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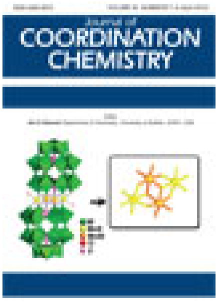

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Structural characterization of polymeric potassium salts with 2-thiobarbituric acid: influence of organotin(IV) chlorides on potassium cation solvation

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Structural characterization of polymeric potassium salts with 2-thiobarbituric acid: influence of organotin(IV) chlorides on potassium cation solvation

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Slow evaporation of the filtrate derived from the reaction in water between 2-thiobarbituric acid (H_2TBA) and equimolar amount of potassium hydroxide results in the formation of crystals of two coordination polymers: unhydrated $[K(\mu_3\text{-S,O-HTBA})]_n$ (**1**) and hydrated $[K(\mu_2\text{-S,O-HTBA})(\mu_2\text{-S,O-}H_2TBA)(\mu\text{-}H_2O)]_n$ (**2**), which depend on the absence (**1**) or presence (**2**) of methanol solutions of organotin chloride. The hydrate **2** was isolated from the filtrates when di-*n*-butyltin dichloride, dimethyltin(IV) dichloride, diphenyltin(IV) dichloride, tri-*n*-butyltin chloride, or triphenyltin(IV) chloride were used during the reaction. The crystal structures show that coordination of potassium occurs through the S and O donors. The potassiums have distorted tetragonal bipyramidal and distorted cubic coordination environments in **1** and distorted square antiprism coordination in **2**. Both structures exhibit intermolecular N–H $\cdots$ O hydrogen-bond interactions, which form TBA chains while the water in **2** produces a richer hydrogen-bonded structure.

Keywords: Coordination polymers; Thiobarbituric acid; Potassium complex; Hydrates

1. Introduction

2-Thiobarbituric acid (H_2TBA) is a hydroxyl substituted thiouracil, wherein three out of total of four hydrogen atoms are mobile [1, 2]. Generally, experimental and spectroscopic data for the neutral forms of H_2TBA reveal an equilibrium between the keto-thione (N1) and hydroxyl-keto-thione (N10) tautomeric forms (scheme 1).

The equilibrium of H_2TBA is derived by conversion of one of the keto-groups associated with the proton transition to the enol group [1–3]. H_2TBA is used as a scavenger of the radicals formed in the course of lipids peroxidation [4, 5]. We have also recently reported on the synthesis and tumor cell screening results of the tri-*n*-butyltin(IV) complex $[(n\text{-Bu})_3Sn(\text{O-HTBA}) \cdot H_2O]$ against leiomyosarcoma cells (LMS) [6]. The $\{[Ph_3Sn(\text{O-HTBA})]\}_n$ complex has also been synthesized and tested

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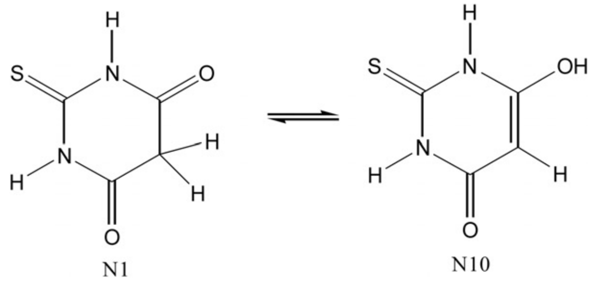

Scheme 1. Tautomeric forms of 2-thiobarbituric acid (H_2TBA).

against human cancer cell lines: HeLa (cervical), OAW-42 (ovarian), MCF-7 (breast, ER positive), MDA-MB-231 (breast, ER negative), A549 (lung), Caki-1 (renal), and additionally, the normal human lung cell line MRC-5 (normal human fetal lung fibroblast cells) and normal immortalized human mammary gland epithelial cell line MTSV17 [7]. During the studies the hydrated potassium salt of H_2TBA $[K(\mu_2\text{-S,O-HTBA})(\mu_2\text{-S,O-}H_2TBA)(\mu\text{-}H_2O)]_n$ (**2**) was obtained in the filtrate as a by-product of the synthesis of $\{[Ph_3Sn(O\text{-HTBA})] \cdot 0.7(H_2O)\}_n$. Therefore, we have performed a comparative reaction without Ph_3SnCl – but adding methanol which was used as a solvent for Ph_3SnCl – and in this case the product **1** was obtained. The product turned out not to be a hydrate and contains only the deprotonated HTBA ligands. That leads to a supposition that the presence of Ph_3SnCl results in the formation of the hydrated form of potassium salt. The assumption was subsequently supported by appropriate reactions with other tin compounds such as di-*n*-butyltin dichloride, tri-*n*-butyltin chloride, and dimethyltin dichloride. In each case **2**, a hydrate, was obtained.

2. Experimental

2.1. *Materials and instruments*

All solvents used were of reagent grade, while H_2TBA and di-*n*-butyltin dichloride (Aldrich, Merck) were used with no purification. Infrared (IR) spectra from 4000 to 370 cm^{-1} were obtained in KBr discs. The ^1H-NMR spectra were recorded on a Bruker AC 250 MHFT NMR instrument in DMSO-d_6 solution.

2.2. *Synthesis and crystallization of $[K(\mu_3\text{-S,O-HTBA})]_n$ (1) and $[K(\mu_2\text{-S,O-HTBA})(\mu_2\text{-S,O-}H_2TBA)(\mu\text{-}H_2O)]_n$ (2)*

A suspension of H_2TBA (1 mmol, 0.144 g) in 5 mL distilled water solution was treated with 1 N potassium hydroxide solution (1 mL, 1 mmol) and a clear solution was immediately formed. 5 mL methanol (**1**) or 5 mL methanol solution of $(n\text{-}C_4H_9)_2SnCl_2$, (0.152 g, 0.5 mmol) (**2**) was then added. The same hydrate **2** was also isolated from the filtrates when 0.5 mmol of dimethyltin(IV) dichloride, diphenyltin(IV) dichloride or

1 mmol of tri-*n*-butyltin chloride, triphenyltin(IV) chloride were used for the reaction. Crystals of **1** and **2** suitable for X-ray analysis were grown by slow evaporation of the filtrates.

2.3. *X-ray crystallography*

Although the crystallographic data for the unit cell of **2** have been reported earlier [7] the full X-ray analysis of the complex was absent. We report the full X-ray analyses of **1** and **2**. X-ray diffraction data were collected for **1** at 100(1) K on an XCALIBUR diffractometer with EOS detector using graphite-filtered Mo-Kα radiation ($\lambda = 0.71073$ Å) and for **2** at 130(1) K on a SuperNova diffractometer with Atlas detector and Cu-Kα ($\lambda = 1.54178$ Å) radiation. The data were corrected for Lorentz-polarization as well as for absorption effects [8]. Accurate unit-cell parameters were determined by least-squares fit of 7496 (**1**), and 3297 (**2**) reflections of highest intensity, chosen from the whole experiment. The calculations were mainly performed within the WinGX program system [9]. The structures were solved with SIR92 [10] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-97 [11]. Scattering factors incorporated in SHELXL-97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A \cdot P)^2 + B \cdot P]$, where $P = [\text{Max}\ (F_o^2, 0) + 2F_c^2]/3$. The final values of A are listed in table 1. All hydrogen atoms were located by difference Fourier synthesis. Non-hydrogen atoms were refined anisotropically; all hydrogen atoms were also freely refined with the isotropic thermal parameters. For molecular graphics the programs SHELXTL [11] and Mercury 2.2 [12] were used. Relevant crystal data are listed in table 2, together with refinement details.

3. Results and discussion

Compounds **1** and **2** form in reactions differing solely by the presence or absence of organotin(IV) chloride compounds (Me_2SnCl_2, (n-Bu)$_2$SnCl$_2$, Ph_2SnCl_2, (n-Bu)$_3$SnCl, Ph_3SnCl) during the reaction (see Section 2). The asymmetric parts of **1** and **2** together with the labeling schemes are shown in figures 1 and 2, respectively. Both structures constitute 3-D coordination polymers that extend throughout each crystal.

Complex **1** crystallizes in the monoclinic space group $P2/c$ with two potassiums and one anion of thiobarbituric acid in the asymmetric unit (figure 1). Potassium cations occupy the special positions on different two-fold axes and the environments of the cations are different. The coordination of K1 is close to a distorted tetragonal bipyramid (figure 3a). The angle O4–K1–O41 is 177.80(3)° and the angle S22–K1–S23 is 172.20(2)° (further geometrical parameters are listed in table 1). The environment of K2 can be described as a distorted cube (figure 3b, table 1). The angle O6–K2–O61 is 171.70(4)° whereas the angle S22–K2–S23 is 169.25(2)°.

Compound **2** crystallizes in the triclinic space group P-1 with a potassium cation, an additional water molecule, one H_2TBA neutral molecule, and one anion in the asymmetric unit (figure 2). Similar to **1**, coordination of potassium occurs through the S and O donors of TBA and oxygen of water. The potassium cation **2** exhibits a distorted square antiprism environment (figure 3c, table 1).

Table 1. Selected geometric parameters (Å, °) for **1** and **2**.

Complex **1**			
K1–O4	2.8537(12)	O4^{i}–K1–O4^{v}	94.92(5)
K1–O4^{i}	2.7514(11)	S2^{ii}–K1–S2^{iii}	173.20(2)
K1–S2^{ii}	3.2419(6)	S2^{ii}–K1–O4	82.99(2)
O4–K1–O4^{iv}	90.53(5)	S2^{ii}–K1–O4^{iv}	101.86(2)
O4–K1–O4^{i}	177.81(3)	S2^{ii}–K1–O4^{i}	97.45(2)
O4–K1–O4^{v}	87.28(3)	S2^{ii}–K1–O4^{v}	77.88(2)
K2–O6	2.7321(12)	O6–K2–O6^{xi}	105.53(6)
K2–O6^{ix}	3.1051(13)	O6–K2–S2^{iii}	67.74(3)
K2–S2^{vi}	3.2372(6)	O6–K2–S2^{viii}	107.05(2)
K2–S2^{iii}	3.6739(7)	O6–K2–S2^{vii}	67.24(3)
O6–K2–O6^{x}	171.70(4)	O6–K2–S2^{vi}	106.50(3)
O6–K2–O6^{ix}	82.76(3)	S2^{vi}–K2–S2^{iii}	169.25(2)
Complex **2**			
K1–O1	2.720(2)	O1–K1–O6B	89.72(6)
K1–O6B	2.7426(15)	O1–K1–O4A	74.98(5)
K1–O4A	2.7688(16)	O1–K1–S2A	147.41(5)
K1–S2A	3.3034(10)	O1–K1–S2B	112.43(5)
K1–S2B	3.3502(8)	S2A–K1–S2B	81.21(2)
K1–S2B^{xiii}	3.4432(8)	O6B–K1–S2A	75.61(4)
K1–S2B^{xiv}	3.5045(9)	O6B–K1–S2A^{xii}	140.73(4)
K1–S2A^{xii}	3.4963(8)	O1–K1–O6B	89.72(6)

Symmetry codes: i: $x, 1+y, -1/2-z$; ii: $-x, -y, -z$; iii: $x, -y, -1/2+z$; iv: $-x, y, -1/2-z$; v: $x, 1+y, z$; vi: $1-x, -1-y, -z$; vii: $1-x, -y, -z$; viii: $x, -1-y, -1/2+z$; ix: $x, -1+y, z$; x: $1-x, -1+y, -1/2-z$; xi: $1-x, y, -1/2-z$; xii: $-x, 1-y, -z$; xiii: $-1-x, 1-y, -z$; xiv: $1-x, 1-y, -z$.

The most significant differences between H_2TBA and anion are seen in the C4–C5 and C5–C6 bond lengths and intraannular angle of C5. In the neutral molecule (A) the C4A–C5A, C5A–C6A distances correspond to single bonds (1.501(3) Å and 1.496(3) Å, respectively) and the angle at C5A is 116.2(2)°, close to the typical value for neutral acid molecule [13]. In the anion, the angle of C5(B) corresponds to sp^2 hybridization [121.1(2)] and the C4B–C5B, C5B–C6B distances [1.394(3), 1.404(2)] are close to the typical values for the aromatic ring.

In the structure of **1**, the sulfur and potassium form parallel, 2-D networks along the [10] direction (figure 4). Perpendicular to the direction are sulfur–potassium chains and anions of H_2TBA that are situated between the networks (figure 5a). The sulfur and potassium form a parallel ladder structure perpendicular to the [10] direction and the thiobarbituric rings and water molecules coordinated to potassium lie between the ladders (figure 5b). It is evident that the presence of water significantly affects the crystal packing.

In **1**, where all the sulfurs are coordinated to three potassium cations, the sulfur–potassium bond lengths are quite different [3.2373(4) Å to 3.6740(5) Å]. Furthermore, each oxygen is coordinated to two potassiums and the O–K distances are in range 2.751(1)–3.105(1) Å. Despite the different values, the distances are in the typical ranges for the kinds of bonds, as determined in the Cambridge Structural Database [13] (figure 6). In the structure of **2**, sulfur is coordinated to two and oxygen to one potassium, while the S–K and O–K distances are shorter than those in **1**. The oxygen–potassium bond lengths range from 2.718(2) to 2.768(2) and sulfur–potassium distances range from 3.303(1) Å to 3.504(1) Å. The relatively large spread of the S–K and O–K bond lengths in **1** is probably a result of the different coordination involved in the interactions and, therefore, different steric demands. A similar geometry has been found in [Co(Htbba)(ethane-1,2-diamine)$_2$]ClO$_4 \cdot 2H_2O$ (**2**) [14].

Table 2. Relevant crystal data and the details of structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$(C_4H_3N_2O_2S)K$	$(C_8H_9N_4O_5S_2)K$
Formula weight	182.24	344.41
Crystal system	Monoclinic	Triclinic
Space group	$P2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.235(2)	6.7758(8)
b	3.8689(11)	10.2313(16)
c	14.556(2)	10.3893(12)
α	90	109.055(12)
β	97.48(1)	91.005(10)
γ	90	107.745(12)
Volume (Å^3), Z	627.3(2), 4	642.88(15), 2
Calculated density (Mg m^{-3})	1.93	1.78
Absorption coefficient (mm^{-1})	1.11	6.93
$F(000)$	368	352
θ range for data collection (°)	2.82–29.0	4.54–74.06
Limiting indices	$-14 \le h \le 14$; $-5 \le k \le 5$; $-19 \le l \le 19$	$-7 \le h \le 8$; $-12 \le k \le 12$; $-12 \le l \le 12$
Reflections collected	11,830	4514
Independent reflection	1566 [R(int) = 0.0181]	2506 [R(int) = 0.0270]
Reflections with $I > 2\sigma(I)$	1459	2314
Weighting scheme		
A	0.0307	0.0905
B	0.3038	0.2277
Number of parameters	104	217
$R(F)$ [$I > 2\sigma(I)$]	0.0225	0.0404
$R(F)$ (all data)	0.0248	0.0433
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0604	0.1152
$wR(F^2)$ [all data]	0.0614	0.1179
Goodness-of-fit on F^2	1.077	1.001
Largest difference peak and hole (e Å^{-3})	0.34 and −0.25	0.37 and −0.42

Intermolecular hydrogen-bonding (figure 7) is crucial in the determination of the crystal packing of both structures. Hydrogen-bond parameters are given in table 3. A hydrogen-bonded chain is formed in **1** by interactions between N(1)–H and N(3)–H donors and O6 and O4 acceptors of thiobarbituric anions. The hydrogen bonds are nearly linear [N–H $\cdots$ O angles of 177(2)°] while the distances are typical for medium–strength interactions. These hydrogen bonds close the centrosymmetric rings across two different inversion centers, with the graph set notation of rings being described as $R_2^2(8)$. The two kinds of rings in turn connect the cations into two $C_2^2(10)$ chains.

To some extent a similar hydrogen-bond pattern is observed in **2**; however, the number of hydrogen bonds increases owing to the presence of water molecule that acts as an additional hydrogen-bond donor. One can describe the hydrogen-bond system in the structure as a stepwise construction. At the first level the HTBA and H_2TBA form hydrogen-bonded pairs, which further extend into chains of centrosymmetric dimers. Two such chains make a double layer with water sticking outside the layers ($R_2^2(8)$, $C_2^2(10)$, figure 8a). One of the hydrogen atoms of water takes part in a hydrogen-bonding interaction that connects neighboring layers into pairs (figure 8b), while the other hydrogen is also involved in hydrogen-bonding interactions that expand the structural building blocks into a 3-D structure. An analysis of the hydrogen-bond

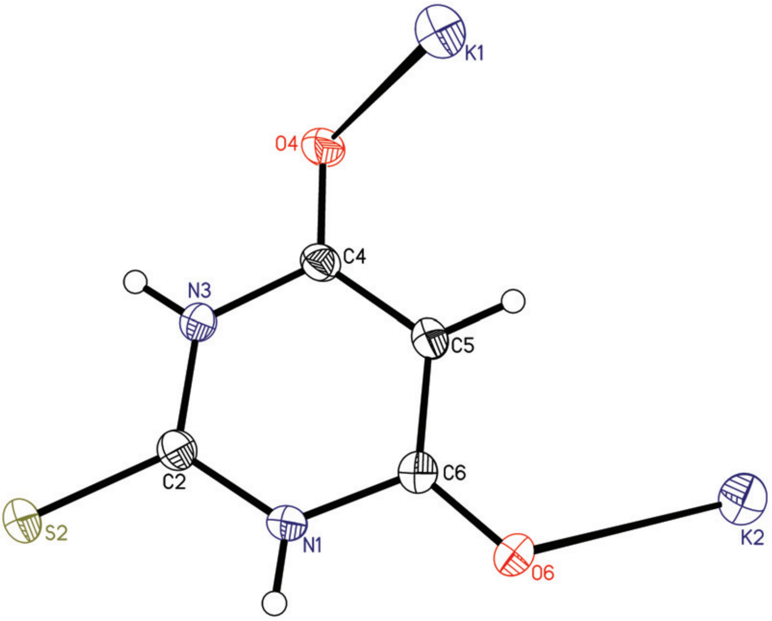

Figure 1. Asymmetric part of the unit cell of **1** with numbering scheme. The ellipsoids are drawn at 50% probability level; hydrogen atoms are shown as spheres of arbitrary radii.

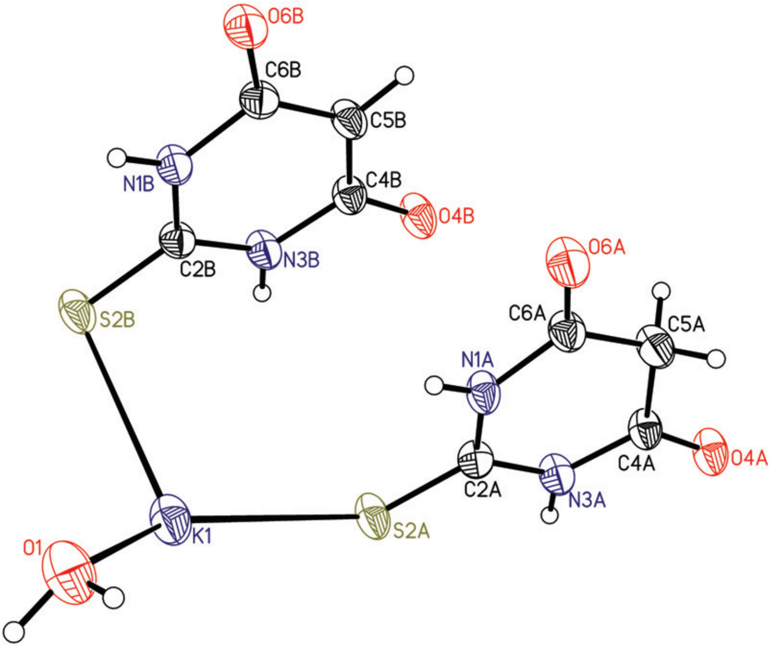

Figure 2. Asymmetric part of the unit cell of **2** together with numbering scheme. The ellipsoids are drawn at 50% probability level; hydrogen atoms are shown as spheres of arbitrary radii.

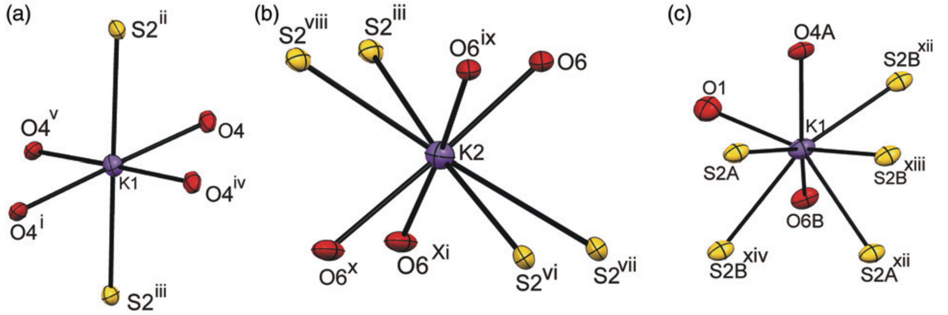

Figure 3. Coordination modes of potassium cations: (a) K1 in **1** (symmetry codes: $^{\text{i}}$: $-x, 1+y, -1/2-z$, $^{\text{ii}}$: $-x, -y, -z$, $^{\text{iii}}$: $x, -y, -1/2+z$, $^{\text{iv}}$: $-x, y, -1/2-z$, $^{\text{v}}$: $x, 1+y, z$); (b) K2 in **1** (symmetry codes: $^{\text{vi}}$: $1-x, -1-y, -z$, $^{\text{vii}}$: $1-\ x, -y, -z$, $^{\text{viii}}$: $x, -1-y, -1/2+z$, $^{\text{ix}}$: $x, -1+y, z$, $^{\text{x}}$: $1-x, -1+y, -1/2-z$, $^{\text{xi}}$: $1-x, y, -1/2-z$); (c) K1 in **2** (symmetry codes: $^{\text{xii}}$: $-x, 1-y, -z$, $^{\text{xiii}}$: $-1-x, 1-y, -z$, $^{\text{xiv}}$: $1-x, 1-y, -z$).

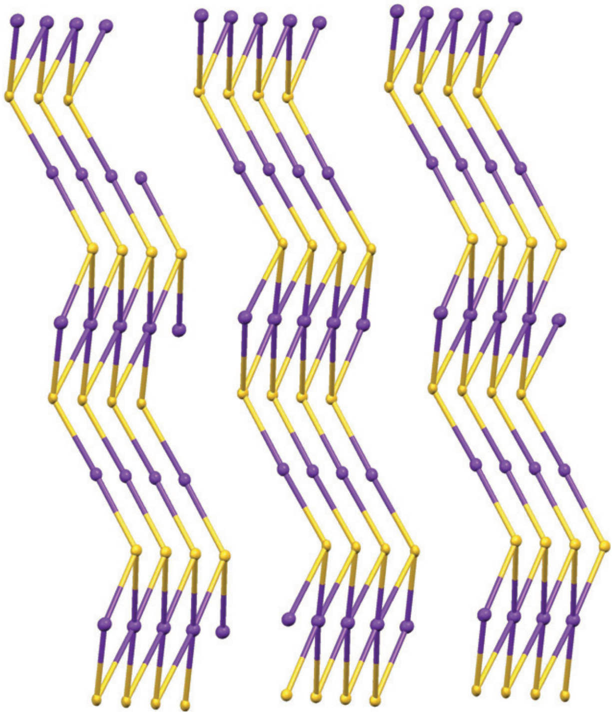

Figure 4. Perspective view of S–K network in **1**.

parameters of **2** indicates that the water forms weaker interactions than the hydrogen bonds between thiobarbiturate anions. The self-associated hydrogen bonds between TBA$^-$ molecules, which form TBA network, have also been described in codeinone derivatives of thiobarbituric acids [15] and $[Ph_3PAuSC_4H_3N_2O_2]$ [16].

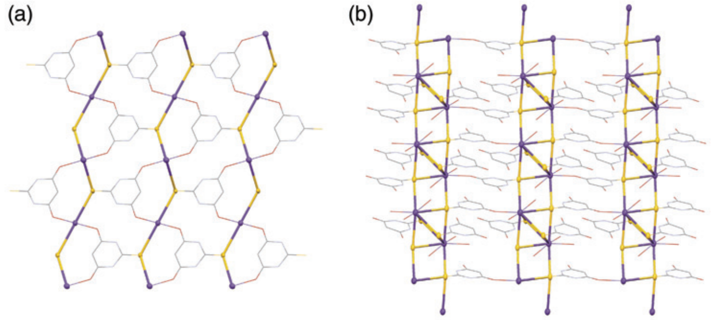

Figure 5. Packing diagrams: (a) for **1** and (b) for **2**.

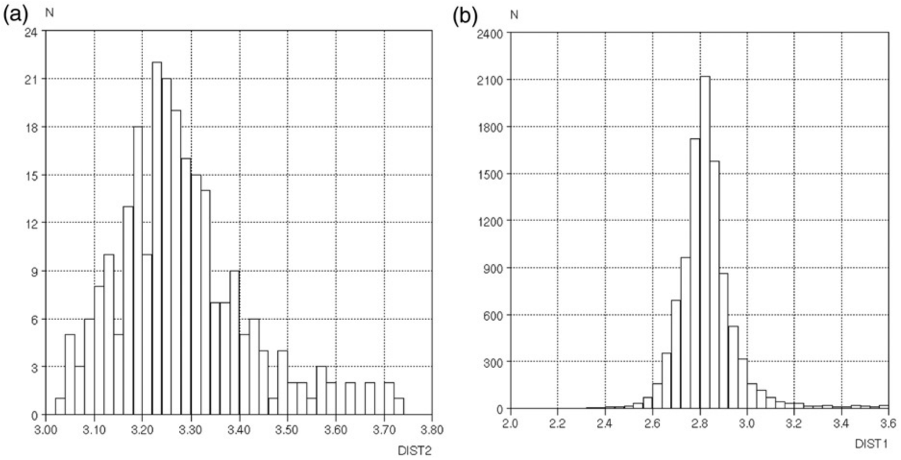

Figure 6. Histograms presenting the results of the Cambridge Structural Database search for (a) S–K distances and (b) O–K distances (limited to compounds in which S and O are connected with carbon; in part b the search range 2.0–3.6 Å).

3.1. *IR spectroscopy*

Characteristic IR bands of **1**, **2**, and the ligand are listed in table 4. The IR bands of **1** and **2** show distinct vibrational bands at 1410–1490 and 1305–1240 cm^{-1}, which are assigned to ν(CN) vibrations (thioamide I and II bands) and bands at 1020–995 and 930–740 cm^{-1} that can be attributed to ν(CS) vibrations (thioamide III and IV bands). The bands are shifted to lower frequencies toward the corresponding bands in the spectrum of the free ligand, supporting donation of the ligand as well. In both IR spectra of **1** and **2** bands due to ν(NH) vibration are also observed at 3000–3500 cm^{-1}, indicating no deprotonation of the nitrogen atoms. The broad band at 3483 cm^{-1} in the IR spectrum of **1** is due to ν(O–H) involved in hydrogen-bonding interactions (table 4, supplementary figure S1). However, the sharp band at 3563 cm^{-1} in **2** is characteristic of ν(OH) of coordinated H_2O. The assignment of the IR vibrational bands to the corresponding normal modes is based on detailed data for similar complexes where *ab initio* or DFT calculations are performed and X-ray data are also available [17].

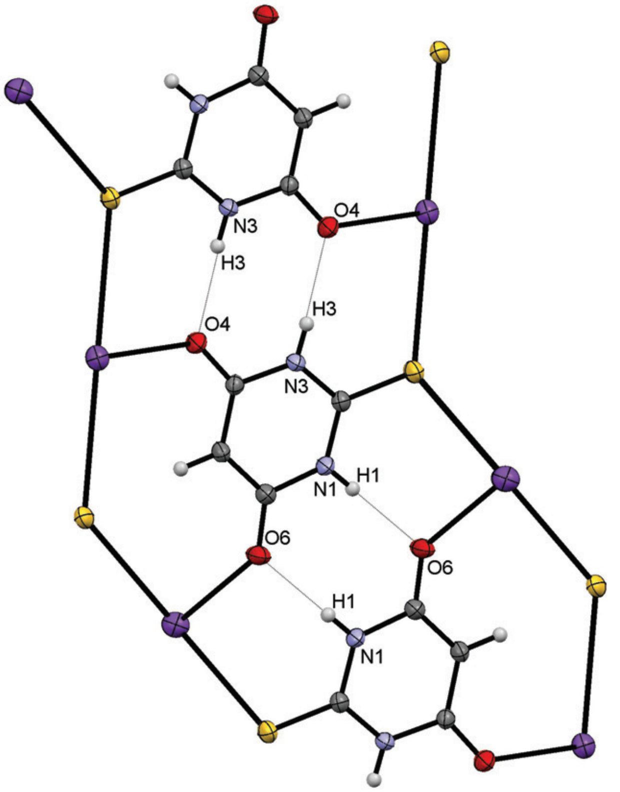

Figure 7. Hydrogen-bond pattern in **1**. Hydrogen bonds are depicted as dashed lines.

Table 3. Hydrogen-bond data for **1** and **2**.

D–H $\cdots$ A	D–H (Å)	A $\cdots$ H (Å)	D $\cdots$ A (Å)	D–H $\cdots$ A (°)
Complex **1**				
N1–H1 $\cdots$ 06^{i}	0.80(2)	2.01(2)	2.812(1)	177(2)
N3–H3 $\cdots$ 04^{ii}	0.82(2)	2.03(2)	2.846(1)	177(2)
Complex **2**				
N1A–H1A $\cdots$ 06B^{iii}	0.79(3)	2.17(5)	2.826(2)	176(4)
N1B–H1B $\cdots$ 06A^{iii}	0.84(3)	2.07(3)	2.906(2)	177(3)
N3A–H3A $\cdots$ 04B^{iv}	0.88(4)	1.96(4)	2.837(2)	173(4)
N3B–H3B $\cdots$ 04A^{iv}	0.85(3)	2.05(4)	2.881(2)	168(3)
O1–H1 $\cdots$ 06A^{v}	0.83(5)	2.17(5)	2.928(3)	152(4)
O1–H1’ $\cdots$ 04B^{vi}	0.91(7)	1.91(6)	2.798(3)	163(5)

Symmetry codes: ^{i} $1-x, -y, -z$; ^{ii} $-x, -1-y, -z$; ^{iii} $1-x, 1-y, 1-z$; ^{iv} $-x, -y, -z$; ^{v} $-x, 1-y, 1-z$; ^{vi} $x, 1+y, z$.

3.2. *Thermal decomposition*

TG-DTA analysis (under nitrogen) shows that unhydrated **1** remains stable up to 350°C, beyond which decomposition occurs by two exothermic steps 350–560°C (supplementary figure S2 (top)). The hydrated **2**, however, is less stable. Thus, TG-DTA

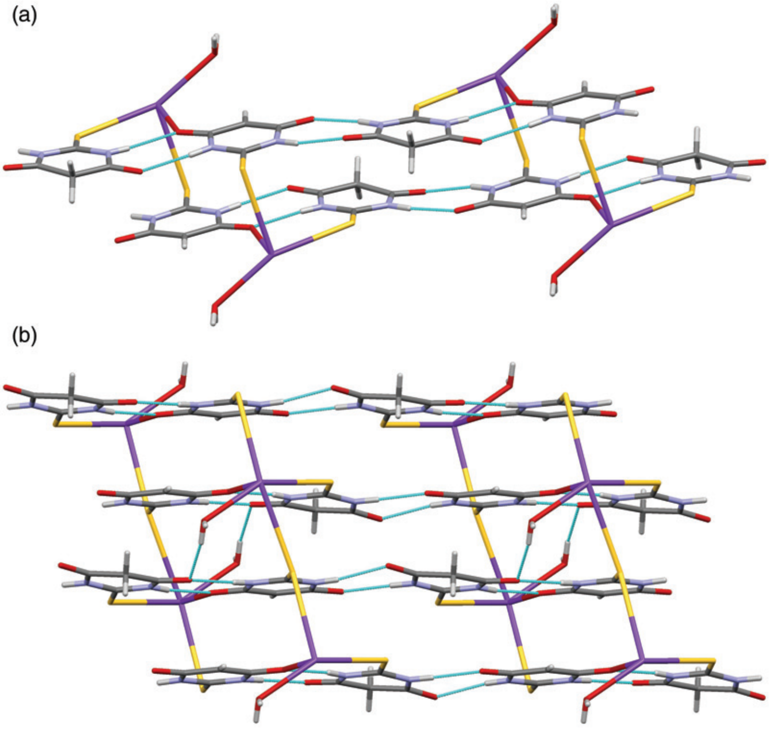

Figure 8. Hydrogen-bond patterns in **2**: (a) formation of the bilayer by means of N–H · · · O hydrogen bonds and (b) water molecules join the bilayers into pairs of O–H · · · O hydrogen bonds.

Table 4. Characteristic IR bands of **1** and **2**.

	TBA	Complex **1**	Complex **2**
ν(O–H)	–	3483.68	3563
ν(N–H)	3663.73	3068.94	3562.78
Thioamide band I	1527.02	1397.64	1459.10
Thioamide band II	1350.13	1303.95	1301.81
Thioamide band III	1153.69	992.76	1017.85
Thioamide band IV	800.64	795.30	799.99

analysis shows an endothermic decomposition step between 150°C and 250°C (supplementary figure S2 (bottom)), which corresponds to the loss of water molecule.

4. Conclusion

The unhydrated **1** and corresponding hydrate **2** have been isolated from slow evaporation of the filtrate derived from the reaction in water between H_2TBA and equimolar potassium hydroxide, depending on the absence or presence of methanol solutions of organotin chlorides. The crystal structures show that coordination occurs through the S and O donors. The potassiums have distorted tetragonal bipyramidal and distorted cubic coordination environments in **1** and distorted square antiprism coordination environment in **2**. Thermal analysis shows that the unhydrated **1** is more stable than the corresponding hydrate **2**.

Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos CCDC-830893 (**1**) and CCDC-830894 (**2**). Copies of the information may 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: www.ccdc.cam.ac.uk).

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