pt is left. The TGA curve of **2** reveals an initial weight loss of 1.8% at 47–104 °C corresponding to the loss of a water molecule (calc. 1.7%). An almost continuous weight loss is then observed in the range 171–650 °C, probably due to a complex event caused by the decomposition of het and the counter ion. The curve of **3** is similar to that of **2** with the decomposition starting at 184 °C, however no initial loss of water is observed. Crystalline samples of **1** and **2** were heated to 70 °C under reduced pressure for 1 h to remove the water. The dehydrated compounds both give sharp peaks in the X-ray powder diffraction pattern, indicating that the samples remain crystalline when the crystallized water molecules are absent.

Conclusion

The present study shows that coordination of anions to het and hpt results in a 1-D double-chain cross-linked by $PtCl_6^{2-}$ anions in **1** and a 3-D cationic framework with channels filled by HgI_4^{2-} anions and water guests in **2**, which are distinct from the supramolecular structures in the C2-free thiamine–anion systems, and a molecular column in **3** similar to that in the

Table 5 Details of crystal data and structure refinements for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{14}H_{26}Cl_6N_4O_4PtS$	$C_{14}H_{24}HgI_4N_4O_3S$	$C_{15}H_{24}Br_6Hg_2N_4O_2S$
M	754.24	1036.62	1205.08
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a/Å	21.022(5)	10.109(2)	11.049(5)
b/Å	11.702(2)	20.755(3)	15.229(4)
c/Å	21.519(5)	12.601(2)	8.243(2)
α/°	90	90	95.61(2)
β/°	105.87(2)	92.64(2)	98.67(3)
γ/°	90	90	94.53(3)
U/Å^3	5092(2)	2641.1(8)	1358.4(8)
Z	8	4	2
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	6.25	10.60	20.21
Reflections collected	6430	6734	6914
Unique reflections (R_{int})	5871 (0.010)	6068 (0.008)	6224 (0.019)
R [$F > 4\sigma(F)$]	0.034	0.046	0.059
wR (all data)	0.093	0.140	0.178

thiamine–platinate anion complexes[7,11] but accommodating relatively large $Hg_2Br_6^{2-}$ anions, and thus the anions have remarkable effects upon the supramolecular construction. In addition, the inherent *S* conformation of the C2-substituted thiamine offers intermolecular connections distinguished from the C2-free thiamine complexes in the *F* conformation. Thus significant topological changes have been achieved by changes in the nature of the anions and molecular conformation. Based on the understanding of these factors, it is possible to achieve precise structure design by appropriate choice of anions and ligands in the thiamine–anion systems.

Experimental

Synthesis

Ligands. 2-(α-Hydroxyethyl)thiamine hydrochloride, (het)Cl_2, was prepared from acetaldehyde and thiamine hydrochloride by literature methods[17] and 2-(α-hydroxypropyl)thiamine hydrochloride, (hpt)Cl_2, was obtained by a similar method but using propionaldehyde as starting material. The products were washed with acetone and recrystallized from methanol. Yield 64% for (het)Cl_2 and 48% for (hpt)Cl_2 based on thiamine hydrochloride.

(het)($PtCl_6$)·2H_2O 1. A methanolic solution (5 ml) of (het)Cl_2 (0.1 mmol) was added to an aqueous solution (5 ml) of $PtCl_4$ (0.1mmol). The mixture (pH *ca*. 3) was allowed to stand at room temperature. Reddish orange crystals formed after three weeks. Yield 28 mg, 37%. Found: C, 22.28; H, 3.65; N, 7.13. Calc. for $C_{14}H_{26}Cl_6N_4O_4PtS$: C, 22.29; H, 3.47; N, 7.43%. IR (KBr)/cm^{-1}: 3313w, 3126w, 2953w, 1660vs, 1604vs, 1535s, 1392m, 1360m, 1331w, 1229m, 1119m, 1051s, 764w, 706w and 505w.

(het)(HgI_4)·H_2O 2. The same method as for **1**, using (het)Cl_2 (0.1 mmol) and K_2HgI_4 (0.1 mmol) (pH *ca*. 4.5), gave light-yellow crystals after two weeks. Yield 46 mg, 44%. Found: C, 16.39; H, 2.61; N, 5.28. Calc. for $C_{14}H_{24}HgI_4N_4O_3S$: C, 16.22; H, 2.33; N, 5.40%. IR (KBr)/cm^{-1}: 3399w, 3127w, 2881w, 1683s, 1655s, 1626s, 1591m, 1535s, 1431w, 1390w, 1319m, 1114m, 1038s, 904w, 876w, 771m, 648w and 507w.

(hpt)(Hg_2Br_6) 3. This was prepared by reacting (hpt)Cl_2 (0.1 mmol) dissolved in methanol (5 ml) and $HgBr_2$ (0.1 mmol) dissolved in water (5 ml). Colorless crystals were obtained from the mixture (pH *ca*. 5) at room temperature after two weeks. Yield 23 mg, 57%. Found: C, 15.31; H, 2.05; N, 4.38. Calc. for $C_{15}H_{24}Br_6Hg_2N_4O_2S$: C, 14.95; H, 2.01; N, 4.65%. IR (KBr)/cm^{-1}: 3369m, 3145w, 2883w, 1676vs, 1619vs, 1539s, 1431w, 1365w, 1327w, 1230m, 1119m, 1041s, 987m, 891m, 768s, 690w and 567m.

X-Ray crystallography

Intensity data measurements were performed on a Rigaku AFC7R diffractometer with an 18 kW rotating anode generator, using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The unit cell parameters were derived from a least-squares fit to the setting angles of 25 high-angle reflections. The ω–2θ scan technique was employed for data collection to a maximum of 2θ = 55°. The intensity data were corrected for Lorentz and polarization effects and absorption effects. The crystal data and other details of the structure determination are listed in Table 5.

The heavy-atom positions were determined by direct methods using the SHELXS97 program[18a] and the structures were expanded by difference Fourier techniques and refined by full-matrix least-squares using the SHELXL97 program.[18b] In **1**, the O(21) atom of the C(2)-substituent is disordered over two positions and three of the water molecules are partially occupied. An iodine atom, I(2), and a water molecule in **2** are disordered each over two positions. The occupancy factors of all the disordered atoms in **1** and **2** were refined. All non-hydrogen atoms were refined anisotropically, except for some disordered atoms. The hydrogen atoms were added to the structures according to the calculated coordinates with isotropic displacement parameters, except those attached to hydroxyl groups in **1** and water molecules in **1** and **2**, which were not located.

CCDC reference numbers 189677–189679.

See http://www.rsc.org/suppdata/dt/b2/b206765j/ for crystallographic data in CIF or other electronic format.

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