

Solvent-induced supramolecular isomerism in $[\text{Pt}(\text{S}=\text{C}(\text{NH}_2)_2)_4]^{2+}$ croconate salts

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The role of solvent (and other species) in the formation of networks from tetrakis(thiourea)platinum(II) cations and croconate anions is examined, with crystallisations from DMSO giving rise to a structure containing solvent filled channels.

The term “supramolecular isomerism” was coined to describe the existence of more than one type of network superstructure formed from the same building blocks.¹ Polymorphism and pseudopolymorphism are phenomena of paramount importance to the production and applications of solid compounds in the explosives, pigments and pharmaceutical industries. Solvent-dependent framework formation in coordination networks is well documented, with solvent molecules frequently included within structures.^{2,3} Nevertheless, examples of this type of behaviour in metal organic frameworks which do not include any guest molecules and other types of structure highlight the role of solvents in synthon formation and crystallisation.^{4,5} There are fewer examples of this phenomenon involving hydrogen-bonded networks, with only a handful of examples of solvent templated three-dimensional hydrogen bonded networks being reported.⁶

Tetrakis(thiourea)platinum(II) complex provides a set of four coordinated thiourea groups in a semiflexible square planar arrangement with a positive net charge. We decided to co-crystallise this cation complex with the croconate dianion as a rigid hydrogen bond acceptor moiety in order to obtain solid state structures containing channels or voids. Tetrakis(thiourea)platinum(II) complexes with simple dicarboxylates have been reported previously by us.⁷ Interest in the use of croconate and other oxocarbon dianions in crystal engineering has increased over recent years. For example in 2002, Braga and co-workers reported the structures of the alkali metal salts of $\text{C}_5\text{O}_5^{2-}$.⁸ Mak and co-workers have co-crystallised tetrabutylammonium croconate ($\text{C}_5\text{O}_5^{2-}$) and other oxocarbon dianion salts with urea and thiourea derivatives with different stoichiometries, yielding a variety of anionic host lattices in which the tetrabutylammonium cations are included in a guest-like fashion.⁹ In the structures discussed in this communication, and previously,⁷ the thiourea sulfur is coordinated to the platinum(II) centre and all hydrogen bonding interactions occur between the thiourea NH groups and the anions in the structure. The expected product is a neutral structure, thus avoiding the need to accommodate counter-ions, whilst the excess hydrogen bond donors may result in the incorporation of hydrogen bond acceptor guests.

Slow diffusion of acetone into a 1 : 1 mixture of tetrakis(thiourea)platinum(II) dichloride and croconic acid disodium salt in DMSO–water yielded crystals of **1** suitable for X-ray diffraction studies.[†] The structure corresponded to the complex salt $[\text{Pt}(\text{SC}(\text{NH}_2)_2)_4][\text{C}_5\text{O}_5] \cdot 4\text{DMSO}$, which forms a three dimensional hydrogen-bonded assembly containing two types of channel that accommodate the solvent molecules (Fig. 1 and 2). The croconate dianions are found in a quite symmetrical hydrogen bond environment, interacting with six thiourea molecules attached to six different platinum complexes. These hydrogen bond interactions form a network corresponding to a graph set of four $\text{R}_2^2(9)$ plus two D contacts. Hydrogen bonding distances range from 2.812(3) Å to 2.911(3) Å ($\text{N}\cdots\text{O}$) with $\text{N}-\text{H}\cdots\text{O}$ bond angles of 163.7° to 151.6°. All carbon–carbon and carbon–oxygen

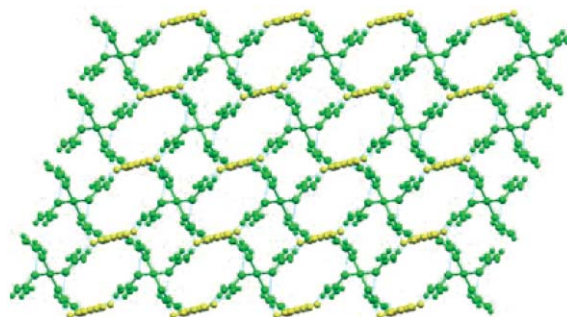


Fig. 1 Crystal structure of compound **1** viewed along the *b* axis (DMSO molecules omitted for clarity). The platinum complexes are represented in green and the croconate anions in yellow.

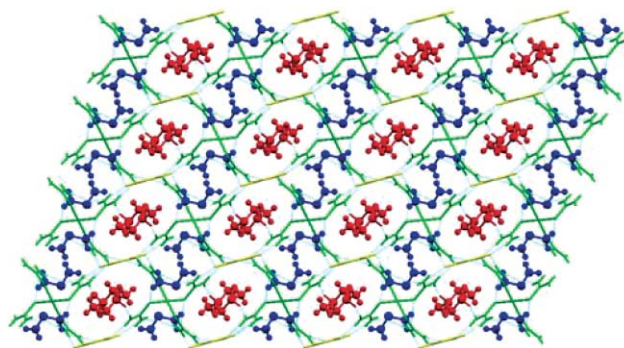


Fig. 2 Crystal structure of compound **1** viewed down the *b* axis. The platinum complexes are represented in green and the croconate anions in yellow. The DMSO molecules occupying the larger channel are shown in red whilst the DMSO molecules occupying the smaller channel are shown in blue.

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bond distances are very similar within the croconate anion, supporting an aromatic D_{5h} structure.¹⁰ The thiourea ligands adopt a 1,2-alternate conformation (*i.e.* two adjacent thioureas are oriented up from the PtS_4 plane whilst the other two are oriented down) around each metal and the hydrogen bond environment of every platinum complex cation comprises four croconate anions bound *via* $R^2_2(9)$ contacts and two croconate rings attached in a terminal fashion. The large croconate anions result in a platinum–platinum separation of 12.59(7) and 9.86(6) Å in the *bc* and *ab* directions respectively. There are four molecules of dimethyl sulfoxide, two of them are bridging two thiourea groups in a *cis* arrangement, whilst the other two are linked to the other two thiourea groups in a terminal fashion.

Two types of channels are found within the structure, the DMSO molecules within the smaller channel are held by two hydrogen bonds meanwhile the larger channels contain solvent held by only one hydrogen bond. § The volume occupied by the solvent is 54% of the unit cell volume.

Crystallisation experiments were repeated several times to assess the reproducibility of the structure, using DMSO and DMSO–water mixtures to dissolve the starting materials and allowing slow diffusion of acetone or acetonitrile into these samples. In all cases **1** appeared to be the unique crystalline product, however, during one of these experiments, whilst the majority of crystals were found to be complex **1**, a very small number of differently shaped crystals were isolated and their structure elucidated by crystallography. ¶

These crystals were found to be the serendipitous compound **1a**, with an empirical formula of $\text{C}_{80}\text{H}_{157}\text{Cl}_8\text{K}_5\text{O}_{46}\text{Pt}_9$ || resulting from the inclusion of K^+ and PtCl_4^{2-} from the starting materials of the platinum tetrakis(thiourea) chloride and adventitious methanol, in addition to the platinum tetrakis(thiourea) cation, croconate anions and DMSO. Of note in the structure is the formation of chloride containing capsules formed by two platinum tetrakis(thiourea) cations both in the cone conformation ($\text{N}\cdots\text{Cl}$ distances in the range 3.28(4)–3.484(4) Å) with the cation thiourea groups bridged by four croconate anions (Fig. 3). This compound also forms a network containing channels, in this case filled with K^+ cations and PtCl_4^{2-} anions (Fig. 4).

To further assess the influence of the crystallisation solvent on the final network, we repeated the crystallisation from water. ** In this case a crystalline material is readily obtained upon mixing solutions of tetrakis(thiourea)platinum(II) dichloride and croconic acid disodium salt, and crystals suitable for X-ray diffraction were obtained by leaving this solution standing overnight.

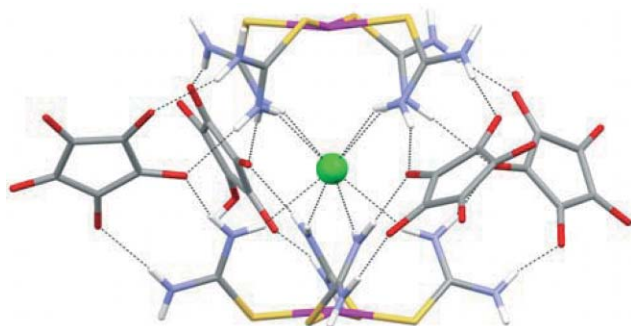


Fig. 3 The chloride templated capsule $[(\text{Pt}(\text{SC}(\text{NH}_2)_2)_4)_2 \cdot (\text{C}_5\text{O}_5)_3 \cdot (\text{C}_5\text{O}_4\text{OH}) \cdot \text{Cl}]^{4-}$ present in the solid-state structure of **1a**.

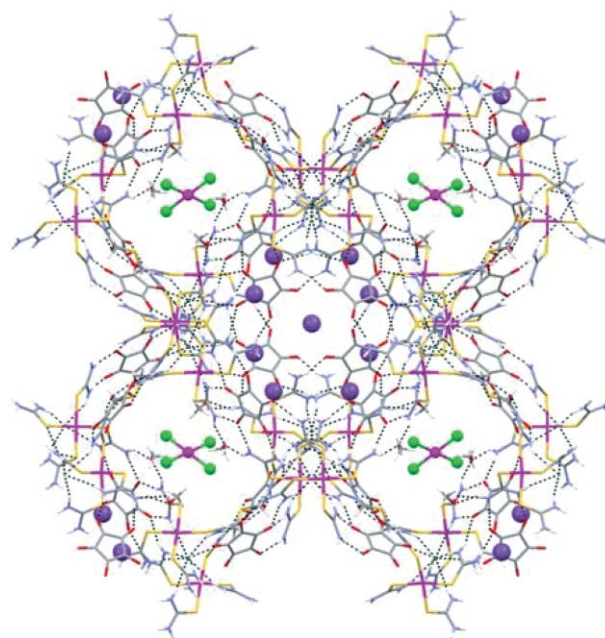


Fig. 4 A view of the packing present in the solid state in **1a** down the *c*-axis. Channels in the structure are filled with the K^+ and PtCl_4^{2-} guests. Pt: magenta, K: purple, Cl: green

This material was found to be $[\text{Pt}(\text{SC}(\text{NH}_2)_2)_4] \cdot [\text{C}_5\text{O}_5] \cdot 2.5\text{H}_2\text{O}$. †† The switch from DMSO to water had a dramatic effect on the network. The complex forms a three-dimensional hydrogen bonded structure containing no channels or voids with the water molecules integral to the network (Fig. 5 and 6). Thiourea groups are found in a 1,2-alternate arrangement, with one molecule of water bridging two platinum complexes. The hydrogen bond environment of the croconate dianion includes eight urea groups corresponding to eight different platinum complexes and two molecules of water. The main hydrogen bonding motifs are discrete contacts, including six of the urea groups, meanwhile the other two are found forming rings (graph set $R^2_2(9)$). All of these are strong interactions, with $\text{N}\cdots\text{O}$ distances ranging from 2.859(4) Å to 3.019(5) Å and bond angles from 171.3° to 138.6°. Two water molecules complete the

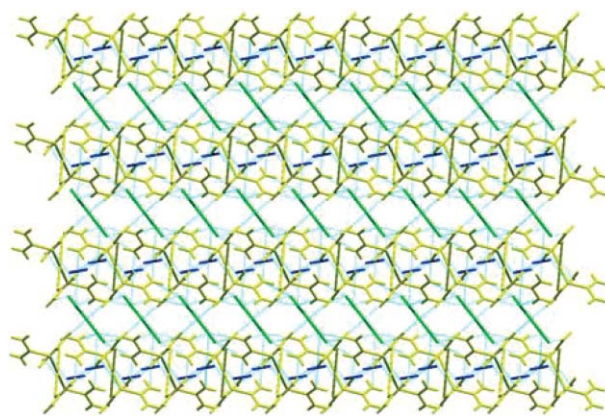


Fig. 5 Crystal structure of **2** viewed along the *b* axis. The platinum complexes are represented in yellow, croconate anions in green and water in blue.

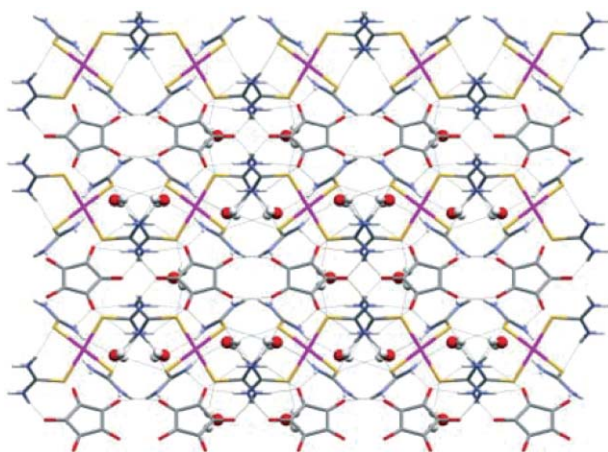


Fig. 6 Crystal structure of **2** viewed along the *c* axis showing hydrogen bonding interactions. Water is shown in a ball and stick representation.

hydrogen-bonding environment around the dianion, bridging two thiourea groups of one of the platinum complexes as well. This more asymmetric hydrogen bonding environment stabilizes more efficiently a charge localized form of the croconate dianion (the C(4)–O(2) bond distance is significantly larger at 1.258(6) Å than the other two carbon–oxygen distances: C(5)–O(3) 1.239(6) Å and C(3)–O(1) 1.243(8) Å).

We have seen the profound influence of solvent (and a salt) on the structure obtained in platinum(II) tetrakis(thiourea) complexes with croconate. The potential of these and similar systems to generate porous structures is currently under investigation in our laboratory. The results of these studies will be reported in due course.

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Notes and references

† X-Ray crystal data were collected on a Bruker Nonius KappaCCD mounted at the window of a Mo rotating anode following standard procedures. CCDC 284038–284040. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513059j

‡ $C_{17}H_{40}N_8O_8S_8Pt$, $M_r = 952.14$, $T = 120(2)$ K, monoclinic, space group $C2/c$, $a = 17.315(4)$, $b = 9.4289(19)$, $c = 23.344(5)$ Å, $\beta = 107.70(3)^\circ$, $V = 3630.6(13)$ Å³, $\rho_{\text{calc}} = 1.742$ g cm⁻³, $\mu = 4.377$ mm⁻¹, $Z = 4$, reflections collected: 21798, independent reflections: 4155 ($R_{\text{int}} = 0.0412$), final R indices [$I > 2\sigma(I)$]: $R1 = 0.0254$, $wR2 = 0.0598$, R indices (all data): $R1 = 0.0326$, $wR2 = 0.0633$.

§ TGA analysis of the crystals showed losses of mass which were complete at 157 and 215°C corresponding to 16.4% and 32.6% of the total mass respectively. This presumably corresponds to loss of DMSO.

¶ **1**: 29.4 mg, 0.05 mmol of tetrakis(thiourea)platinum(II) dichloride dissolved in 1.5 mL of DMSO were mixed with a solution of 9.5 mg, 0.051 mmol of croconic acid disodium salt in 0.5 mL of water. Slow diffusion of acetonitrile afforded yellow crystals after three days. Yield: 30.4 mg (63.3%). Elemental analysis (%) calcd. for **1**·4DMSO: 21.44 C, 4.23 H, 11.78 N; found: 20.99 C, 3.85 H, 12.01 N. **1a**: These crystals grew during the crystallisation of **1**. Chlorine analysis of bulk samples only

showed residual percentages of this element. Experiments aimed at the rational synthesis of **1a** and other types of guest-containing compounds are currently under way in our laboratory.

|| Crystal data for **1a** $C_{80}H_{157}Cl_8K_5N_6O_{46}Pt_9S_{34}$, $M_r = 6076.65$, $T = 120(2)$ K, monoclinic, space group $C2/c$, $a = 38.36(2)$, $b = 38.80(2)$, $c = 24.643(5)$ Å, $\beta = 105.63(3)^\circ$, $V = 35322(27)$ Å³, $\rho_{\text{calc}} = 1.413$ g cm⁻³, $\mu = 3.915$ mm⁻¹, $Z = 4$, reflections collected: 155406, independent reflections: 3116 ($R_{\text{int}} = 0.1481$), final R indices [$I > 2\sigma(I)$]: $R1 = 0.1821$, $wR2 = 0.4752$, R indices (all data): $R1 = 0.2822$, $wR2 = 0.5153$.

** **2**: Two solutions containing 13.5 mg, 0.023 mmol of tetrakis(thiourea)platinum(II) dichloride in 1 mL of water and 4.4 mg, 0.023 mmol of croconic acid disodium salt in 0.5 mL of water were mixed and left standing at room temperature for four days. Long yellow needles were formed during this time. Yield: 12.3 mg (78.2%). Elemental analysis (%) calcd. for **1**·2.5H₂O: 15.79 C, 3.09 H, 16.37 N; found: 15.84 C, 2.94 H, 16.55 N.

†† $C_9H_{21}N_6O_7S_4Pt$, $M_r = 684.67$, $T = 120(2)$ K, monoclinic, space group $C2/c$, $a = 17.518(4)$, $b = 13.767(3)$, $c = 9.0857(18)$ Å, $\beta = 91.32(3)^\circ$, $V = 2190.5(8)$ Å³, $\rho_{\text{calc}} = 2.076$ g cm⁻³, $\mu = 6.838$ mm⁻¹, $Z = 4$, reflections collected: 12592, independent reflections: 2506 ($R_{\text{int}} = 0.0637$), final R indices [$I > 2\sigma(I)$]: $R1 = 0.0318$, $wR2 = 0.062$, R indices (all data): $R1 = 0.0513$, $wR2 = 0.069$. This structure contains a half occupied water that is disordered over 2 positions.

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