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Unsymmetrically-substituted 2,4,6-trimercaptotriazine: supramolecular self-assembly through C=S···H–N hydrogen bonds in the crystal structures of $C_3N_3S_3H_2Na\cdot 3H_2O$ and $C_3N_3S_3H_2Cu(PPh_3)_2$

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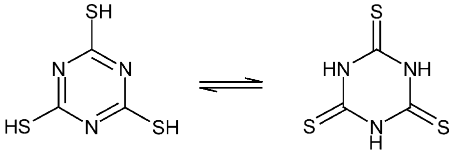
Abstract

The monosodium salt of trithiocyanuric acid, $C_3N_3S_3H_2Na$, has been isolated as its trihydrate (**1**) by partial neutralisation of $C_3N_3S_3H_3$ with NaOH. Each sodium in the structure displays a novel *cis*-S_2NaO_4 coordination sphere and is hydrogen bonded to the anion, which adopts its thione form. Compound **1** has been used to synthesise other unsymmetrically-metallated trithiocyanuric acid derivatives, typified by $[C_3N_3S_3H_2Cu(PPh_3)_2]$ and whose structure has also been determined. The nickel complex $[C_3N_3S_3H_2NiCl(PPh_3)_2]\cdot 0.5CH_2Cl_2$ was also obtained, but only tri-substituted compounds $C_3N_3S_3[Au(PPh_3)]_3\cdot 2CH_2Cl_2$ and $C_3N_3S_3(SnMe_3)_3$ were formed when **1** was reacted with $(Ph_3P)AuCl$ and Me_3SnCl, respectively.

Keywords: Trithiocyanuric acid; Sodium salt; Copper salt; X-ray; C=S···H–N hydrogen bonds

1. Introduction

In this paper we wish to report further on the chemistry of 1,3,5-triazine-2,4,6-trithiol (**I**) (also referred to as 2,4,6-trimercaptotriazine or trithiocyanuric acid, H_3TMT). Compound **I**, which can exist in either thiol (**Ia**) or thione (**Ib**) forms, is an analytical reagent which has attracted renewed general interest in recent years because of its use in removing heavy metals (Ag^+, Hg^{2+}, Cd^{2+}, Pd^{2+}, Cu^{2+}) from waste waters [1–3]. Despite this, the structural chemistry of metallo-derivatives of **I** remains limited (partly due to reasons of solubility) [4,5] and is mainly confined to derivatives of *s*-(Li^+, Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}) [3,6–8] and *d*-block elements [4,5,9–13] where it can behave as either a chelating [9] or bridging [11–13] ligand. More recent work has furnished the structures of gold $[(Ph_3P)Au]_3[C_3N_3S_3]$ [12], $(AuC_3N_3S_3)(AuL)_2]_2$ (L = Me_2PhP [12], ^tBuNC [13] $[C_3N_3S_3H_2Au(PPh_3)_3](DMF)$ [14]), nickel $[Ni(pmdien)(HC_3N_3S_3)(H_2O)]$ (pmdien = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) [15], mercury $[(MeHg)_3(C_3N_3S_3)]$ [16] and copper derivatives $[(CuPPh_3)_3(C_3N_3S_3)]_2$ [11], while we have synthesised several organotin derivatives and determined the structures of $(R_3Sn)_3(C_3N_3S_3)$ (R = Me, Ph) [17]. The use of metal complexes of **I** for the formation of nanoparticulate metal sulphides has also been noted [18].



(**Ia**) (**Ib**)

Additional interest in **I** stems from the fact that recrystallisation from polar solvents (DMSO, MeOH, Me_2CO) or in the presence of species such as melamine

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or 4,4′-bipyridyl yields supramolecular arrays built up from N–H···O, N–H···N, N–H···S and S···S interactions [19–21]. Similarly, in addition to molecular species such as 'manxane' $M_3C_3N_3S_3$ ($M = R_3Sn$ [17], R_3PAu [13]), metal derivatives of **I** e.g. $[(AuC_3N_3S_3)(AuL)_2]_2$ ($L = Me_2PhP$ [12], ^tBuNC [13]) can also form supramolecular arrays. It was thus of interest to us to study further the chemistry of partially metallated species starting from either $C_3N_3S_3H_2Na$ or $C_3N_3S_3HNa_2$, the results of which we now report. Both salts have previously been cited in patents [22,23]. The only structural reports directly relevant to these findings are $[C_3N_3S_3H_2]_2M$ (M = Mg, Ca, Sr, Ba) [3,8], $C_3N_3S_3H_2Li\cdot 2HMPA$ [6] and $[C_3N_3S_3H_2Au(PPh_3)_3](DMF)$ [14].

2. Experimental

The starting materials were purchased from a commercial source (Aldrich). Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), Perkin–Elmer 599B (IR). For all compounds, infrared spectra were recorded as nujol mulls on KBr plates and all NMR data were recorded on saturated solutions at room temperature (r.t.); chemical shifts are in ppm relative to either Me_4Si (^1H, ^{13}C) or H_3PO_3 (^{31}P), coupling constants are in Hz.

The starting materials were purchased from a commercial source (Aldrich). $(Ph_3P)AuCl$ was prepared according to literature methods [24].

$(Ph_3P)_4Cu(OAc)$ was obtained by the reaction of stoichiometric amounts of $Cu(OAc)_2\cdot H_2O$ and PPh_3 in MeOH under reflux, followed by crystallisation from MeOH at low temperature. Yield: 84%, m.p. 152 °C. *Anal*. Found (Calc. for $C_{74}H_{63}CuO_2P_4$): C, 75.6 (75.9); H, 5.4 (5.4)%. ^1H NMR ($CDCl_3$): 7.26–7.10 (m, 30H, Ph), 1.87 (s, 3H, CH_3CO_2). ^{13}C NMR: 179.0 ($CH_3\mathit{C}OO$), 134.3, 123.1 (*3*-Ph), 130.1 (*4*-Ph), 129.0, 128.9 (*2*-Ph), 23.8 ($\mathit{C}H_3COO$). ^{31}P NMR: δ 0.00. IR (Nujol): 1583 m, 1571 m, 1549 s, 1476 vs, 1434 vs, 1338 w, 1178 w, 1156 w, 1118 w, 1094 s, 1068 w, 1026 m, 996 w, 926 w, 752 s, 742 s, 702 s, 694 vs, 666 s.

2.1. Synthesis of $C_3N_3S_3H_3$ (**I**)

The reaction of $C_3N_3S_3Na_3\cdot 9H_2O$ (1 equiv.) with concentrated HCl (3 equiv.) in aqueous solution gave the product as a fine yellow precipitate, in good yield (88%). A product of satisfactory purity can be obtained by washing the precipitate with water and drying it at r.t. overnight. m.p. > 290 °C. *Anal*. Found (Calc. for $C_3H_3N_3S_3$): C, 20.3 (20.3); H, 1.7 (1.7); N, 23.3 (23.7)%. NMR (DMSO): ^1H: 13.7 (s, broad, NH), 3.39 (s, H_2O); ^{13}C: 172.2 (C–S); IR (Nujol): 3130 s (br), 1576 s, 1532 vs, 1298 m, 1258 m, 1123 w, 983 w, 786 w, 744 ms.

2.2. Synthesis of $C_3N_3S_3H_2Na\cdot 3H_2O$ (**1**)

A suspension of $C_3N_3S_3H_3$ (1 equiv.) in aqueous NaOH (1 equiv.) solution was stirred at r.t. for 30 min during which time almost complete dissolution occurred. After removing the small amount of remaining solid, the pale yellow filtrate was allowed to evaporate slowly at r.t. to give the product as a yellow crystalline solid, in satisfactory yield (66%), m.p. 280 °C (dec.).

Alternatively, an aqueous solution of $C_3N_3S_3Na_3\cdot 9H_2O$ (1 equiv.) and HCl (2 equiv.) were stirred at r.t. for 1 h. The resulting pale yellow clear solution was allowed to evaporate slowly at r.t. to give the product as yellow crystalline solid. Depending on the concentration of the reaction mixture, the product might also deposit during the reaction as a microcrystalline yellow precipitate. Yield: 80%. *Anal*. Found (Calc. for $C_3H_8N_3NaO_3S_3$): C, 14.2 (14.2); H, 3.2 (3.2); N, 16.2 (16.6)%. ^1H NMR (DMSO): 12.23 (s, broad, NH), 3.56 (s, H_2O); ^{13}C NMR: 176.9 (C–S); IR (Nujol): 3458 s (br), 3100 m, 1623 w, 1588 w, 1554 s, 1276 w, 1239 s, 1149 vs, 882 m, 812 m, 774 w.

2.3. Synthesis of $[C_3N_3S_3H_2Cu(PPh_3)_2]\cdot CH_2Cl_2$ (**2**)

$C_3N_3S_3H_2Na\cdot 3H_2O$ (0.5 g, 2.0 mmol) was stirred as a suspension in a CH_2Cl_2 solution (70 ml) of $(PPh_3)_4Cu(OAc)$ (2.3 g, 2.0 mmol) for 6 h at r.t. After removing the solid residue, the yellow solution was concentrated to low volume and stored at low temperature for 2–3 days to give the product as yellow crystalline solid. Yield: 1.05 g, 62%, m.p. 180 °C (dec.).

As an alternative method, EtOH solution (30 ml) of $C_3N_3S_3H_2Na\cdot 3H_2O$ (0.4 g, 1.6 mmol) was added dropwise to $(PPh_3)_4Cu(OAc)$ (1.8 g, 1.5 mmol) in EtOH (20 ml). Pale yellow solid precipitated at once. After stirring the mixture at r.t. for 1 h, the mother liquid was removed and the precipitate was washed with EtOH and dried in vacuo. Yield: 0.80 g, 63%. *Anal*. Found (Calc. for $C_{40}H_{34}Cl_2CuN_3P_2S_3$): C, 56.6 (56.6); H, 4.1 (4.0); N, 5.0 (5.0)%. ^1H NMR (DMSO), recorded on a sample re-crystallised from CH_2Cl_2/MeOH: 3.30 (s, CH_3, MeOH), 5.70 (s, CH_2, CH_2Cl_2), 7.26 (s, broad, 30H, Ph), 13.33 (s, br, 2H, NH); ^{13}C NMR: 55.2 (CH_2Cl_2), 128.9 (*2*-Ph), 130.2 (*4*-Ph), 133.6 (*3*-Ph); ^{31}P NMR: −17.1; IR (Nujol): 3100 m, 1583 w, 1547 s, 1524 s, 1233 s, 1174 s, 1141 vs, 1117 s, 1094 m, 1049 w, 1024 w, 995 w, 892 w, 743 s, 693 vs.

2.4. Synthesis of $[C_3N_3S_3H_2][(PPh_3)_2NiCl]\cdot 0.5CH_2Cl_2$ (**3**)

$C_3N_3S_3H_2Na\cdot 3H_2O$ (0.27 g, 1.07 mmol, 7% excess) was stirred as a suspension in a dark greenish–black CH_2Cl_2 solution (50 ml) of $(PPh_3)_2NiCl_2$ (0.33 g, 0.5 mmol) at r.t. for 6 h. After removing the solid residue,

C_6H_{14} was added to the dark brown solution (approximately 15 ml) and the mixture concentrated to low volume to yield the product as a microcrystalline brick-brown precipitate. The mother liquid was removed by filtration and the product was dried in vacuo. Yield: 0.2 g, 40%. *Anal*. Found (Calc. for $C_{39.5}H_{31}Cl_2N_3NiP_2S_3$): C, 56.4 (56.8); H, 4.0 (3.7); N, 5.9 (5.0)%. IR (nujol): 1586 w, 1573 w, 1543 s, 1438 vs, 1399 m, 1245 m, 1189 s, 1144 s, 1094 s, 1069 w, 1021 w, 998 w, 749 m, 741 m, 704 m, 692 vs, 668 m.

2.5. Synthesis of $C_3N_3S_3[Au(PPh_3)]_3 \cdot 2CH_2Cl_2$ (4)

$C_3N_3S_3H_2Na \cdot 3H_2O$ (0.15 g, 0.6 mmol, approximately 20% excess) was stirred for 24 h as a suspension in a CH_2Cl_2 solution (20 ml) of $(PPh_3)AuCl$ (0.23 g, 0.47 mmol). The solid residue was removed and the pale yellow filtrate was mixed with C_6H_{14} (1:1) and stored at low temperature for 1–2 weeks to yield the product as pale yellow microcrystalline solid. Yield: 0.1 g, 35%, m.p. 174 °C. *Anal*. Found (Calc. for $C_{59}H_{49}Au_3Cl_4N_3P_3S_3$): C, 41.1 (41.1); H, 2.8 (2.8); N, 2.8 (2.4)%.

3. Crystallography

Crystallographic data for compounds **1** and **2** are summarised in Table 1. In both cases, data collections were implemented on a Nonius KappaCCD diffractometer. One of the water molecules in compound **1** was seen to been disordered in a 1:1 ratio between sites O(3) and O(3A); this precluded location of the associated hydrogen atoms which were therefore not included in the final refinement. The hydrogen atoms in the remaining 2 water molecules were readily located however, and refined at a distance of 0.89 Å from the relevant parent atoms, and at a distance of 1.45 Å from each other in individual waters.

Table 1
Crystallographic data for **1** and **2**

	1	2
Empirical formula	$C_3H_8N_3NaO_3S_3$	$C_{40}H_{34}Cl_2CuN_3P_2S_3$
Formula weight	253.29	849.26
Temperature (K)	150(2)	150(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/n$
a (Å)	7.7860(2)	14.9240(2)
b (Å)	12.6940(4)	16.2290(2)
c (Å)	10.3850(4)	16.6720(2)
β (°)	109.087(3)	102.1710(8)
V (Å^3)	969.98(5)	3947.22(9)
Z	4	4
Absorption coefficient (mm^{-1})	0.787	0.962
Reflections collected	5613	61 287
Reflections observed ($> 2\sigma$)	1829	7497
Independent reflections	1944 [$R_{int} = 0.0416$]	9029 [$R_{int} = 0.0470$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0729$, $wR_2 = 0.2221$	$R_1 = 0.0336$, $wR_2 = 0.0818$
R indices (all data)	$R_1 = 0.0758$, $wR_2 = 0.2234$	$R_1 = 0.0459$, $wR_2 = 0.0894$
Goodness-of-fit on F^2	1.350	0.979

In **2**, one of the chlorines in the solvate molecule also exhibited disorder between positions Cl(2), Cl(2A) and Cl(2B) in respective 48:32:20 ratios. In the final least-squares cycles, these partial chlorines were restrained to have similar distances from the carbon in the solvate, C(4). The solvent hydrogens included in the refinement are based on the position of the major disordered chlorine component.

Non-hydrogen atoms were refined anisotropically without exception. All data were corrected for Lorentz, polarisation and extinction. An absorption correction (multiscan) was applied to data for **2** (maximum and minimum transmission factors 1.044, 0.949; respectively). Software used: SHELXS-86 [25], SHELXL-97 [26], ORTEX [27].

4. Results and discussion

We have prepared and isolated $C_3N_3S_3H_2Na$ as its trihydrate (**1**) either from neutralisation of $C_3N_3S_3H_3$ with 1 equiv. of NaOH or by the addition of 2 equiv. of HCl to $C_3N_3S_3Na_3$. Attempts to prepare $C_3N_3S_3HNa_2$ by the same routes failed. Reactions of both $C_3N_3S_3H_3$ (1 equiv.) with NaOH (2 equiv.) and $C_3N_3S_3Na_3.9H_2O$ (1 equiv.) with HCl (1 equiv.), respectively gave the monosodium salt **1** in satisfactory yield (66–80%). It has been noted by others that the dianion $[C_3N_3S_3H]^{2-}$ is dominant in aqueous solutions of approximately pH 10 while the monoanion $[C_3N_3S_3H_2]^{-}$ is dominant at approximately pH 7 [18].

The structure of **1** is shown in Fig. 1; two of the water molecules are well resolved while the third [based on O(3)] is disordered. Within the disordered water, O(3) and O(3A) are sited close to each other [O(3)–O(3A): 0.76(1) Å] so only the coordination of O(3) will be discussed further. The anion exists in its thione form with two of the nitrogen atoms being protonated. The C=S bonds are relatively short [S(1)–C(1) 1.681(6), S(2)–C(2) 1.679(6), S(3)–C(3) 1.684(6) Å] and overall are shorter than those found in S-substituted species such as $C_3N_3S_3(SnMe_3)_3$ [1.743(3) Å] [17]. Each sodium adopts a *cis*-S_2NaO_4 coordination sphere in which the two soft sulphur atoms are more weakly bound [Na(1)–S(1″): 2.955(3); Na(1)–S(3) 3.186(3) Å] than the four hard oxygens [Na(1)–O(1): 2.379(5); Na(1)–O(1′): 2.384(5); Na(1)–O(2′): 2.391(6); Na(1)–O(3)/O(3A): 2.401(11), 2.337(11) Å]. This is a unique coordination

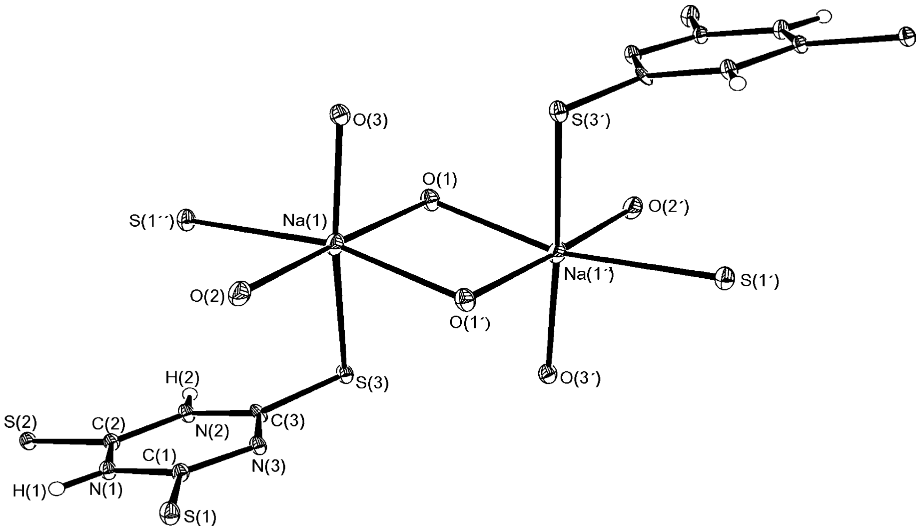

Fig. 1. The structure of **1** showing the atomic labelling; O(3A), the complimentary position for O(3) in the disordered water, has been omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected metrical data: S(1)–C(1) 1.681(6), S(2)–C(2) 1.679(6), S(3)–C(3) 1.684(6), N(1)–C(2) 1.352(8), N(1)–C(1) 1.375(8), N(2)–C(2) 1.354(8), N(2)–C(3) 1.384(8), N(3)–C(1) 1.344(8), N(3)–C(3) 1.346(8), Na(1)–O(1) 2.379(5), Na(1)–O(1′) 2.384(5), Na(1)–O(2) 2.391(6), Na(1)–O(3) 2.401(11), Na(1)–S(1″): 2.955(3); Na(1)–S(3) 3.186(3) Å (symmetry operations: ′ $-x, -y, -z$; ″: $1/2+x, 1/2-y, z$).

mode in TMT molecules of this type, though it resembles the $SNaO_5$ coordination in $Na_3(TMT)\cdot 9H_2O$ [7], and contrasts with the all-oxygen coordination in $Mg(H_2O)_6(TMTH_2)$ [8], $M(H_2O)_8(TMTH_2)$ ($M = Ca, Sr$) [3] and various barium derivatives which embrace S, N and O-donors [3,8]. $Li(HMPA)_2(TMTH_2)$ is monomeric with a four-coordinate lithium, attached to the nitrogen of the heterocycle (thione form) [6].

The lattice structure of **1** is a self-assembled supramolecular achitecture made up of alternating layers of $[TMTH_2]^-$ and hydrated cations (Fig. 2a), which is typical of s-block complexes containing TMT [3,8]. Also common with these structures is a complex pattern of hydrogen bonds (Fig. 2b; Table 2). The two N–H units hydrogen bond to sulphur both to generate eight-membered $(SCNH)_2$ rings, graph set $[R_2^2(8)]$, and link the $[C_3N_3S_3H_2]^-$ ions into ribbons. Rather surprisingly, it is the sulphurs which engage in coordination to sodium [S(1), S(3)] that are involved in these hydrogen bonds. A dimeric sub-unit of these ribbons appears in the structure of **2** (Fig. 4). The water based on O(1) hydrogen bonds as a donor to the remaining sulphur [S(2)] and $H_2O(2)$, while $H_2O(2)$ acts as a hydrogen bond donor to the anionic nitrogen [N(3)] and $H_2O(3A)$. The role of O(3)/O(3A) is less clear as the disorder made it impossible to locate the associated hydrogen atoms, but the closest lattice contacts to O(3) are other water molecules [O(3)–O(1): 3.190; O(3)–O(3′): 3.067 Å].

Attempts to utilise **1** as a precursor for other partially-metallated derivatives of $[C_3N_3S_3H_2]^-$ proved only moderately successful. From the reaction of **1** with $(Ph_3P)_4Cu(OAc)$ we have succeeded in isolating $C_3N_3H_2Cu(PPh_3)_2$. This precipitates directly when the reaction is carried out in ethanol, or it crystallises slowly as a 1:1 solvate with CH_2Cl_2 (**2**), in which it is soluble. Compound **2** has trigonal planar copper (sum angles = 359.98°) bonded to the heterocycle via nitrogen [Cu(1)–N(1) 2.019(2) Å] while the remaining two nitrogens are protonated (Fig. 3). The ligand thus exists in its thione form as with **1**, with similar C=S distances [S(1)–C(1) 1.677(2), S(2)–C(2) 1.662(2), S(3)–C(3) 1.653(2) Å]. The N–H units are involved in C=S···H–N– hydrogen bonding leading to self-assembly into dimeric supramolecules. The dimer is formed by hydrogen bonds involving N(3)–H(3)···S(1) [H(3)–S(1): 2.401 Å] which generates an eight-membered ring, graph set $[R_2^2(8)]$ (Fig. 4), and which is also a component of the anionic ribbons in **1**.

The hydrogen associated with N(2) forms very weak hydrogen bonds with the disordered dichloromethane solvent [(H(2)–Cl(2A): 2.949; H(2)–Cl(2B): 3.010 Å] but these interactions effectively cap the two extremes of the dimer. Nevertheless, this dimer is clearly related to the ribbons of hydrogen-bonded $[C_3N_3S_3H_2]^-$ anions visible in the structure of **1** (Fig. 2b).

The only compound directly comparable with **2** is $[C_3N_3S_3H_2Au(PPh_3)_3](DMF)$ [14] though in this species the soft gold is S-bonded to the ligand which is in its thiol form (**Ia**). Divalent metal complexes $(C_3N_3S_3H_2)_2M$ have also been prepared but lack structural characterisation in the cases where M = Cu, Co [18] while for the Group 2 metals such complexes are largely ionic, as described above [3,8]. The structures of the nickel compounds $[Ni(bapen)(C_3N_3S_3H)]\cdot 2H_2O$

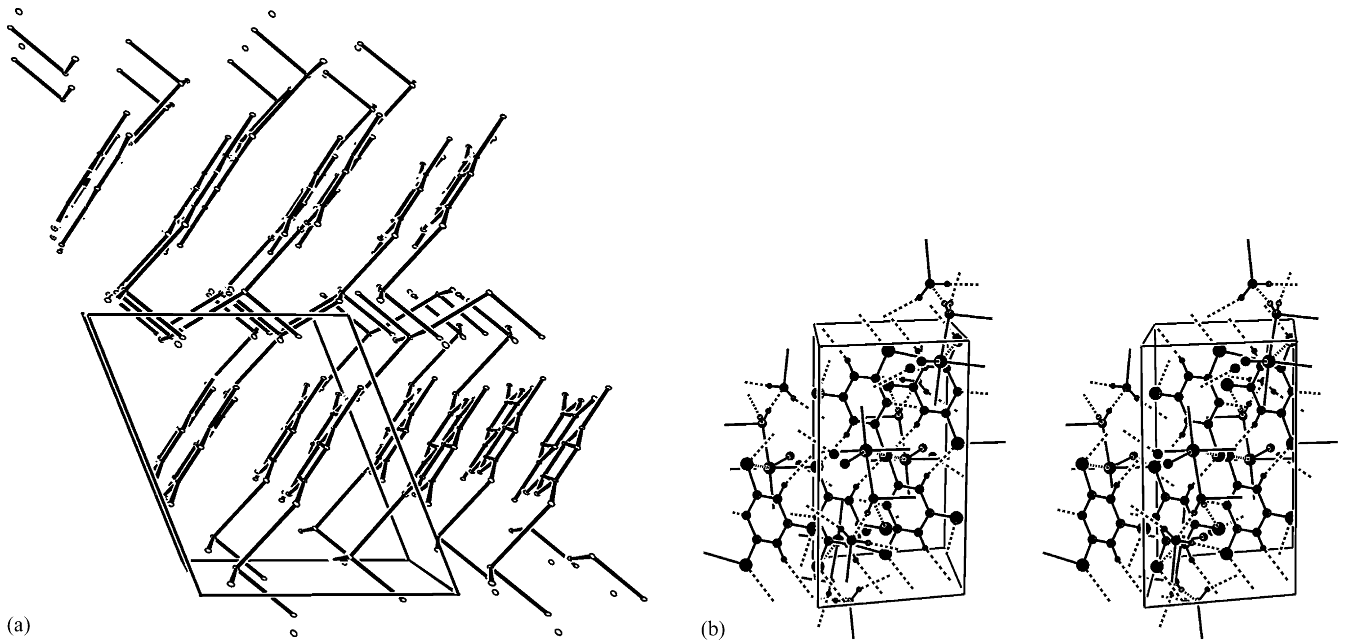

Fig. 2. The lattice structure of **1** showing (a) the alternating layers of hydrated cations and $[TMTH_2]^-$ anions and (b) a stereo view of the cell in which hydrogen bonds involving water molecules can be seen.

Table 2
Hydrogen bonding in **1**

D–H	A	d(D–H)	d(H–A)	d(D···A)	<D–H···A	Symmetry
N1–H1	S3	0.880	2.409	3.266	164.9	$-x+1/2, y+1/2, -z+1$
N2–H2	S1	0.880	2.468	3.326	165.1	$-x+1/2, y\text{-}1/2, -z+1$
O1–H1A	S2	0.896	2.449	3.323	165.3	$-x+1/2, y\text{-}1/2, -z+1$
O1–H1B	O2	0.894	1.937	2.826	172.4	
O2–H2A	O3A	0.879	2.250	2.916	132.4	$-x+1, -y, -z$
O2–H2B	N3	0.885	1.934	2.809	169.6	$-x, -y, -z$

(bapen = N,N'-bis(3-aminopropyl)ethylenediamine) [28], [Ni(taa)($C_3N_3S_3H$)] (taa = tris(2-aminoethylamine) [29] [Ni(pmdien)($C_3N_3S_3H$)(H_2O)] (pmdien = N,N,N',N',N''-pentamethyldiethylenetriamine) [15], and [Ni(dpta)($C_3N_3S_3H$)]·H_2O (dpta = dipropylenetriamine) [30] have also been reported.

The reaction of **1** with $(Ph_3P)_2NiCl_2$ afforded a brown–black product analysing most closely to $[C_3N_3S_3H_2][(PPh_3)_2NiCl]\cdot 0.5CH_2Cl_2$ (**3**). Unfortunately, we have been unable to grow crystals of this compound to authenticate its composition.

However, when **1** was reacted with $(Ph_3P)AuCl$ the only product isolated was $C_3N_3S_3[(Ph_3P)Au]_3\cdot 2CH_2Cl_2$ (**4**). The IR spectrum or **4** lacks the bands in the 1550–1500 cm^{-1} region characteristic of the $[C_3N_3S_3H_2]^-$ group and shows a strong band at approximately 850 cm^{-1} typical of a fully substituted $[C_3N_3S_3]^{3-}$ moiety. Similarly, after a methanol solution of $C_3N_3S_3H_2Na\cdot 3H_2O$ and Me_3SnCl (1:1) was stirred at room temperature for 2 h, slow evaporation of the resulting solution gave a yellow powder. The product was extracted into hexane (50 ml) and crystallised at low temperature to afford $C_3N_3S_3(SnMe_3)_3$ [17] as a colourless crystalline solid, while the hexane insoluble material proved to be $C_3N_3S_3H_3$.

5. Conclusions

$C_3N_3S_3H_2Na$ (**1**) has been isolated as its trihydrate and has proved moderately successful in allowing other partially-metallated derivatives such as $C_3N_3H_2Cu(PPh_3)_2$ and $[C_3N_3S_3H_2][(PPh_3)_2NiCl]\cdot 0.5CH_2Cl_2$ to be synthesised. However, such systems are often in equilibrium with fully-metallated species and $C_3N_3S_3[(Ph_3P)Au]_3\cdot 2CH_2Cl_2$ and $C_3N_3S_3(SnMe_3)_3$ are the key products isolated in reactions of **1** with $(Ph_3P)AuCl$ and Me_3SnCl. Similarly, we have so far been unable to isolate $C_3N_3S_3HNa_2$.

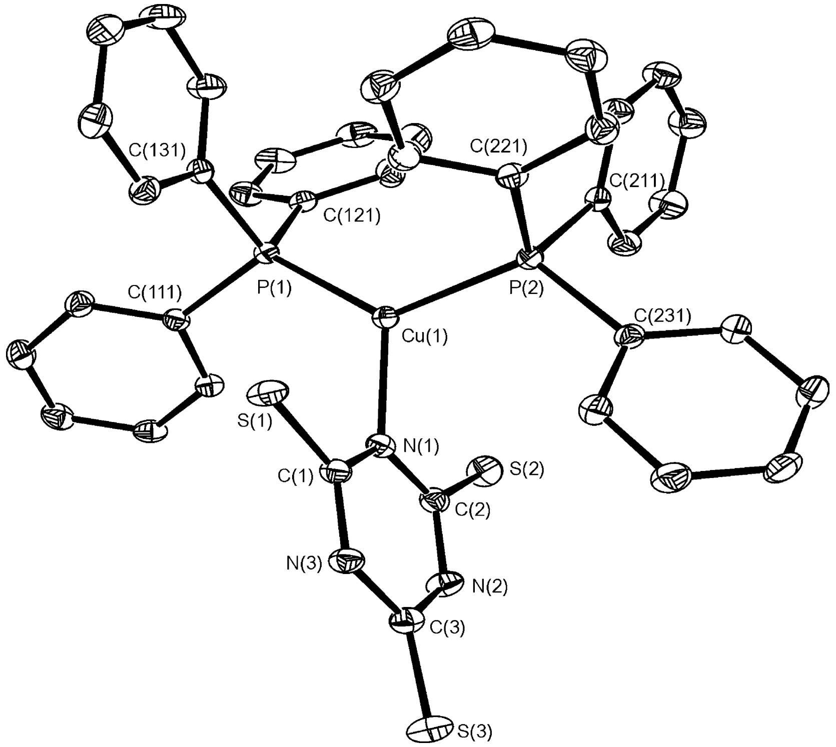

Fig. 3. The structure of **2** showing the atomic labelling. Thermal ellipsoids are at the 30% probability level. Selected metrical data: Cu(1)–N(1) 2.019(2), Cu(1)–P(1) 2.2318(5), Cu(1)–P(2) 2.2526(5), S(1)–C(1) 1.677(2), S(2)–C(2) 1.662(2), S(3)–C(3) 1.653(2), N(1)–C(1) 1.347(2), N(1)–C(2) 1.348(3), N(2)–C(2) 1.384(3), N(2)–C(3) 1.362(3), N(3)–C(1) 1.369(2), N(3)–C(3) 1.359(2) Å; N(1)–Cu(1)–P(1) 121.28(5), N(1)–Cu(1)–P(2) 111.06(5), P(1)–Cu(1)–P(2) 127.64(2)°.

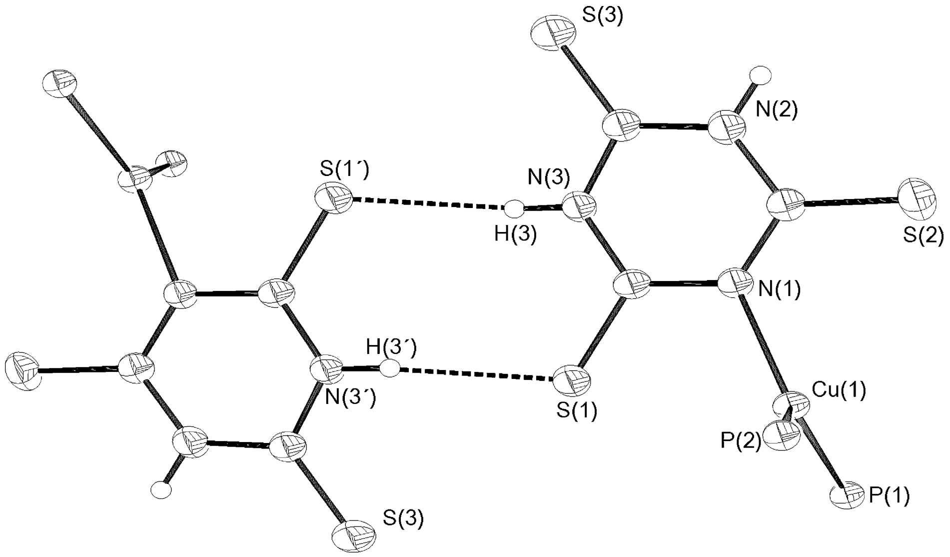

Fig. 4. The hydrogen-bonded dimer of **2**; phenyl groups attached to phosphorus and the CH_2Cl_2 solvent molecules have been omitted for clarity.

6. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 189198 and 198199, compounds **1** and **2**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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