Synthesis of zinc and cadmium O-alkyl thiocarbonate and dithiocarbonate complexes and a cationic zinc hydrosulfide complex

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Treatment of Zn(II) and Cd(II) hydroxide complexes of the tris(2-pyridylmethyl)amine (TPA) ligand with COS or CS₂ in protic solvents (MeOH or EtOH) resulted in [(TPAZn–SC(S)OCH₃)ClO₄ (1), [(TPAZn–SC(S)OCH₃)BF₄ (2), [(TPAZn–SC(S)OCH₃)ClO₄ (1), [(TAPA)Zn–SC(S)OCH₃)ClO₄ (6). The molecular structures of 1, 2, 3 and 6 were determined by X-ray crystallography. Complexes 2, 3 and 4, unlike 1, 5 and 6, are easily hydrolyzed upon treatment with water in CH₃CN to give zinc hydrosulfide complexes of the form [(TPAZn–SH)X (X = BF₄⁻ (7) and ClO₄⁻ (8)], as evidenced by spectroscopic methods and the crystal structure of 7. These complexes may be prepared more directly by (a) reacting equimolar amounts of TPA, Zn(ClO₄)₂, 6H₂O and Me₂NH₂·SH₂O with COS in CH₃CN or (b) treating [(TPAZn–SH)X (X = BF₄⁻ (7) and ClO₄⁻ (8)].

1. Introduction

Extensive research efforts have been directed at understanding carbon dioxide (CO₂) insertion into coordination complexes because of its biological significance to carbonic anhydrase (CA) [1]. CA, which is a zinc-containing enzyme common to animals, plants and bacteria, catalyzes the reversible hydration of CO₂ to bicarbonate [2]. The enzyme is involved in numerous processes within living organisms, such as cellular respiration, photosynthesis, and pH regulation [3]. However, research aimed at understanding insertion of sulfur-containing heterocumulenes, such as carbonyl sulfide (COS) and carbon disulfide (CS₂), into zinc-containing complexes has been rather limited [4,5]. This is surprising since studies have shown atmospheric COS is fixated by CA in plants, lichens and algae [6] and CS₂ is fixated by CS₂ hydroxide (3TEN), a zinc-containing enzyme similar to CA, in thermophilic archaea [7]. Furthermore, few studies [8] have examined heterocumulene insertion into cadmium-containing complexes, even though a cadmium carbonic anhydrase (3BOB) is formed by marine diatoms in zinc-poor environments [9].

The active site of CA consists of a tetrahedral Zn²⁺ ion coordinated by three histidine residues (His-94, His-96 and His-119) and a water molecule [10]. The proposed mechanism of COS fixation by CA [4], which is shown in Scheme 1, involves deprotonation of the coordinated water molecule (pKₐ ≈ 7) to form a zinc hydroxide complex (B). Insertion of COS into the metal–hydroxide bond results in the formation of [[His]₂Zn–SC(O)OH]⁺ (C) that readily decomposes to form the cationic zinc hydrosulfide complex [[His]Zn–SH]⁺ (D). The proposed final step is protonation of the hydrosulfide ligand and release of H₂S at neutral pH. However, many questions remain unresolved regarding desulfurization of the zinc hydrosulfide complex (D) and how it occurs near a neutral pH.

Prior studies by Parkin and co-workers [11], Vahrenkamp and co-workers [5,12] and Anders and co-workers [13] to make [(L)Zn–SH]n (where n = 0 or +1) complexes, akin to intermediate D in Scheme 1, made use of substituted tris(pyrazolyl)borate (Tp³Me) and neutral azamacrocyclic ([12]aneN₃) tripodal ligands (Chart 1). The authors found that the Tp³Me ligand was the only ligand capable of stabilizing the [Zn–SH]⁺ moiety [14]. For instance, an attempt by Ender et al. to make a cationic [[12]aneN₃Zn–SH]⁺ complex with the neutral [12]aneN₃ ligand (Chart 1) resulted in ZnS formation [13]. As such, a number of Tp³MeZn–SH complexes have been characterized [5,11,12]. The remarkable stability of the Tp³MeZn–SH complexes...
has been attributed to the ability of the TpR,Me ligand to encapsulate the labile hydrosulfide ligand and, thus, prevent demetallation and formation of insoluble zinc sulfides.

The tris(2-pyridylmethyl)amine (TPA) ligand (Chart 1) was chosen as the supporting ligand in this study primarily because [(TPA)Zn(SC(S)OMe)]ClO4 has already been shown to undergo insertion reactions with heterocumulenes, such as CO2, under basic conditions [15]. Additional reasons why we chose to use the TPA ligand is that (a) it can be modified with steric substituents [16] and hydrogen bond donors [17] and (b) it would result in a cationic rather than a neutral hydrosulfide complex. TPA has the advantage of yielding a cationic active site model, rather than Tp which is an anionic biomimetic ligand. As such, there is potential with TPA to better model the CA chemistry.

Herein, we describe the insertion reactions of [(TPA)M2(μ-OH)2]BF4 where M = Zn, Cd with Cs2 and COS in protic (MeOH, EtOH) and aprotic solvents (CH3CN). Overall, O-alkyl diithiocarbonates and thiocarbonate complexes are formed under protic conditions (MeOH and EtOH). Particularly important, complexes [(TPA)Zn(SC(O)OMe)] and [(TPA)Cd–SC(O)OMe]+ were formed and, according to the Cambridge Structural Database, represent the first structurally characterized examples of Zn or Cd complexes containing an M–SC(O)OR fragment. In addition, new synthetic methods under aprotic (CH3CN) conditions resulted in cationic complexes of the general formula [(TPA)Zn–SH]+. These complexes were characterized by 1H and 13C NMR, IR, and electrospray mass spectrometry (ESI-MS) and, in one example, by X-ray crystallography. Furthermore, theoretical calculations were used to compare the electronics and predict the reactivity of the TPA/Tp ZnSH complexes. Taken together, the results provide new detail for routes to synthetic Zn–SH complexes and the relative characterisics of the two predominant CA models (Tp and TPA).

2. Experimental

2.1. General data

All reactions were performed using standard Schlenk techniques under an atmosphere of dry nitrogen gas. Solvents and reagents were obtained from commercial sources in analytical grade quality and used as received unless noted otherwise. The solvents tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH) and acetonitrile (CH3CN) were dried with CaH2 and distilled prior to use. NMR spectra were recorded on a Bruker AVANCE III 600 NMR. Chemical shifts (δ) for 1H or 13C NMR spectra were referenced to residual protium in the deuterated solvent. IR spectra were measured using a Perkin Elmer Spectrum 100 spectrometer. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA. High resolution electrospray mass spectra were recorded on a Bruker Daltonics Maxis QTof instrument. The ligand tris(2-pyridylmethyl)amine (TPA) was made by following a previously reported procedure [18].

2.2. Synthesis and characterization

2.2.1. Preparation of [(TPA)ZnSC(S)OMe]ClO4 (1)

To a solution of tris(2-pyridylmethyl)amine (290 mg, 1.00 mmol) dissolved in dry methanol (40 mL) was added Zn(ClO4)2·6H2O (373 mg, 1.00 mmol). After stirring for 5 min, KOH (56 mg, 1.00 mmol) was added which caused immediate formation of a white precipitate. Carbon disulfide (228 mg, 3.00 mmol) was then added and the reaction was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (15 mL) and filtered through Celite. The volume was reduced (~3 mL) and addition of diethyl ether (20 mL) caused the formation of a pale yellow solid. The solid was collected, washed with diethyl ether (10 mL) and dried under vacuum (409 mg, 75%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into acetone at room temperature. 1H NMR (CD3CN, 600 MHz): δ 7.82 (d, 3H), 8.06 (t, 3H), 7.59 (t, 3H), 7.54 (d, 3H), 4.24 (s, 6H), 3.87 (s, 3H). 13C NMR (CD3CN, 150 MHz): δ 225.2, 155.0, 148.6, 141.2, 125.0, 124.6, 60.07, 56.97. IR (ATR, cm−1): 2981, 1609, 1576, 1485, 1446, 1436, 1373, 1314, 1295, 1272, 1190, 1131, 1111, 1081, 1066, 1052, 1022, 1001, 990, 944, 907, 836, 774, 761, 732, 719. Anal. Calc. for C20H21ZnClN4O5S2: C, 42.71; H, 3.76; N, 9.96. Found: C, 42.52; H, 3.71; N, 9.84.

2.2.2. Preparation of [(TPA)ZnSC(O)OMe]BF4 (2)

To a solution of tris(2-pyridylmethyl)amine (800 mg, 2.80 mmol) dissolved in dry methanol (50 mL) was added zinc tetrafluoroborate (658 mg, 2.80 mmol). After stirring for 5 min, KOH (155 mg, 2.80 mmol) was added and the headspace gases were removed by vacuum. Carbonyl sulfide was then bubbled through the solution and the reaction was allowed to stir under a COS atmosphere for 24 h at room temperature, during which time a white precipitate formed. The solid was collected and extracted with dichloromethane (2 × 20 mL). The dichloromethane solution was concentrated (5 mL) and addition of diethyl ether (20 mL) resulted in a pale yellow solid. The solid was collected, washed with diethyl ether (3 mL) and dried under vacuum (602 mg, 41%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into methanol at room temperature. 1H NMR (CD3CN, 600 MHz): δ 8.73 (d, 3H), 8.07 (t, 3H), 7.61 (t, 3H), 7.57 (d, 3H), 4.19 (s, 6H), 3.57 (s, 3H). 13C NMR (CD3CN, 150 MHz): δ 176.5, 155.2, 148.9, 141.2, 125.0, 124.7, 56.3, 52.8. IR (ATR, cm−1): 2946, 1609, 1575, 1482, 1435, 1375, 1319, 1298, 1273, 1184, 1164, 1114, 1048, 1022, 978, 956, 909, 835, 812, 770, 73, 687. Anal. Calc. for C20H21ZnBF4N3O2S: C, 45.01; H, 3.76; N, 9.10. Found: C, 45.12; H, 3.71; N, 9.10.

2.2.3. Preparation of [(TPA)ZnSC(O)OMe]ClO4 (3)

To a solution of tris(2-pyridylmethyl)amine (250 mg, 0.86 mmol) dissolved in dry methanol (40 mL) was added Zn(ClO4)2·6H2O (320 mg, 0.86 mmol). After stirring for 5 min, KOH (48 mg, 0.86 mmol) was added and the headspace gases were
removed by vacuum. Carboxyl sulfide was then bubbled through the solution and the reaction was allowed to stir under a CO2 atmosphere for 24 h at room temperature, during which time a white precipitate formed. The solid was collected and extracted with dichloromethane (20 mL). The dichloromethane solution was concentrated (~5 mL) and addition of diethyl ether (15 mL) resulted in a pale yellow solid. The solid was collected, washed with diethyl ether (5 mL) and dried under vacuum (138 mg, 30%).

1H NMR (CD3CN, 600 MHz): δ 8.73 (d, 3H), 8.07 (t, 3H), 7.61 (t, 3H), 7.55 (d, 3H), 4.19 (s, 6H), 3.98 (q, 2H), 0.92 (t, 3H). 13C NMR (CD3CN, 150 MHz): δ 175.7, 155.2, 148.9, 141.2, 125.0, 124.7, 61.9, 56.3, 13.4. IR (ATR, cm−1): 3435, 2963, 2870, 1543, 1461, 1361, 1216, 1294, 1253, 1230, 1202, 1047, 1023, 976, 908, 838, 784, 768, 730, 686. Anal. Calc. for C20H21CdClN4O6S: C, 39.42; H, 3.92; N, 11.47. Found: C, 39.19; H, 3.48; N, 9.00%.

2.2.4. Preparation of [(TPA)Zn–SH]ClO4 (7)

To a solution of tris(2-pyridylmethyl)amine (250 mg, 0.86 mmol) dissolved in dry ethanol (50 mL) was added zinc tetrafluoroborate (206 mg, 0.86 mmol). After the addition of KOH (48 mg, 0.86 mmol), the headspace gases were removed by vacuum. Carboxyl sulfide was then bubbled through the solution and the reaction was allowed to stir under a CO2 atmosphere for 24 h at room temperature. The solvent was then removed under reduced pressure and the residue extracted with dichloromethane (10 mL) and filtered through Celite. The dichloromethane solution was concentrated (3 mL) and addition of diethyl ether (20 mL) resulted in a white solid. The solid was collected, washed with diethyl ether (3 mL) and dried under vacuum (160 mg, 39%).

1H NMR (CD3CN, 600 MHz): δ 8.98 (d, 3H), 8.07 (t, 3H), 7.63 (t, 3H), 7.54 (d, 3H), 4.16 (s, 6H), −1.52 (SH, s, 1H). 13C NMR (CD3CN, 150 MHz): δ 155.2, 148.8, 141.1, 125.0, 124.6, 56.4. IR (ATR, cm−1): 3454, 3067, 2981, 1605, 1575, 1484, 1437, 1374, 1315, 1294, 1268, 1106, 1049, 1021, 906, 839, 765, 733. HRMS (ESI, Pos) calculated for [C18H19N4SZn]+: 387.0619, found 387.0616. Anal. Calc. for C18H19ZnBF4N4S: C, 45.45; H, 4.03; N, 11.78. Found: C, 45.28; H, 4.09; N, 11.67%.

2.2.8. Preparation of [(TPA)ZnSH]ClO4 (8)

2.2.8.1. Method A. To a solution of [(TPA)ZnSC(O)OMe]ClO4 (120 mg, 0.22 mmol) dissolved in acetonitrile (30 mL) was added 80 μL of water (4.44 mM, 20 equiv.). The reaction was allowed to stir for 1 week. The acetonitrile solution was then concentrated and addition of diethyl ether (20 mL) resulted in a white solid.

2.2.8.2. Method B. To a solution of tris(2-pyridylmethyl)amine (250 mg, 0.86 mmol) dissolved in dry acetonitrile (60 mL) was added Zn(ClO4)2·6H2O (0.32 g, 0.86 mmol). (CH3)4NOH (5 mL) and addition of diethyl ether (5 mL) and addition of diethyl ether (20 mL) resulted in a white solid. The solid was collected, washed with diethyl ether (5 mL) and dried under vacuum (138 mg, 30%).
were removed by vacuum. After stirring for 15 min, COS was then bubbled through the solution and the reaction was allowed to stir under a COS atmosphere for 24 h at room temperature. The solution was filtered and the filtrate solven was concentrated (5 mL) and addition of diethyl ether (20 mL) resulted in a pale yellow solid. The solid was collected, washed with diethyl ether (4 mL) and dried under vacuum to give 8 (310 mg, 73%).

2.2.10. Preparation of [(TPA)2Cd(ClO4)2], (9)

To a solution of tris(2-pyridylmethyl)amine (300 mg, 1.03 mmol) dissolved in dry acetonitrile (40 mL) was added Cd(ClO4)2·6H2O (384 mg, 1.03 mmol). After the addition of KOH (58 mg, 1.03 mmol), the headspace gases were removed by vacuum. Hydrogen sulfide was then bubbled through the solution and the reaction was allowed to stir under a H2S atmosphere for 24 h at room temperature, during which time a white precipitate formed. The solid was collected and extracted with dichloromethane (2 × 10 mL). The dichloromethane solution was concentrated (5 mL) and addition of diethyl ether (15 mL) resulted in a white solid. The solid was collected, washed with diethyl ether (5 mL) and dried under vacuum to give 8 (150 mg, 30%). The 1H and 13C NMR spectra are identical to the spectra of 8 generated from Method A.

2.2.11. Reaction of 8 with CH3I to form [(TPA)2ZnI]ClO4, (10)

To a solution of 8 (50 mg, 0.10 mmol) dissolved in dry acetonitrile (15 mL) was added 5 equiv. of CH3I (32 μL, 0.51 mmol). The solution was stirred for 10 days at room temperature to ensure complete conversion to product. The solution was then removed under reduced pressure leaving a white residue. Diethyl ether (2 × 10 mL) was added and the solid was triturated into a fine crystalline powder. The powder was collected and dried under vacuum (45 mg, 78%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into acetonitrile at room temperature. The unit cell parameters are identical to the structure of [(TPA)2ZnI]ClO4 reported by Canary and co-workers [19]. 1H NMR (CD3CN, 600 MHz): δ 9.26 (d, 3H), 8.08 (t, 3H), 7.69 (t, 3H), 7.57 (d, 3H), 4.20 (s, 6H). 13C NMR (CD3CN, 150 MHz): δ 155.0, 149.4, 141.6, 125.0, 124.9, 56.4. IR (ATR, cm−1): 3725, 3704, 3633, 3030, 1610, 1574, 1483, 1437, 1369, 1316, 1297, 1272, 1227, 1159, 1129, 1077, 1054, 1023, 1001, 980, 966, 908, 896, 837, 780, 762, 731.

2.2.12. Reaction of 8 with nBuLi to form [(TPA)2CdClO4](31)

To a stirred solution of 8 (100 mg, 0.20 mmol) dissolved in dry acetonitrile (15 mL) at −70 °C, 10.0 equiv. of nBuLi (0.33 mL, 1.6 M in hexanes) was added dropwise. The resulting cloudy mixture was allowed to slowly warm to room temperature and stirred for 24 h. The solution was then removed under reduced pressure and the residue extracted with dichloromethane (10 mL) and filtered through Celite. The volume was reduced (~3 mL) and addition of diethyl ether (5 mL) caused the formation of a white solid. The solid was collected, washed with diethyl ether (3 mL) and dried under vacuum (45 mg, 57%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into dichloromethane at room temperature. 1H NMR (CD3CN, 600 MHz): δ 8.70 (d, 3H), 7.83 (t, 3H), 7.37 (m, 6H), 3.90 (s, 6H). 13C NMR (CD3CN, 150 MHz): δ 158.7, 149.4, 138.2, 123.2, 123.2, 58.0. IR (ATR, cm−1): 3966, 3028, 2877, 2846, 2191, 1991, 1643, 1600, 1573, 1480, 1431, 1375, 1316, 1297, 1274, 1212, 1155, 1135, 1086, 1098, 1048, 1008, 975, 958, 937, 902, 831, 761. Anal. Calc. for C18H29LiClN3O4·C: C, 54.49; H, 4.57; N, 14.12. Found: C, 54.83; H, 4.73; N, 14.56%.

2.2.13. Reaction of 8 with NaH to form [Na2(TPA)2(ClO4)2], (12)

To a stirred solution of 8 (100 mg, 0.20 mmol) dissolved in dry acetonitrile (15 mL), 20 equiv. of NaH (100 mg, 4.0 mmol) was added. The resulting cloudy mixture was stirred for 24 h at room temperature. The solution was filtered and the solvent was removed under reduced pressure. The residue was then extracted with dichloromethane (12 mL) and filtered through Celite. The volume was reduced (~3 mL) and addition of diethyl ether (8 mL) caused the formation of a white solid. The solid was collected, washed with diethyl ether (3 mL) and dried under vacuum (40 mg, 48%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into dichloromethane at room temperature. 1H NMR (CD3CN, 600 MHz): δ 8.59 (d, 3H), 7.73 (t, 3H), 7.32 (t, 3H), 7.26 (d, 3H), 3.76 (s, 6H). 13C NMR (CD3CN, 150 MHz): δ 158.2, 149.9, 137.2, 123.7, 122.6, 59.3. IR (ATR, cm−1): 3841, 3757, 3675, 3651, 3616, 2846, 1597, 1571, 1479, 1437, 1371, 1315, 1300, 1270, 1215, 1156, 1095, 1062, 1048, 1004, 989, 977, 959, 926, 903, 835, 764. Anal. Calc. for C18H28Na2Cl2N6O8·C: C, 52.37; H, 4.40; N, 13.57. Found: C, 52.65; H, 4.48; N, 13.51%.

2.3. X-ray crystallography

Suitable crystals were obtained from slow vapor diffusion and mounted on a glass fiber using hydrocarbon oil and cooled under a nitrogen stream to 150(1) K. A Nonius Kappa CCD diffractometer (Mo Kα radiation; i = 0.71073 Å) was used for data collection. Unit cell parameters were determined from 10 data frames with an oscillation range of 1°/frame and an exposure time of 20 s/frame. Indexing and unit cell refinement based on the reflections from the initial set of frames were consistent with monoclinic P lattices for 7, 9, 11 and 12, triclinic P lattices for 1 and 5, an orthorhombic P lattice for 2 and a tetragonal P lattice for 6. The intensity data for each compound was then collected. These reflections were then indexed, integrated and corrected for Lorenz, polarization and absorption effects using DENZO-SMN and SCALEPAC [20]. The
space group for each compound was determined from the systematic absences in the diffraction data. The structures were solved by a combination of direct and heavy atom methods using SIR 97 [21]. Compound 2 contains a BF$_4$ anion disordered over two positions with an 83:17 occupancy ratio. Compound 5 contains two crystallographically independent molecules per unit cell. Compound 6 contains a CH$_3$OH molecule that is within H-bonding distance of an atom. The structures were solved by direct and heavy atom methods using SIR 97 [21]. A summary of the crystallographic data and parameters is given in Table 1 and for 9, 11 and 12 in Table S1.

### 2.4. Computational methods

All calculations were carried out using Gaussian 03 [23]. Geometry optimizations were carried out using the 6-31 + G(d,p) basis set for all atoms, except for Zn, for which the Stuttgart effective core potential basis set was used [24]. Among various density functionals considered here, TPSSH [25] was chosen as the functional for geometric and electronic analysis given that gas phase optimizations were best able to reproduce geometries from crystallographic data and parameters for a combination of direct and heavy atom methods using SIR 97 [21].

### 3. Results and discussion

#### 3.1. Synthesis of alkyl thiocarbonate and dithiocarbonate complexes 1–6

Our aim was to prepare [(TPA)M–SH]$^+$ complexes (where M = Zn or Cd) via insertion of COS or CS$_2$ into the metal hydroxide bond followed by elimination of CO$_2$ or COS to give the cationic metal hydrosulfide complexes. Instead, the formation of O-alkyl thiocarbonate and dithiocarbonate complexes was observed. [(TPA)Zn–SC(S)OCH$_3$]BF$_4$ (1), [(TPA)Zn–SC(O)OCH$_3$]BF$_4$ (2), [(TPA)Zn–SC(O)OCH$_3$]ClO$_4$ (3), [(TPA)Zn–SC(O)OCH$_3$]BF$_4$ (4), [(TPA)Cd–SC(S)OCH$_3$]ClO$_4$ (5) and [(TPA)Cd–SC(O)OCH$_3$]ClO$_4$ (6) were synthesized in 27–75% yield using the synthetic route outlined in Scheme 2. The compounds were obtained by the reaction of equimolar amounts of TPA, the appropriate metal salt, and KOH in either dry methanol or ethanol followed by bubbling of COS or addition of CS$_2$. Compounds 1–6 were characterized by $^1$H and $^{13}$C NMR, IR, elemental analysis (CHN) and, for 1, 2, 5 and 6, by single-crystal X-ray crystallography. One possible mechanism for formation of products 1–6 could be the esterification of [(TPA)M–SC(E)OH]$^+$ (M = Zn, Cd; E = O, S) by the protic solvent (MeOH or EOH), where [(TPA)M–SC(E)OH]$^+$ is the product initially formed after heterocumulene insertion into the M-OH bond. However, we cannot rule out the possibility that 1–6 may result from heterocumulene insertion into an M-OR (R = alkyl group) rather than an M-OH bond. Trace amounts of a metal alkoxide species may be in equilibrium with the metal hydroxide in alcoholic solvents, as observed with the TP$_2$Me$_2$ systems [30].

The spectroscopic data for complexes 1–6 are very similar, supporting the assignment that complexes 3 and 4, for which crystals

### Table 1

Summary of X-ray crystallographic data and parameters.$^a$

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$a$ Radiation used: Mo Kα (λ = 0.71073 Å).

$b$ $R_1 = \sum|F_o|-|F_c|)/\sum|F_o|; wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^2]^{1/2}$, where $w = 1/[\sigma(F_o^2)]^2 = (ap)^2 + bP^2.$
suitable for X-ray crystallography have not been obtained, have atom sequences similar to complexes 1, 2, 5 and 6. Particularly diagnostic in the $^1$H and $^{13}$C NMR is the observation of the -OCH$_3$ resonances for 1-3 and 5-6 and the -OCH$_2$CH$_3$ resonances for 4. Evidence for the thiocarbonate group in complexes 2-4 and 6 and the dithiocarbonate group in complexes 1 and 5 is provided by $^{13}$C NMR, with the observation of carbon resonances at ~177 ppm and 228 ppm, respectively. In the FTIR, a band at ~1645 cm$^{-1}$ was assigned as the C=O vibration of the thiocarbonate ligand for complexes 2-4 and 6. However, the C=S vibration for the dithiocarbonate ligand was not observed in complexes 1 and 5 due to overlapping vibrations associated with the ClO$_4^-$ and BF$_4^-$ anions.

3.2. X-ray structures of complexes 1, 2, 5 and 6

The molecular structures of [(TPA)Zn–SC(S)OCH$_3$]ClO$_4$ (1) and [(TPA)Zn–SC(O)OCH$_3$]BF$_4$ (2) are shown in Figs. 1 and 2. A summary of the X-ray crystallographic data and refinement parameters for the two complexes is provided in Table 1. Complexes 1 and 2 are monomeric and the zinc ion in each complex is coordinated by four nitrogen atoms from the TPA ligand and a sulfur atom from the dithiocarbonate ligand. The dithiocarbonate and thiocarbonate ligands in 1 and 2 are oriented such that the more sterically demanding -OCH$_3$ unit of the ligands is pointed away from zinc. The coordination environment around the zinc ion in each complex can be described as distorted trigonal bipyramidal. The tertiary amine nitrogen atom of the TPA ligand and the sulfur atom of the dithiocarbonate ligand occupy the axial positions. The $\tau_5$ values of 0.83 for 1 and 0.89 for 2 (where $\tau_5=0$ is expected for an idealized square pyramidal geometry and $\tau_5=1.0$ for an idealized trigonal bipyramidal geometry [31]) are similar and indicate the same degree of distortion from an idealized trigonal bipyramidal geometry. Surprisingly, a search of the Cambridge Structural Database for a complex containing the fragment M-SC(O)OR where M = Zn or Cd resulted in no structures. However, examples of metal complexes, besides Zn or Cd complexes, containing an alkyl thiocarbonate group have been reported [32].

The binding mode of the dithiocarbonate and thiocarbonate ligands in 1 and 2 can be described as monodentate. In 1, the Zn1-51 and Zn1-52 distances are 2.3590(4) and 3.2994(5) Å, while in 2, the Zn1-51 and Zn1-52 distances are 2.3332(5) and 3.273(16) Å. The Zn1-52 distance in 1 and Zn1-52 distance in 2 are clearly too long for any type of interaction. The S1-Zn1-N2 bond angles in 1 and 2 are almost linear (175.30(3)$^\circ$ for 1 and 172.98(4)$^\circ$ for 2) consistent with monodentate binding modes for the dithiocarbonate and thiocarbonate ligands. The Zn-5 distances are similar between the two complexes (2.3590(4) Å in 1 and 2.3332(5) Å in 2) and compare well with other five-coordinate zinc complexes [33]. However, the Zn-S distance in both complexes is significantly longer when compared to the values of four-coordinate Tp$^\text{III}$,Me$^+$-Zn–SC(S)OR complexes (when R' = Et, 2.264 Å; R' = Me, 2.244 Å) [30b,34].
The molecular structures of [(TPA)Cd–SC(S)OCH₃]ClO₄ (5) and [(TPA)Cd–SC(O)OCH₃]ClO₄ (6), which are the cadmium analogs of 1 and 2, were also determined by X-ray crystallography. Their structures are shown in Figs. 3 and 4 and their crystallographic data and refinement parameters are listed in Table 1. When compared to 1 and 2, the structures of 5 and 6 are similar but differences do exist between the zinc and cadmium analogs. For instance, the dithiocarbonate ligand in 1 is monodentate but in 5 the dithiocarbonate ligand could be considered as weakly anisobidentate. The two Cd–S distances of the dithiocarbamate ligand are 2.516(5) Å and 3.053(5) Å. The Cd–N–S2 distance (3.053(5) Å) is longer than the sum of the covalent radii (2.96 Å), but significantly shorter than the sum of the van der Waals radii (3.38 Å), indicative of a weak interaction. The S1–Cd1–N2 angle (163.13(4)°) in 5 compared to the S1–Zn1–N2 angle in 1 (175.30(3)°) is also considerably smaller. The smaller S1–M–N2 (M = Zn or Cd) angle in 5 illustrates how the large cadmium atom has adjusted for the Cd–S2 interaction at the expense of the S1–Cd1–N2 angle.

Fig. 4 shows the structure for [(TPA)Cd–SC(O)OCH₃]ClO₄ (6). Complex 6 is, to the best of our knowledge, the first structurally characterized cadmium complex containing an O-alkyl thio-carbonate ligand. The geometry of the cadmium center is distorted trigonal bipyramidal (τ = 0.86), where three pyridine nitrogen atoms (N2, N3 and N4) make up the equatorial positions and N2 and S1 the axial positions. In addition, a methanol molecule is hydrogen bonded to O1 of the thiocarbonate ligand. The Cd ion in 6 is located 0.69 Å (compared to 0.76 Å for 5) above the equatorial plane defined by the three pyridine nitrogen atoms, which is significantly farther than the Zn ion in 1 and 2 (~0.47 Å). The Cd1–S1 and Cd1–O1 distances of the thiocarbonate ligand are 2.4715(6) Å and 2.978(2) Å, respectively. The Cd1–O1 distance is approximately the same as the van der Waals distance (3.10 Å) indicating the thiocarbonate ligand in 6, similar to 2, has a monodentate coordination mode. The Cd1–S1 distance (2.4715(6) Å) is shorter than the Cd1–S1 distance (2.5160(5) Å) in 5 but is similar to Cd–S distances observed in cadmium complexes with thiolate ligands (2.47–2.55 Å) [35] but shorter than cadmium complexes with bidentate alkyl dithiocarbonate ligands (2.65–2.86 Å) [33a].

3.3. Synthesis of cationic zinc hydrosulfide complexes

Three general routes to cationic zinc and cadmium hydrosulfide complexes of the form [(TPA)M–SH]+ (M = Zn or Cd) were explored (Scheme 3) [14]. Of these routes, methods A and B represent new methods for making Zn–SH complexes, while method C has been used to make Tpzn–SH complexes [12] but not cationic [LZn–SH]+ (where L = ligand) complexes.

Method A investigated the hydrolytic stability of complexes 1–6 towards water. Prior studies by Vahrenkamp had shown that TpBu₄Zn–OC(O)OR complexes are easily hydrolyzed to TpBu₄Zn–OH [36]. Interestingly, the related TpCumMeZn–OC(O)OR complexes are stable in water/alcohol mixtures, suggesting the more encapsulating TpCumMe ligand is responsible for the increased stability [5]. The stability of complexes 1–6 towards hydrolysis was initially examined by 'H NMR. Treatment of 2, 3 and 4 in CD₂CN with water results in the quantitative formation of [(TPA)Zn–SH]X (X = BF₄⁻ or ClO₄⁻) within 48 h. The hydrolysis of 3 on a preparative scale yielded 8 in a 47% yield. A detailed description of the characterization of 7 and 8, including the X-ray structure of 7, follows in the next section. Interestingly, under the same conditions, 1, 5 and 6 show no signs of hydrolysis, even after 8 days.

Method B involves the reaction of equimolar amounts of TPA, M(ClO₄)₂ ⋅ 6H₂O and Me₄NOH with COS or CS₂ in CH₃CN. This procedure is similar to the procedure used to make 1–6 except the protic solvent (MeOH or EtOH) and KOH have been replaced with CH₃CN and Me₄NOH ⋅ 5H₂O (Me₄NOH ⋅ 5H₂O was used as the base because of the poor solubility of KOH in acetonitrile). The rationale for switching the solvent to acetonitrile was to prevent incorporation of the solvent into the products, as was observed with the formation of 1–6 in alcoholic solvents. Treatment of TpZnCl₂ ⋅ 6H₂O and Me₄NOH ⋅ 5H₂O with COS yielded [(TPA)Zn–SH]ClO₄ (8) in a 73% yield. Surprisingly, replacing COS with CS₂, under the same reaction conditions, does not result in a zinc hydro-sulfide (as evidenced by the absence of a SH resonance in the 'H NMR) but an unidentified mixture of products.

The reaction was also run using Cd(ClO₄)₂ ⋅ 6H₂O and Me₄NOH with COS or CS₂ in CH₃CN. This procedure is similar to the procedure used to make 1–6 except the protic solvent (MeOH or EtOH) and KOH have been replaced with CH₃CN and Me₄NOH ⋅ 5H₂O (Me₄NOH ⋅ 5H₂O was used as the base because of the poor solubility of KOH in acetonitrile). The reason for switching the solvent to acetonitrile was to prevent incorporation of the solvent into the products, as was observed with the formation of 1–6 in alcoholic solvents. Treatment of TpCdCl₂ ⋅ 6H₂O and Me₄NOH ⋅ 5H₂O with COS yielded [(TPA)Cd–SC(S)OCH₃]ClO₄ (9) in a 89% yield. Surprisingly, replacing COS with CS₂, under the same reaction conditions, does not result in a cadmium hydro-sulfide (as evidenced by the absence of a SH resonance in the 'H NMR) but an unidentified mixture of products.
obtained by Bebout et al. crystallized in a different space group (P1), as a result of a co-crystallized toluene molecule. Method C explored the direct method of treating the cadmium and zinc hydroxide complexes with H2S. This procedure is used to make TpR,MeZn–SH complexes from TpR,MeZn–OH [5]. Bubbling of H2S through a CH3OH solution of [(TPA)Zn]2(μ-OH)2(X)2 (where X = BF4 or ClO4) led to the formation of 7 and 8 in a 39% and 30% yield, respectively. Repeated attempts to make a cadmium hydrosulfide from [(TPA)Cd]2(μ-OH)2(ClO4)2 and H2S always resulted in insoluble CdS.

3.4. Characterization of [(TPA)Zn–SH]+ complexes 7 and 8

Complexes [(TPA)Zn–SH]BF4 (7) and [(TPA)Zn–SH]ClO4 (8) were characterized by 1H and 13C NMR, IR, elemental analysis (CHN), electrospray mass spectrometry (ESI-MS) and, for 7, by X-ray crystallography. The compounds are stable in acetonitrile but begin to decompose within one day after dissolution in chloroform. The spectroscopic data for complexes 7 and 8 are identical, supporting the claim that 8 is similar in structure to 7. In the 1H and 13C NMR, the three pyridyl groups in both complexes are equivalent, indicative of tridentate coordination of the TPA ligand to the zinc center. The SH resonance for 7 and 8 is observed in CD3CN as a singlet at 1.5 ppm. Exchange of this resonance with deuterium occurs with D2O or D3OD, consistent with the assignment of the 1.5 ppm resonance as the SH proton. The 1H NMR chemical shift value for the SH proton in 7 and 8 also falls within the range (−2.1 to −1.0 ppm) observed by the zinc hydrosulfide complexes TpRMeZn–SH (R = phenyl, 3-pyridyl, 4-picolyl and t-butyl) [12]. The IR spectra of 7 and 8 did not show a v(SH) vibration.

The structure of the cationic portion of the X-ray structure of [(TPA)Zn–SH]BF4 (7) is shown in Fig. 5. The complex is mononuclear and the zinc ion is five-coordinate and displays approximately trigonal bipyramidal geometry. The hydrogen atom of the SH ligand is not located in the difference Fourier map, but its presence is supported by one tetrafluoroborate anion per cation and by 1H NMR (singlet at −1.5 ppm). The hydrosulfide and tertiary amine occupy the axial positions, while the three pyridyl rings occupy the equatorial positions. The structure is identical to [(TPA)Zn–SH]BPh4, which has just recently been published [14].
A comparison of the metrical parameters around the zinc ion between the active site structure of human carbonic anhydrase II (HCA II) bound with anionic hydrogen sulfide (1CAO) [38] and the model complexes [(TPA)Zn–SH]BF4 (7) and TpRM2Zn–SH (R = phenyl, 3-pyridyl or 4-picolyll) [12] shows important differences and similarities. For instance, the Zn–S distance (2.3207(14) Å) in 7 is significantly longer compared to the Zn–S distance in HCA II (2.2 Å) and TpRM2Zn–SH (Zn–Savg = 2.214 Å). The longer Zn–S bond can be attributed to the coordination of the tertiary amino nitrogen of the TPA ligand which elongates the trans Zn–SH bond distance. In addition, we would like to note that there are three potential hydrogen bonding interactions to the SH ligand in the 1CAO active site (Thr199 side chain hydroxyl group and crystalized waters HOH338 and HOH218) that may affect how SH ligates to Zn2+ in 1CAO. As such, not having such interactions in the TPA and Tp complexes means that the structural comparisons, while interesting, should be considered with this caveat in mind. Finally, the Zn–Npyridine bond distances (Zn–Navg = 2.09 Å) and S–Zn–Npyridine angles (S–Zn–Navg = 103.6°) in 7 are more similar to HCA II (Zn–Navg = 2.13 Å and S–Zn–Navg = 110.8°) compared to TpRM2Zn–SH (Zn–Navg = 2.06 Å and S–Zn–Navg = 123.8°).

3.5. Computational comparison between [(TPA)Zn–SH]+ and TpZn–SH

DFT calculations provide evidence for a stronger ligation of hydrosulfide to the zinc center in TpZn–SH than in [(TPA)Zn–SH]+ (Table 2). The Zn–S distance in the former is shorter by 0.061 Å in the gas phase and similarly by 0.053 Å in acetonitrile. This is consistent with the Zn–S Wiberg bond index being 0.054 greater in the Tp complex in the gas phase and 0.061 greater in acetonitrile. Likewise, there is a greater polarity in the SH–Zn bond in the TPA complex. Examination of the Mulliken charge populations on Zn and the hydrosulfide ligand (Table 3) in the two complexes reveals a greater difference in charge between the metal center and SH ligand in the TPA complex versus the Tp complex. This measure of bond polarity shows a small increase in going from the gas phase to acetonitrile solvent. The same trend is observed if NPA charges are considered (Table S3). Finally, Fukui nucleophilicity indices for the hydrosulfide ligand in TpZn–SH and [(TPA)Zn–SH]+ (Table 4) indicate that the SH ligand is more nucleophilic in the Tp complex, consistent with the reactivity trend observed upon methylating the two hydrosulfide complexes with methyl iodide [12].

3.6. Reactivity of [(TPA)ZnSH]ClO48

Preliminary reactivity studies were performed with [(TPA)Zn–SH]ClO4 (8) and comparisons were made to the more thoroughly studied TpRM2Zn–SH system. Prior studies by Rombach and Vahrenkamp [12] had shown that the zinc-bound hydrosulfide in the TpPhME2Zn–SH system is alkylated by CH3I to give TpPhMe2Zn and methanethiol. In contrast to TpPhMe2Zn–SH, the reaction of CH3I and 8 at room temperature is extremely slow, requiring about 9 days for completion, as evidenced by 1H NMR. This result is supported by the DFT calculations, which suggest a decreased nucleophilicity for [(TPA)Zn–SH]+ compared to TpZn–SH. Treatment of 8 on a preparative scale in CH3CN with CH3I (~5 equiv.) resulted in the isolation of [(TPA)ZnI]ClO4 (10) in a 78% yield. The product was identified by 1H and 13C NMR and X-ray crystallography. Formation of 10 was evident in the 1H NMR by the absence of the SH resonance present in 8 and the downfield shift of the TPA resonances. Crystals of the product were obtained and gave identical unit cell parameters for [(TPA)ZnI]ClO4, which has been previously characterized by X-ray crystallography [19].

Attempts to make an unknown metallothiolate via deprotonation of the hydrosulfide ligand in 8 using n-butyllithium and NaH failed. The deprotonation reactions resulted in the elimination of zinc sulfide and formation of the products [(TPA)LiClO4] (11) and [(TPA)Na2(μ-Clo4)2] (12), respectively. The composition of 11 and 12 were determined by spectroscopic methods (NMR, IR), elemental analysis and X-ray crystallography. The structures for both complexes are provided in Figs. S2 and S3 in the Supporting information. Compound 11 is monomeric and the lithium ion is bound by the TPA ligand and the perchlorate anion in a trigonal bipyramidal geometry. Conversely, 12 is dimeric with each sodium ion coordinated to a TPA ligand and two bridging perchlorate anions. Interestingly, the TpCum,MeZn–SH reaction with n-butyllithium results in SH substitution to form TpCum,MeZn–C4H9 instead of ZnS elimination [12].

4. Conclusion

The insertion of COS and CS2 into the M-OH bond of [(TPA)M2(μ-OH)2]ClO4 (M = Zn, Cd) in alcoholic media results in O-alkyl thiocarbonate and dithiocarbonate zinc and cadmium complexes. These complexes were characterized by spectroscopic methods and, in several cases, by X-ray crystallography. Complexes 2 and 6 represent the first examples of structurally characterized Zn and Cd complexes containing a M-S(C)O6(R = alkyl group) fragment. The O-alkyl thiocarbonate zinc complexes were determined to be susceptible to hydrolysis resulting

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in zinc hydrosulfide complexes of the general formula [(TPA)Zn–SH]. Other synthetic routes were also described for making [(TPA)Zn–SH]+ complexes. Furthermore, reactivity and DFT studies comparing cationic [(TPA)Zn–SH]+ with neutral TpZn–SH were conducted and many similarities and differences between the two complexes were found.

Acknowledgements

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Appendix A. Supplementary material

Computational details and the molecular structures and crystallographic data and refinement parameters for 838220, 838221, and 838222 contain the supplementary crystallographic data for 1 2 5 6 7 9 11. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.01.040.

References

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