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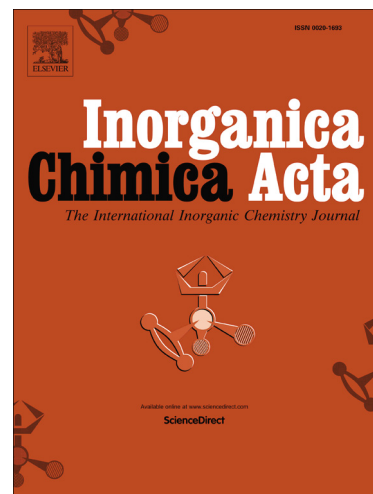
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Research paper

Cadmium(II) thiosaccharinate (tsac) complexes: Crystal structures of [Cd(tsac)₂(abtH)₂] (abtH = 2-aminobenzothiazole), [Cd(tsac)₂(bimsH)₂] (bimsH = 2-mercaptobenzimidazole) and [Cd(μ -tsac)(tsac)(κ^2 -aapH)]₂ (aapH = 2-acetylaminopyridine)

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Cadmium(II) thiosaccharinate (tsac) complexes: Crystal structures of [Cd(tsac)₂(abtH)₂] (abtH = 2-aminobenzothiazole), [Cd(tsac)₂(bimsH)₂] (bimsH = 2-mercaptobenzimidazole) and [Cd(μ -tsac)(tsac)(κ^2 -aapH)]₂ (aapH = 2-acetylaminopyridine)

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Abstract

A range of new cadmium(II) thiosaccharinate (tsac) complexes have been prepared from reactions of the synthon [Cd(tsac)₂.H₂O] with a variety of two-electron donor ligands including amino- and acetyl-amino heterocycles, 2-mercaptobenzoimidazole, 2-mercaptobenzothiazole and 2-phenylpyridine, as well as the bidentate small bite-angle diphosphane, bis(diphenylphosphino)methane (dppm), and the tridentate ligand 2,6-diacetylaminopyridine (daapH₂). Four types of complex have been isolated, namely [Cd(tsac)₂L₂], [Cd(tsac)₂L], [Cd(tsac)₂(μ -dppm)]₂ and [Cd(tsac)₂(κ^3 -daapH₂)(H₂O)]. Crystal structures of three, namely [Cd(tsac)(μ -tsac)(κ^2 -aapH)]₂ (aapH = 2-acetylaminopyridine), [Cd(tsac)₂(abtH)₂] (abtH = 2-aminobenzothiazole) and [Cd(tsac)₂(bimsH)₂] (bimsH = 2-mercaptobenzimidazole) have been carried out. In all the tsac ligand(s) bind exclusively through coordination of the thiocarbonyl sulfur atom highlighting the chalcogenophilic nature of cadmium. In [Cd(tsac)(μ -tsac)(κ^2 -aapH)]₂ the tsac ligands adopt both bridging and terminal coordination modes, the former being relatively rare.

Keywords: cadmium; thiosaccharinate; crystal structures; amino; diphosphane;

1. Introduction

The saccharinate (sac) anion is a versatile ligand binding to a wide range of transition metal centres in a variety of different coordination modes [1-7], while in contrast the coordination chemistry of the related thiosaccharinate (tsac) anion has been far less extensively explored [8-31]. While the most common coordination mode for saccharinate binding is through nitrogen, the thiosaccharinate ligand predominantly binds as thiolate type ligand through the thiocarbonyl sulfur (**Chart 1**).

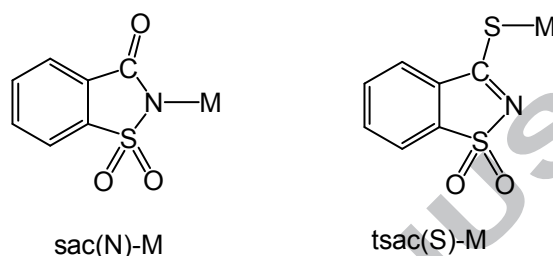


Chart 1

The coordination chemistry of cadmium has attracted interest due to its toxicological properties which primarily arise from the affinity of Cd(II) towards compounds bearing thiol groups, such as metallothioneins and glutathione, although binding to residues through oxygen and nitrogen sites is also possible [32,33]. Thus, Cd(II) is believed to be able to displace several essential metal ions in biological systems, including Ca(II), Cu(II) or Zn(II), giving rise to a range of disorders [34-37]. Consequently it is important to remove cadmium from water, the maximum contaminant level goal (MCLG) being set at 5 ppb, and also to be able to treat cadmium poisoning using chelation agents, generally those with sulfur binding sites [38].

The coordination chemistry of thiosaccharinate to cadmium is relatively unexplored, although studies by Baran and co-workers [8,14,39,40] suggest that it is able to vary its coordination environment depending upon the co-ligands present. Thus, in $[\text{Cd}(\text{tsac})_2(\text{im})_2]$ (im = imidazole) [8] and $[\text{Cd}(\text{tsac})_2(\text{bzim})_2]$ (bzim = benzimidazole) [39] a distorted tetrahedral geometry is noted, the tsac ligands binding through the thiocarbonyl sulfur in both cases. In contrast, in $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ [14] cadmium is five-coordinate, binding to water and four symmetry related tsac ligands, two through the thiocarbonyl sulfur and the other two through one of the sulfonyl oxygen atoms. Addition of pyridine to $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ yields $[\text{Cd}(\text{tsac})_2(\text{py})_3]$ which contains a six-coordinate metal center with a *fac* arrangement of

pyridine ligands. Most interestingly, the two tsac ligands adopt different coordination modes, one binding in a monodentate fashion through sulfur, while the second chelates through both sulfur and nitrogen binding sites [40]. Herein as part of our studies aimed at developing the coordination chemistry of the thiosaccharinate anion we report the synthesis and characterization of a series of new Cd-tsac complexes with heterocyclic amine, acetamide, thiole and diphosphane co-ligands. Crystal structures on three examples reveal a previously unreported Cd₂-tsac binding mode, and show that the nature of the product is highly dependent upon the binding properties and steric bulk of the co-ligands.

2. Experimental

2.1. Materials and instrumentation

IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer and ¹H and ³¹P{¹H} NMR spectra on Varian Unity and Gemini 2000 spectrometers. Melting points were measured on Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at Al-Albait University, Jordan. Conductivity measurements were measured on digital conductivity meter using dmso as a solvent. 2-Aminobenzohiazole (abtH), 2-mercaptobenzoimidazole (bimsH), 2-mercaptobenzothiazole (btzsH), 2-phenylpyridine (2-Phpy), bis(diphenylphosphino)methane (dppm) were purchased and used as supplied. 2-Acetylamino pyridine (aapH) [41], 2-acetylamino pyrimidine (aapmH) [42], 2,6-diacetylamino pyridine (daapH₂) [39], acetylaminothiazole (aatzH) [43], thiosaccharin (Htsac) [44] and [Cd(tsac)₂(H₂O)] [14] were prepared by literature methods.

2.2. Synthesis and characterization

For complexes **1-8**, a warm solution of ca. two equivalents of ligand (0.151 mmol) in absolute EtOH (10 cm³) was added to a warm solution of [Cd(tsac)₂(H₂O)] (0.040 g, 0.076 mmol) in absolute EtOH (10 cm³). The mixture was heated to reflux for 3 h. After cooling to room temperature it was filtered and evaporated to half volume. Further slow evaporation of EtOH over several days gave a yellow solid which was collected, washed with absolute EtOH and dried under vacuum.

[Cd(tsac)₂(abtH)₂] (**1**): Pale yellow crystals, 52%. Anal. Calc. for C₂₈H₂₀CdN₆O₄S₆: C, 41.55, H, 2.49, N, 10.38. Found: C, 41.53, H, 2.43, N, 10.66. Molar conductivity (DMSO): 6.9 (Ω⁻¹ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆): δ 6.98 (t, ³J 7.01, 2H, abt), 7.18 (t, ³J 7.77, 2H, abt), 7.31 (d, ³J 7.92, 2H, abt), 7.42 (s, 4H, 2NH₂), 7.61-7.68 (m, 6H, 4tsac+2abt), 7.61-7.68 (m, 2H, Ar), 7.72 (dd, ³J 5.73, ⁴J 2.98, 2H, tsac), 7.92 (dd, ³J 5.92, ⁴J 2.75, 2H, tsac). IR (KBr): 3394vs, 3286w, 3193w, 3099w. 2962w, 1627m, 1525s, 1490m, 1400s, 1298s, 1234m, 1157s, 1124m 1004s, 810m, 760m, 592m, 561m, 432w cm⁻¹. Mp: 204 °C.

[Cd(tsac)₂(bimsH)₂] (**2**): Yellow crystals, 60%. Anal. Calc. for C₂₈H₂₀CdN₆O₄S₆: C, 41.55, H, 2.49, N, 10.38. Found: C, 41.83, H, 2.53, N, 10.51. Molar conductivity (DMSO): 7.2 (Ω⁻¹ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆): δ 7.08-7.11 (m, 8H, 2bimsH), 7.63-7.70 (m, 2H, tsac), 7.75 (d, ³J 6.0, 2H, tsac), 7.92 (dd, ³J 5.92, ⁴J 3.75, H, tsac), 12.49 (s, 4H, 4NH). IR (KBr): 3166w, 3109w, 3085w. 2981, 1622m, 1510s, 1465s, 1400s, 1292s, 1226s, 1155s, 1004s, 811m, 744m, 592m, 422m cm⁻¹. Mp: 206-208 °C.

[Cd(tsac)₂(2-Phpy)₂] (**3**): Yellow crystals, 63 % yield. Anal. Calc. for C₃₆H₂₆CdN₄O₄S₄: C, 52.78, H, 3.20, N, 6.84. Found: C, 52.70, H, 3.51, N, 7.03. Molar conductivity (in DMSO): 7.3 (Ω⁻¹ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆): δ 7.33 (dd, ³J 4.95, ⁴J 2.30, 2H, ppy), 7.40-7.50 (m, 6H, ppy), 7.61-7.68 (m, 4H, tsac), 7.72 (dd, ³J 5.98, ⁴J 2.57, 2H, tsac), 7.86 (dd, ³J 7.81, ⁴J 2.29, 2H, ppy), 7.93(t, ³J 7.89, 4H, 2tsac+2ppy), 8.06(d, ³J 7.81, 4H, ppy), 8.66 (d, ³J 4.72, 2H, ppy). IR (KBr) 3066w, 2923w, 1731m, 1558w, 1460s, 1415s, 1303s, 1234m, 1157s, 1004s, 808m, 764m, 694m, 592w cm⁻¹. Mp: 170 °C.

[Cd(tsac)₂(aapmH)₂] (**4**): Pale yellow solid, 62 % yield. Anal. Calc. for C₂₆H₂₂CdN₈O₆S₄: C, 39.87, H, 2.83, N, 14.31. Found: C, 39.96, H, 2.70, N, 14.22. Molar conductivity (DMSO): 14.2 (Ω⁻¹ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆): δ 2.16 (s, 6H, 2CH₃), 7.14 (t, ³J 4.83, 2H, pym), 7.59-7.63 (m, 4H, tsac), 7.68 (dd, ³J 5.89, ⁴J 2.60 2H, tsac), 7.91 (dd, ³J 6.03, ⁴J 2.40, 2H, tsac), 8.62 (d, ³J 4.83, 4H, Pym), 10.48 (s, 2H, 2NH). IR (KBr): 3305w, 3052w. 2923m, 2831w, 1731m, 1639s, 1514w, 1425s, 1307s, 1157s, 1008s, 813s, 754s, 600w, 590w 425s cm⁻¹. Mp: 264-267 °C.

[Cd(tsac)₂(aapH)₂] (**5**): Yellow crystals, 92% yield. Anal. Calc. for C₂₁H₁₆CdN₄O₅S₃: C, 39.10, H, 2.50, N, 8.69. Found: C, 39.41, H, 2.53, N, 8.60. Molar conductivity (DMSO): 7.4

($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). $^1\text{H NMR}$ (DMSO- d^6): δ 2.39 (s, 3H, CH_3), 7.06 (m, 1H, py), 7.71 (m, 5H, 4tsac + py), 7.80 (m, 2H, tsac), 7.95 (d, 3J 7.2, 2H, tsac), 8.05 (d, 3J 8.4, 1H, py), 8.29 (d, 3J 4.0, 1H, py), 10.35 (s, 1H, NH). IR (KBr): 3325w, 3193w, 3082w, 2925w, 1672s, 1640s, 1531w, 1407s, 1367m, 1315s, 1157s, 1006s, 815 cm^{-1} . Mp: 254-256 $^\circ\text{C}$.

$[\text{Cd}(\text{tsac})_2(\text{ataH})_2]$ (**6**): Pale yellow solid, 91%. Ana. Calc. for $\text{C}_{19}\text{H}_{14}\text{CdN}_4\text{O}_5\text{S}_5$: C, 35.05, H, 2.17, N, 8.61. Found: C, 35.31, H, 2.01, N, 8.34. Molar conductivity (DMSO): 6.5 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). $^1\text{H NMR}$ (DMSO- d^6): δ 2.11 (s, 3H, CH_3), 7.15 (d, 3J 3.54, 1H, ata), 7.43 (d, 3J 3.54, 1H, ata), 7.61-7.68 (m, 4H, tsac), 7.72 (dd, 3J 6.05, 4J 3.15, 2H, tsac), 7.91 (dd, 3J 5.86, 4J 3.85, 2H, tsac), 12.03 (s, 1H, NH). IR (KBr): 3311w, 3186w, 3035w, 2954w, 1655s, 1546w, 1407s, 1362m, 1292s, 1212s, 1149s, 1002s, 815 cm^{-1} . Mp: 242 $^\circ\text{C}$.

$[\text{Cd}(\text{tsac})_2(\text{btzsH})_2]$ (**7**): Pale yellow solid, 66%. Anal. Calc. for $\text{C}_{21}\text{H}_{13}\text{CdN}_3\text{O}_4\text{S}_6$: C, 37.30, H, 1.94, N, 6.2. Found: C, 37.55, H, 2.03, N, 6.41. Molar conductivity (DMSO): 6.6 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). $^1\text{H NMR}$ (DMSO- d^6): δ 7.24-7.40 (m, 4H, btzsH), 7.61-7.68 (m, 4H, tsac), 7.72 (dd, 3J 5.88, 4J 2.96, 2H, tsac), 7.91 (dd, 3J 5.22, 4J 3.12, 2H, tsac), 13.74 (s, H, 1NH). IR (KBr): 3143w, 3082w, 2968w, 1500w, 1461m, 1421s, 1305s, 1157vs, 1004s, 808m, 756m, 690w, 424w cm^{-1} . Mp: 220 $^\circ\text{C}$.

$[\text{Cd}(\text{tsac})_2(\text{daapH}_2)(\text{H}_2\text{O})]$ (**8**): Pale yellow solid, 66%. Anal. Calc. for $\text{C}_{23}\text{H}_{20}\text{CdN}_5\text{O}_7\text{S}_4$: C, 38.42, H, 2.80, N, 9.74. Found: C, 38.36, H, 2.90, N, 9.82. Molar conductivity (DMSO): 7.6 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). $^1\text{H NMR}$ (DMSO- d^6): δ 2.08 (s, 6H, 2 CH_3), 7.60-7.71 (m, 9H, 6tsac+3py), 7.91 (dd, 3J 6.04, 4J 2.56, 2H, tsac), 10.00 (s, 2H, 2NH). IR (KBr): 3307w, 3078w, 2923w, 1641s, 1536m, 1525w, 1452s, 1409s, 1300s, 1234m, 1157s, 1002s, 810m, 592m, 551m cm^{-1} . Mp: 126 $^\circ\text{C}$.

For $[\text{Cd}(\text{tsac})_2(\mu\text{-dppm})_2]$ (**9**), a warm solution of dppm (0.028 g, 0.073 mmol) and $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ (0.040 g, 0.073 mmol) in absolute EtOH (20 cm^3) was stirred at room temperature for 4 h, filtered and the solvent evaporated to a quarter of its original volume on a steam bath. Standing at room temperature afforded a yellow solid which was collected and dried under vacuum (0.032 g, 48 % yield). Anal. Calc. for $\text{C}_{39}\text{H}_{30}\text{CdN}_2\text{O}_4\text{P}_2\text{S}_4$: C, 52.44, H, 3.39, N, 3.14. Found: C, 52.59, H, 3.58, N, 3.14. Molar conductivity (DMSO): 19.8 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). $^1\text{H NMR}$ (DMSO- d^6): δ 4.09 (t, $^2J_{\text{PH}}$ 13.8, 2H, CH_2), 7.30-7.78 (m, 20H, Ph+6tsac),

7.92 (dd, 3J 5.99, 4J 2.47, 2H, tsac). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 25.3 (bs) ppm. IR (KBr): 3058w, 2939w, 1471m, 1417m, 1309s, 1159vs, 1002s, 781m, 742m, 505m, 430w cm^{-1} . Mp: 158 °C.

2.3. Crystallography

Yellow crystals suitable for X-ray crystallographic study were obtained by slow evaporation of concentrated EtOH (**1** and **5**.(EtOH)₂) or EtOH/H₂O (**2**) solutions. Suitable crystals were mounted on glass fibers and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $150 \pm 2 \text{ K}$. Data collection, indexing and initial cell refinements were all done using SMART software. Data reduction were carried out with SAINT PLUS and absorption corrections applied using the programme SADABS [45]. Structures were solved by direct methods or Patterson methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [46].

3. Results and discussion

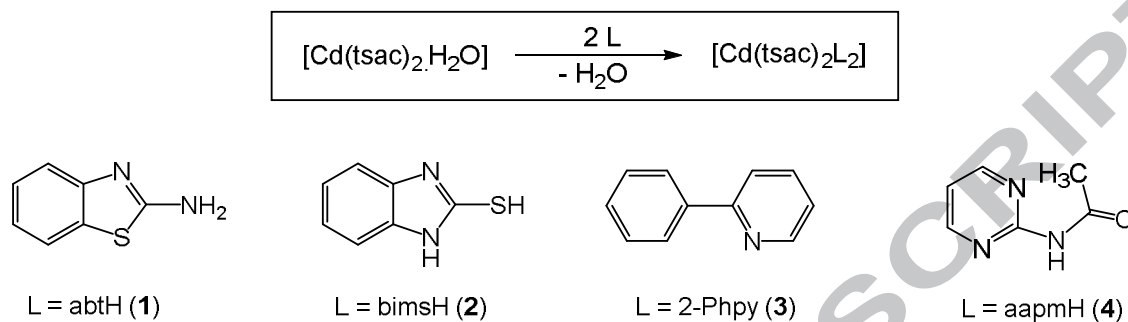
3.1. General synthesis

Five coordinate $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ [**14**] was selected as a synthon since it is easily prepared and stored, and two of the tsac ligands are coordinated weakly through one of the sulfonyl oxygen atoms suggesting they should be easily displaced even by weakly coordinating ligands. Indeed this is the case and in all cases addition of two equivalents of ligand (Scheme 1) in EtOH afforded yellow solutions which after filtration and partial evaporation of volatiles afforded yellow solids in moderate to good yields resulting from coordination of added ligand. Four different types of complexes were isolated of the type; (i) $[\text{Cd}(\text{tsac})_2\text{L}_2]$, (ii) $[\text{Cd}(\text{tsac})(\mu\text{-tsac})\text{L}_2]$, (iii) $[\text{Cd}(\text{tsac})_2(\mu\text{-L})_2]$, (iv) $[\text{Cd}(\text{tsac})_2(\kappa^3\text{-L})(\text{H}_2\text{O})]$ and each is discussed below.

3.2 $[\text{Cd}(\text{tsac})_2\text{L}_2]$ (1-4)

Reactions of $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ with 2-aminobenzothiazole (abtH), 2-mercaptobenzimidazole (bismH), 2-phenylpyridine (2-Phpy) or 2-acetylaminopyrimidine (aapmH) afforded $[\text{Cd}(\text{tsac})_2(\text{abtH})_2]$ (**1**), $[\text{Cd}(\text{tsac})_2(\text{bismH})_2]$ (**2**), $[\text{Cd}(\text{tsac})_2(2\text{-Phpy})_2]$ (**3**) and $[\text{Cd}(\text{tsac})_2(\kappa^2\text{-$

aapmH)₂] (**4**) respectively. In all cases the tsac:L ratio of 1:1 as shown by ¹H NMR spectroscopy and elemental analysis suggest the addition of two equivalents of ligand and loss of water (**Scheme 1**). In order to confirm this, crystal structures were carried out on **1** and **2**, the results of which are summarized in Figures 1 and 2 and Table 1.



Scheme 1

In both **1** and **2**, the Cd(II) cation adopts a distorted tetrahedral environment, with a pair of symmetry related tsac and abtH-bimsH ligands. The tsac anions are bound exclusively through sulfur through their sulfur and Cd-S distances [**1** 2.502(1); **2** 2.5056(7) Å] are close to those found in other cadmium-tsac complexes [**8,14,39,40**]. In **1** the 2-aminobenzothiazole ligands bind through nitrogen and the Cd-N bond length of 2.317(2) Å is somewhat longer than those found in [Cd(tsac)₂(im)₂] [Cd-N 2.226(2) and 2.238(2) Å] [**8**] and [Cd(tsac)₂(bzim)₂] [Cd-N 2.235(2) and 2.256(2) Å] [**39**]. The N-Cd-N bond angle of 86.3(1)^o is significantly smaller than those of 99.97(6) and 98.09(6)^o in [Cd(tsac)₂(im)₂] and [Cd(tsac)₂(bzim)₂] respectively.

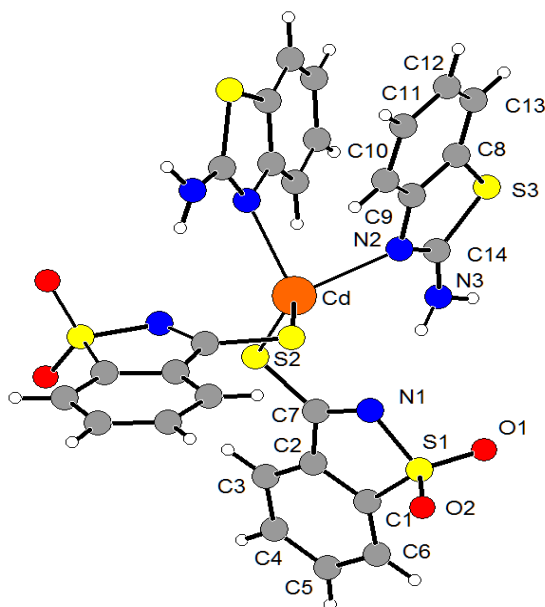


Figure 1. The molecular structure of $[\text{Cd}(\text{tsac})_2(\text{abtH})_2]$ (**1**) with selected bond lengths (Å) and angles ($^\circ$), Cd-N(2) 2.317(2), Cd-S(2) 2.5022(10), N(2)#1-Cd-N(2) 86.30(12), N(2)#1-Cd-S(2) 116.25(7), N(2)-Cd-S(2) 106.82(7), N(2)#1-Cd-S(2)#1 106.82(7), N(2)-Cd-S(2)#1 116.25(7), S(2)-Cd-S(2)#1 119.81(5).

Unlike the CdN_2S_2 coordination environment of **1**, in **2** the metal is coordinated to two neutral 2-mercaptobenzimidazole ligands through sulfur to give an overall CdS_4 coordination environment. The Cd-S distance to the bimsH ligands of 2.6027(7) Å is slightly longer than the normal range of the Cd-S interactions as exemplified by the Cd-S(tsac) distance of 2.5056(7) Å. This highlights the *soft* nature of the Cd(II) cation, favoring a CdS_4 coordination environment over other possible CdS_2N_2 and CdN_4 arrangements.

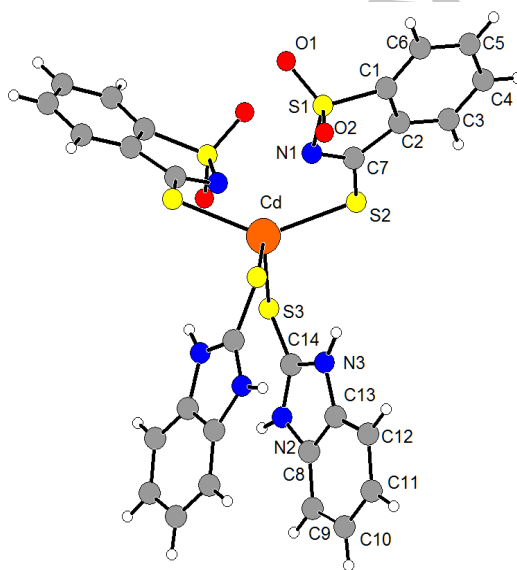


Figure 2. The molecular structure of $[\text{Cd}(\text{tsac})_2(\text{bimsH})]$ (**2**) with selected bond lengths (Å) and angles ($^\circ$), Cd-S(2) 2.5056(7), Cd-S(3) 2.6027(7), S(2)-Cd-S(2)#1 138.86(4), S(2)-Cd-S(3)#1 105.10(2), S(2)#1-Cd-S(3)#1 97.02(2), S(2)-Cd-S(3) 97.02(2), S(2)#1-Cd-S(3) 105.10(2), S(3)#1-Cd-S(3) 114.01(3).

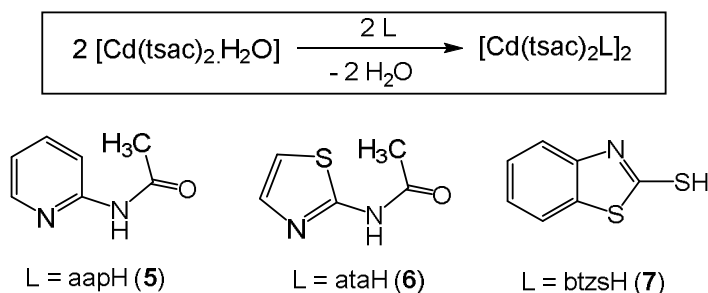
The structure of $[\text{Cd}(\text{tsac})_2(2\text{-Phpy})_2]$ (**3**) could not be confirmed by X-ray crystallography, although a CdS_2N_2 coordination environment as found in **1** is most likely. Formation of **3** contrasts with the related reaction with pyridine which affords a trisubstituted adduct, namely $[\text{Cd}(\text{tsac})_2(\text{py})_3]$ [**40**]. The latter is shown by X-ray crystallography to have a

six-coordinate Cd(II) centre with a *fac* arrangement of pyridine ligands and one of the tsac ligands coordinating in a bidentate and the second in a monodentate fashion. The ^1H NMR spectrum of **3** shows that pairs of tsac and 2-Phpy ligands are equivalent and thus we favour a four-coordinate structure akin to that found in **1** with an overall CdS_2N_2 coordination sphere, the larger size of the 2-Phpy ligand prohibiting the binding of three equivalents.

Similarly we do not have structural data for the 2-acetylaminopyrimidine complex $[\text{Cd}(\text{tsac})_2(\kappa^2\text{-aapmH})_2]$ (**4**). Here, we favour a six-coordinate cadmium centre primarily on the basis of the IR spectrum, the $\nu(\text{CO})$ stretch appearing at 1639 cm^{-1} , being shifted to a lower frequency with respect to the free ligand (1679 cm^{-1}), suggestive of metal coordination. The IR spectrum also contains a medium intensity band at 1514 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ which is also shifted to a lower frequency than that in the free ligand (1521 cm^{-1}). In further support of a six coordinate structure, the chelate coordination of the related 2-acetylpyridine ligand is detailed below.

3.3. $[\text{Cd}(\text{tsac})_2\text{L}]_2$ (**5-7**)

Treatment of $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ with two equivalents of 2-acetylpyridine (aapH), N-(2-thiazoyl)acetamide (ataH) or 2-mercaptobenzothiazole (btzsH) afforded $[\text{Cd}(\text{tsac})(\mu\text{-tsac})(\kappa_2\text{-aapH})_2]$ (**5**), $[\text{Cd}(\text{tsac})(\mu\text{-tsac})(\kappa_2\text{-ataH})_2]$ (**6**) and $[\text{Cd}(\text{tsac})_2(\text{btzsH})_2]$ (**7**) respectively (**Scheme 2**). From analytical and spectroscopic data it is clear that the tsac:L ratio is now 2:1 suggesting addition of only one equivalent of ligand. Characterization of **5** as a dimeric complex with bridging tsac ligands was made primarily on the basis of an X-ray crystal structure of **5**.2EtOH the results of which are summarized in Figure 3 and Table 1. There are no significant intermolecular interactions between ethanol and the molecule and the former will not be discussed further.



Scheme 2

The molecule is dimeric and consists of a pair of Cd(II) centers linked via two S-bound tsac anions. Each cadmium supports a monodentate tsac ligand, also sulfur bound, together with a chelating 2-acetylpyridine (aapH) ligand coordinated through oxygen and the pyridyl nitrogen [47-49]. Thus each metal obtains a CdS_3NO distorted trigonal bipyramid geometry, the trigonal plane containing S(1), S(3) and O(5) with S(1)-Cd-S(3), S(1)-Cd-O(5), S(3)-Cd-O(5) bond angles of $130.51(3)$, $131.55(6)$ and $97.70(6)^\circ$ respectively, and nitrogen N(3) and the second symmetry generated bridging sulfur S(3)# occupying the axial sites [N(3)-Cd-S(3)# $162.58(7)^\circ$]. The Cd-S(1) bond length of $2.539(9)$ Å to the monodentate tsac ligand is similar to those in $[Cd(tsac)_2(im)_2]$ and $[Cd(tsac)_2(bzim)_2]$ [8,39], while the bridging Cd-S(3) and Cd-S(3)# bonds of $2.625(8)$ and $2.7670(7)$ Å respectively are somewhat longer. The chelating aapH ligand is bound through Cd-O and Cd-N bonds of $2.255(2)$ and $2.373(2)$ Å respectively and the bite angle of this ligand, O(5)-Cd-N(3), is $77.06(8)^\circ$. As far as we are aware this is the first example of a tsac ligand bridging Cd(II) centres. That the dimeric structure is maintained in solution is suggested from its 1H NMR spectrum which clearly shows two different tsac environments. Bridging thiolates are common in cadmium chemistry [50]. Somewhat unexpectedly, a single C-S band was observed in the IR spectrum of **5** (and **6** – see below) and must result from the overlap of the C-S vibrations from the two different tsac ligands.

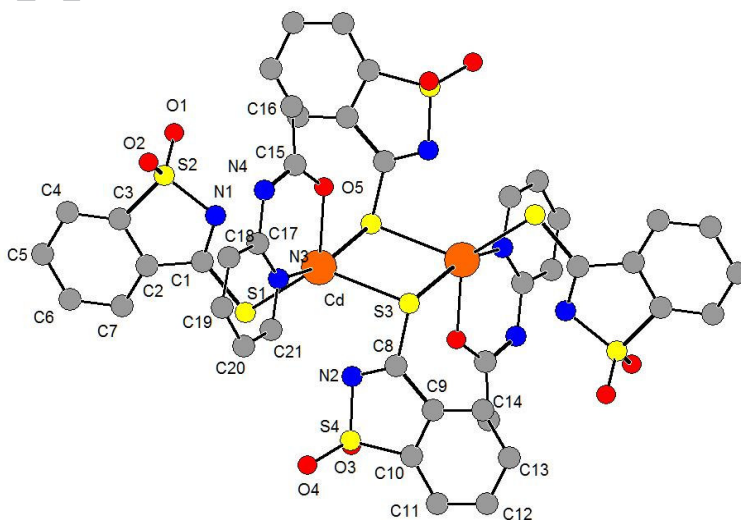


Figure 3. The molecular structure of $[\text{Cd}(\text{tsac})(\mu\text{-tsac})(\kappa_2\text{-aapH})]_2 \cdot 2\text{EtOH}$ (**5**) with selected bond lengths (Å) and angles (°), Cd-N(3) 2.373(2), Cd-O(5) 2.255(2), Cd-S(1) 2.5139(9), Cd-S(3) 2.625(8), O(5)-Cd-N(3) 77.06(8), O(5)-Cd-S(1) 131.55(6), N(3)-Cd-S(1) 93.90(7), O(5)-Cd-S(3) 97.70, N(3)-Cd-S(3) 92.77(7), S(1)-Cd-S(3) 130.51(3).

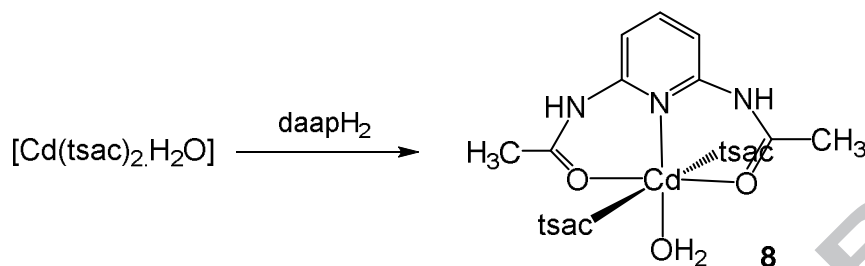
We have been unable to unequivocally establish the solid state structure of $[\text{Cd}(\text{tsac})(\mu\text{-tsac})(\kappa_2\text{-ataH})]_2$ (**6**) but on the basis of spectroscopic data, strongly favor a similar structure to that adopted by **5** as the ^1H NMR spectrum shows two different tsac environments and a tsac:ataH ratio of 2:1. We assume that chelation occurs in a similar manner to that in **5** namely through oxygen and the ring nitrogen. The addition of one equivalent of both aapH and ataH to $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ (despite two equivalents being added) presumably results due to the preferred chelating nature of these ligands.

With 2-mercaptobenzothiazole (btzsH) a similar pale-yellow complex **7** was isolated in 66 % yield. The ^1H NMR spectrum indicates the addition of a single btzsH ligand and analytical data is in accord with this. However, unlike the NMR spectra of **5** and **6** in which two tsac environments are seen, for **7** the two tsac ligands are equivalent. This could be the result of fluxional behaviour, however the sharp nature of all NMR spectra suggest that this is not the case. The presence of a single at δ 13.71 is indicative on an NH group (although SH cannot be completely ruled out). Consequently, assignment of the structure of **7** is speculative but we favour a dimeric structure with bridging btzsH and terminal tsac ligands.

3.4 $[\text{Cd}(\text{tsac})_2(\kappa^3\text{-daapH}_2)(\text{H}_2\text{O})]$ (**8**)

Addition of one equivalent of 2,6-diacetylamidopyridine (daapH₂) in ethanol to $[\text{Cd}(\text{tsac})_2(\text{H}_2\text{O})]$ afforded $[\text{Cd}(\text{tsac})_2(\kappa^3\text{-daapH}_2)(\text{H}_2\text{O})]$ (**8**) in 66 % yield (**Scheme 3**). The ^1H NMR spectrum was particularly informative showing a daapH₂:tsac ratio of 1:2, and the presence of only one tsac environment suggests that these ligands lie *trans* to one another. In the IR spectrum the $\nu(\text{CO})$ of the acetylamide groups appear at 1641 cm^{-1} , being shifted to lower frequency than that the corresponding free ligand (1676 cm^{-1}) indicating coordination to Cd(II) through the carbonyl oxygen. Despite prolonged drying the IR spectrum showed evidence of water and on this basis, and from the best fit of analytical data, it is concluded that water remains bound to cadmium. Thus the complex is formulated as shown in Scheme 4 with an octahedral CdNO₃S₂ coordination environment. It is well-established that the daapH₂

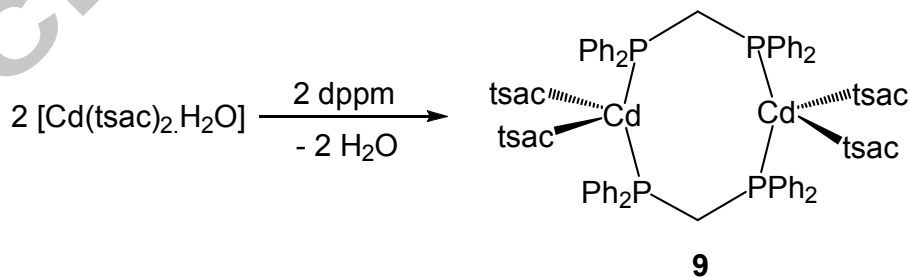
ligand acts as a meridional tridentate ligand binding through the pyridine nitrogen and both oxygen atoms as shown by in a number of crystal structures [51].



Scheme 3

3.5 $[Cd(tsac)_2(\mu\text{-dppm})_2]$ (**9**)

Reaction of $[Cd(tsac)_2(H_2O)]$ with one equivalent of bis(diphenylphosphino)methane (dppm) in EtOH gave a pale-yellow solid characterised as $[Cd(tsac)_2(\mu\text{-dppm})_2]$ (**9**) in 48% yield (Scheme 4). Attempts to generate crystals suitable for X-ray single crystal diffraction analysis were unsuccessful, therefore characterization were made on the basis of analytical and spectroscopic data. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad singlet at 25.3 ppm, the positive chemical shift indicating a bridging behavior of the diphosphane [52]. The ^1H NMR spectrum clear indicates a tsac:dppm ratio of 2:1 and the observation of a triplet for the methylene protons of the diphosphane backbone [δ 4.09 (t, $^2J_{\text{PH}}$ 13.8)] suggests a highly symmetrical structure. While we cannot unequivocally rule out a monomeric species of the formula $[Cd(\kappa^1\text{-tsac})_2(\kappa^2\text{-dppm})]$, we favour a dimeric species (shown) in which two diphosphane ligands span a Cd_2 centre.



Scheme 4

4. Summary and conclusions

In this work we have significantly expanded the chemistry of cadmium thiosaccharinate (tsac) complexes and combined with the earlier work of Baran and co-workers [8,14,39,40] it is becoming clear that while tsac always binds to Cd(II) in a thiol-type interaction through the thiocarbonyl sulfur (**Chart 2a**), it is also able to act as a chelate ligand through the sulfur and nitrogen [40] (**Chart 2b**) and can bridge two cadmiums either through the sulfur atom (**Chart 2c**) or sulfur and one of the oxygens [14] (**Chart 2d**). Further in the presence of tsac, cadmium can adopt 4-, 5- or 6-coordination with a range of atom environments including; CdS_2N_2 , CdS_4 , CdS_3O , CdS_2O_3 , CdS_3NO , $\text{CdS}_2\text{N}_3\text{O}$ and CdS_2NO_3 . These observations make cadmium-tsac chemistry a rich area of chemical and structural study, with our current level of knowledge potentially being the “tip of the iceberg”.

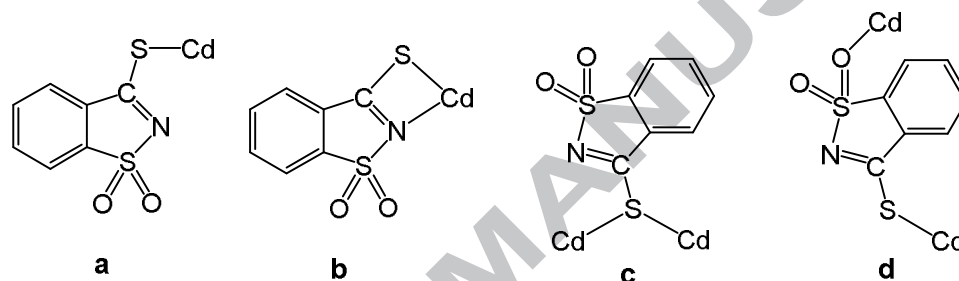


Chart 2

Acknowledgments

We thank the University of Tikrit for support of this work.

Supplementary information

CCDC 1504940-1504942 contains the supplementary crystallographic data for **1**, **2** and **5** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif

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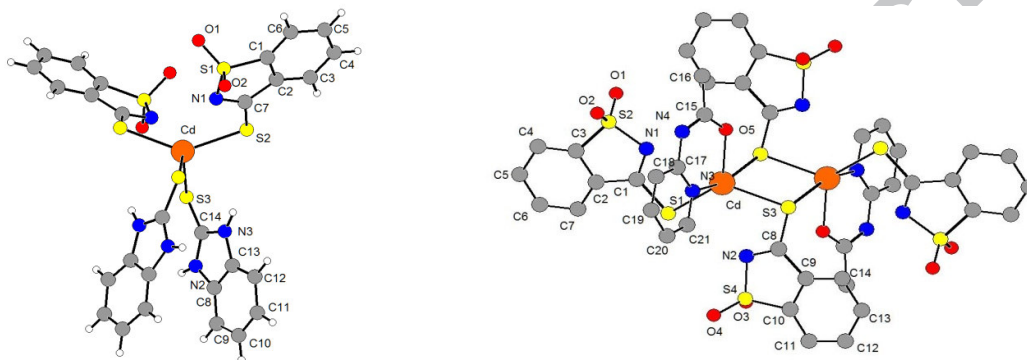
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Table 1. Crystallographic data

Compound	1	2	5. 2EtOH
Empirical formula	C ₂₈ H ₂₀ Cd N ₆ O ₄ S ₆	C ₂₈ H ₂₀ Cd N ₆ O ₄ S ₆	C ₄₆ H ₄₄ Cd ₂ N ₈ O ₁₂ S ₈
Formula weight (Å)	809.26	809.26	1382.17
Temperature (K)	293(2)	200(2)	200(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>Pnab</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit Cell dimensions			
<i>a</i> (Å)	13.920(3)	14.4794(8)	12.7099(8)
<i>b</i> (Å)	10.355(2)	11.9867(5)	10.9099(4)
<i>c</i> (Å)	22.575(5)	18.4569(8)	19.433(1)
α (°)	90	90	90
β (°)	106.23(2)	90	90.352(5)
γ (°)	90	90	90
Volume (Å ³)	3124.5(11)	3203.4(3)	2694.7(2)
Z	4	4	2
Density (calc.) (Mg/m ³)	1.720	1.678	1.703
Absorption coefficient (mm ⁻¹)	1.146	1.118	1.167
F(000)	1624	1624	1392
Crystal size (mm)	0.27 x 0.25 x 0.19	0.34 x 0.18 x 0.12	0.18 x 0.17 x 0.12
Limiting indices	16 ≤ <i>h</i> ≤ 16 -12 ≤ <i>k</i> ≤ 12 -26 ≤ <i>l</i> ≤ 25	-17 ≤ <i>h</i> ≤ 17 -12 ≤ <i>k</i> ≤ 14 -22 ≤ <i>l</i> ≤ 20	-15 ≤ <i>h</i> ≤ 15 -12 ≤ <i>k</i> ≤ 13 -23 ≤ <i>l</i> ≤ 22
θ Range for data collection (°)	3.94 - 25.00	3.84 - 26.00	3.85 - 26.00
Index ranges			
Reflections collected	9306 / 2753	19096 / 3139	14839 / 5275
Independent reflections [<i>R</i> _{int}]	0.0872	0.0622	0.0674
Data / restraints / parameters	2753 / 2 / 212	3139 / 0 / 205	5275 / 1 / 351
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0287, <i>wR</i> 2 = 0.0590	<i>R</i> 1 = 0.0298, <i>wR</i> 2 = 0.0817	<i>R</i> 1 = 0.0286, <i>wR</i> 2 = 0.0608
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0439, <i>wR</i> 2 = 0.0617	<i>R</i> 1 = 0.0394, <i>wR</i> 2 = 0.0865	<i>R</i> 1 = 0.0431, <i>wR</i> 2 = 0.0626
Largest diff. peak and hole (e.Å ⁻³)	0.619 and -0.619	0.878 and -0.706	0.378 and -0.772

Graphic abstract

New cadmium-thiosaccharinate (tsac) complexes and crystal structures of three are presented. In all the tsac ligand(s) bind exclusively through coordination of the thiocarbonyl sulfur atom highlighting the chalcogenophilic nature of cadmium. In $[\text{Cd}(\text{tsac})(\mu\text{-tsac})(\kappa^2\text{-aapH})_2]$ the tsac ligands adopt both bridging and terminal coordination modes, the former being relatively rare.



Highlights

- Synthesis of a series of cadmium-thiosaccharinate (tsac) complexes
- Terminal and bridging tsac coordination
- In all cases the tsac is bound through sulfur

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