Group 2 Complexes of 2,4,6-Trimercaptotriazine (TMT)

Kevin Henke[†] **and David A. Atwood***[,‡]

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University,
Fargo, North Dakota 58105, and Department of Geology and Geological Engineering,
University of North Dakota, Grand Forks, North Dakota 58203

Received July 31, 1997

The 2,4,6-trimercaptotriazine (TMT) ligand system is currently being used as a complexing agent for divalent metals although little is known about its chemistry. This report entails a description of the syntheses and structures of TMT complexes having the formula $M(TMTH_2)_2 \cdot nH_2O$ (M = Ca (**1**), Sr (**2**), and Ba (**3**), where $n = 11$, 11, and 4.5, respectively). In **1** and **2**, the structures consist of alternating layers of hydrated metal cations and π-stacked TMT groups. A wide range of hydrogen-bonding interactions connect these layers. Compound **3** forms as a polymeric molecule with covalent bonds between the Ba atoms and TMT ligands. Each of the compounds was structurally characterized. X-ray data: **1**, $C_{24}H_{104}Ca_4N_{24}O_{44}S_{24}$, triclinic, $P\bar{1}$, $a = 12.9622(7)$ Å, $b = 15.9874(9)$ Å, $c = 24.516(1)$ Å, $\alpha = 81.191(1)°$, $\beta = 89.560(1)°$, $\gamma = 72.433(1)°$, $Z = 2$; **2**, $C_6H_{26}N_6O_{11}S_6$-Sr, triclinic $P\bar{1}$, $a = 8.7454(5)$ Å, $b = 11.7545(6)$ Å, $c = 13.7292(7)$ Å, $\alpha = 66.529(1)°$, $\beta = 73.201(1)°$, $\gamma = 77.034(1)°$, $Z = 2$; **3**, $C_{12}H_{18}Ba_2N_{12}O_9S_{12}$, monoclinic, $P2_1/c$, $a = 8.5576(4)$ Å, $b = 21.028(1)$ Å, $c = 20.276(1)$ Å, $\beta = 96.440(1)°$, $Z = 2$.

Introduction

The contamination of water in the environment is a problem that will continue to grow over the coming years until the impact of regulations in this area begin taking effect. Numerous metal contaminants, such as Ba, Cr, Cd, Pb, Hg, Ag, As, and Se, may cause a great deal of harm in the biosphere.[1] Consider barium, for example; it is used in rat poisons, fireworks, and paints and as a heat stabilizer in plastics. When ingested, barium apparently alters muscle and nerve cells by disrupting the flow of K^+. Ultimately, it behaves like calcium and accumulates in bone.[2] Furthermore, such metals often undergo biomagnification and become potentially hazardous to humans.

The remediation of contaminated waters already in the biosphere represents a problem of collosal proportions.[3] A more manageable strategy, and the one that is currently being enforced by the U.S. Environmental Protection Agency (EPA), is to treat the waste streams at their industrial sources. Many techniques are currently available for the remediation of such effluents, including the use of chelating agents to precipitate the unwanted metals. In an ideal system, the remediator binds the metal, forming an insoluble complex that precipitates from solution and subsequently is removed from the waste stream by filtration. The metal is isolated in an inorganic form, and the chelate is regenerated and used again.

The reagent 2,4,6-trimercaptotriazine ($S_3C_3N_3$ = TMT) in a metalated form ($(TMT)Na_3$) is currently being used to remove univalent (Ag^+) and divalent (Hg^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}) heavy metals from wastewaters.[4] Since the toxicity of these elements can be attributed to a strong affinity for the sulfhydryl groups (S−H) of enzymes, it was thought that the TMT group would bind likewise. In the complexes formed between TMT and these elements, the presence of M−S bonds are assumed. However, no detailed information is known about the chemistry of TMT in relation to these and other metals. The most fully characterized complexes that have been reported in the literature are $(TMT)Na_3 \cdot 9H_2O$[5] and $(Os_3H(CO)_{10})_3(TMT)$.[6] The crystal structure of the first compound reveals a significant amount of water and an extensive network of hydrogen bonding.[5] In the osmium derivative there are no contacts between the molecular units.[6] In an effort to more fully understand this ligand system and its ability to bind "soft" metals, the current study will examine the formation of Ca, Sr, and Ba derivatives. In addition to the possibility of obtaining a good remediation system for barium, these studies should provide insight into the binding of other divalent atoms by the TMT ligand system.

Results and Discussion

Synthesis. The TMT ligand can be delivered in a reaction either as the acid ($TMTH_3$) or as the sodium salt ($(TMT)Na_3$) (Figure 1). In the present study, various stoichiometries of the acid were combined with the appropriate group 2 hydroxides in water. Unequivocal characterization of the compounds resulting from these reactions was not easy. It would appear that a wide range of different Ca, Sr, and Ba compounds form under closely related conditions. For instance, crystals of a compound of formula $Ba_3(TMT)_2 \cdot 8H_2O$ have been obtained from $BaCl_2 \cdot 2H_2O$ and $(TMT)Na_3 \cdot 9H_2O$, but the crystals were

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* Corresponding author. E-mailDatwood@plains.nodak.edu.

† University of North Dakota.

‡ North Dakota State University.

(1) *Code of Federal Regulations*, Parts 141.23 and 261.24, Title 40, 1993.

(2) Harte, J.; Holdren, C.; Schneider, R.; Shirley, C. *Toxics A to Z*; University of California Press: Berkeley, CA, 1991; p 229.

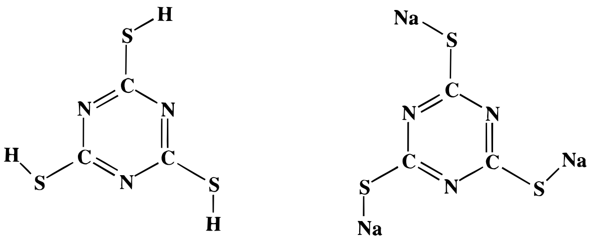
(3) The fact that most water-borne waste is generated as the result of rainfall on cities is an indication of how difficult it will be to find a solution.

(4) *Product information sheets on TMT-15 (15 wt % aqueous solution of $S_3C_3N_3Na_3 \cdot 9H_2O$) and TMT-55 (solid $S_3C_3N_3Na_3 \cdot 9H_2O$)*; Degussa Corp.: Allendale, NJ, 1993.

(5) Henke, K. R.; Bryan, J. C.; Elless, M. P. *Powder Diffr.* **1997**, *12*, 7.

(6) Ainscough, E. W.; Brodie, A. M.; Coll, R. K.; Mair, A. J. A.; Waters, J. M. *Inorg. Chim. Acta* **1993**, *214*, 21.

S0020-1669(97)00954-3 CCC: $15.00



$TMTH_3$
($C_3H_3N_3S_3$)
(a)

$TMTNa_3$
($C_3N_3Na_3S_3$)
(b)

Figure 1. Acid (a) and metalated (b) forms of the TMT ligand system.

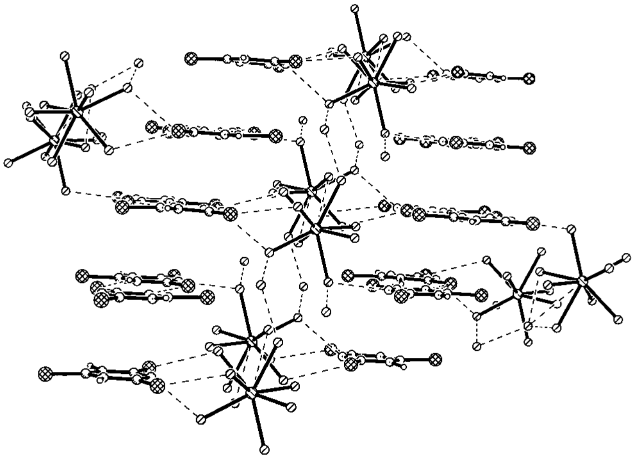


Figure 2. Arrangement of the $TMTH_2$ and $Ca(H_2O)_8$ layers in **1**.

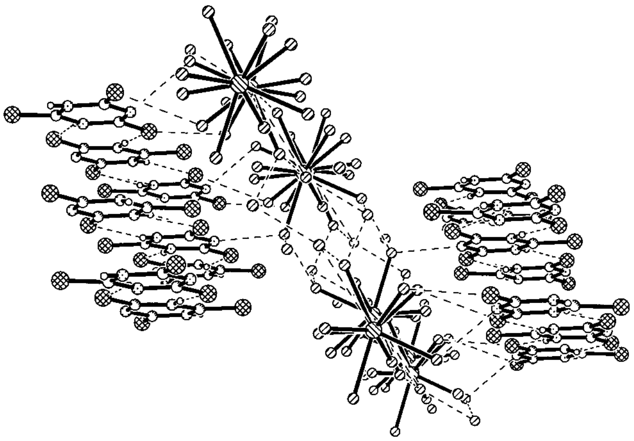


Figure 3. Arrangement of the $TMTH_2$ and $Sr(H_2O)_8$ layers in **2**.

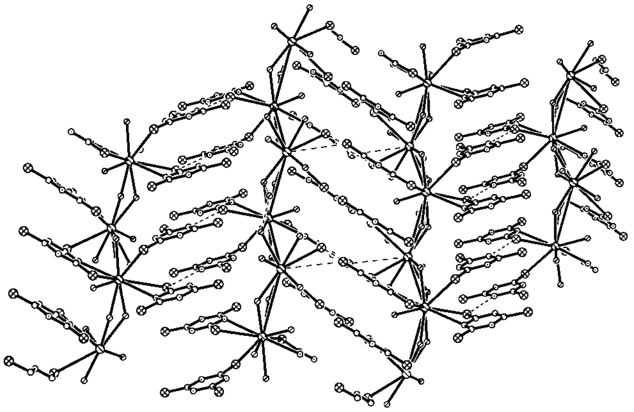


Figure 4. Packing arrangement for **3**.

not large enough for single-crystal X-ray analysis. Reproducibly, however, those of formula $M(H_2TMT)_2{\cdot}nH_2O$ ($n = 4.4$ or 11) could be prepared by combining 2 molar equiv of $TMTH_3$ with the alkaline earth metal hydroxide (eq 1). These conditions

$$2TMTH_3 + M(OH)_2{\cdot}nH_2O \xrightarrow[(M = Ca, Sr, Ba)]{H_2O} M(H_2TMT)_2{\cdot}nH_2O \quad (1)$$

are similar to recovery techniques in which an excess of the remediating agent is used to precipitate a maximal amount of the targeted metal.[4]

Structural Characterization. Due to the degree of hydration of the compounds, a limited amount of information is available spectroscopically. Since the products were isolated in a pure form by growth of single crystals (also confirmed by elemental analyses), X-ray structural data could be used to obtain definitive information on the structure and bonding within the compounds. The molecular structures of **1**−**3** are shown in Figures 2−4, respectively. A common feature of the three structures is the alternating arrangement of the hydrated metals and the TMT ligands. The TMT groups are arranged in a coplanar stack with ring centroid distances of 3.5−4.0 Å. These distances are in the range expected for van der Waals attractions.[7] In **1** and **2**, the TMT groups are anionic and are not bound directly to the Ca and Sr octahydrate units. The remaining two hydrogens on the TMT ligand protonate the nitrogens, making the TMT ligands zwitterionic. In **1** and **2**, the metal coordination spheres are essentially square antiprisms (Figures 2 and 3) with intramolecular spacings of 4.15 and 4.17 Å, respectively. This results in paired octahydrate units. In contrast, the coordination environment of the Ba atom in **3** includes 10 atoms: 3 sulfurs, 2 nitrogens, and 5 water molecule oxygens. Three separate TMT ligands are involved in this bonding array. Two of the waters bridge the barium atoms (in the range 2.80−2.98 Å) and form a continuous zigzag chain of $Ba(H_2O)_5$ units (Figure 4). The Ba−water distances range from 2.804(5) to 2.983(5) Å. In **1** and **2**, these distances decrease as the size of the metal decreases (Sr, 2.588(5)−2.647(5) Å; Ca, 2.409(8)−2.524(9) Å). Unlike **3**, **1** and **2** contain three additional water molecules. The Ba−S distances (3.396(2)−3.629(2) Å) are comparable to those in $Ba(SCN)_2{\cdot}3H_2O$ (3.391(2) Å).[8] However, the Ba−Ba distances are exceptionally long (4.8 Å) when compared to those of other dimeric complexes (e.g., $Ba_2L_4(H_2O)_{1.81}$, 3.90(1) Å (L = 2-methoxy-2,6,6-trimethylheptane-3,5-dionate)).[9]

Hydrogen Bonding. The layers of metal cations and ligand anions for **1** and **2** are connected by an extensive array of hydrogen-bonding contacts. There are five distinct types when they are viewed from the perspective of a single ligand (Figure 5). They can be classified into those involving water molecules and those involving the ligand NH^+ groups. For the three involving the water molecules (A−C), only the N or S···O distances are given since the hydrogens were not found. They are, consequently, ~1 Å longer than what is expected for a hydrogen bond. There is an additional water-only hydrogen-bond contact between the waters of crystallization and those coordinated to the Ca or Sr atoms. The NH^+ contacts are related in that they are both made to an S atom (D and E). They are

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(7) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins College Publishers: New York, 1993; p 290.

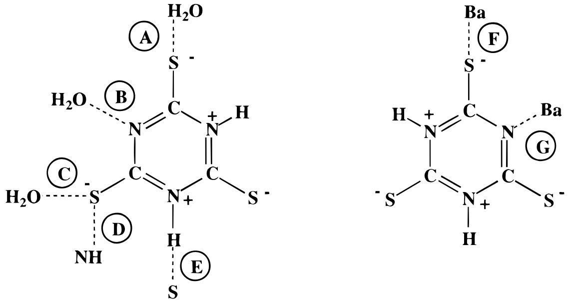
(8) Mereiter, K.; Preijinger, A. *Acta Crystallogr.* **1982**, *B38*, 382.

(9) Ivanov, S.; Snezko, N.; Ilyukhin, A.; Sergienko, V. *Polyhedron* **1997**, *16*, 2527.

Table 1. Crystal Data for $Ca(TMTH_2)_2{\cdot}11H_2O$ (**1**), $Sr(TMTH_2)_2{\cdot}11H_2O$ (**2**), and $Ba(TMTH_2)_2{\cdot}4.5H_2O$ (**3**)

	1	**2**	**3**
empirical formula	$C_{24}H_{104}Ca_4N_{24}O_{44}S_{24}$	$C_6H_{26}N_6O_{11}S_6Sr$	$C_{12}H_{18}Ba_2N_{12}O_9S_{12}$
fw	2363.07	638.31	1133.78
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	12.9622(7)	8.7454(5)	8.5576(4)
b (Å)	15.9874(9)	11.7545(6)	21.028(1)
c (Å)	24.516(1)	13.7292(7)	20.276(1)
α (deg)	81.191(1)	66.529(1)	
β (deg)	89.560(1)	73.201(1)	96.440(1)
γ (deg)	72.433(1)	77.034(1)	
V (Å^3)	4782.5(5)	1229.7(1)	3625.6(3)
Z	2	2	4
D_{calc} (g/cm^3)	1.641	1.724	2.077
λ (Å)	0.7107	0.7107	0.7107
μ (mm^{-1})	0.843	2.757	2.908
temp (K)	298	298	298
2θ range(deg)	0.84−22.50	1.66−18.00	1.40−21.00
$R(F_o^2)^a$	0.0693	0.0705	0.0427
$R_w(F_o^2)^b$	0.2972	0.1601	0.1305

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.



Label	Contact	Distance (Å)		
		Ca	Sr	Ba
A	(H$_2$O) O···S^a	3.27, 3.29	3.28	
B	(H$_2$O) O···N^a	2.84 - 2.87	2.83, 2.86	
C	(H$_2$O) O···S^a	3.29	3.28	
D	(NH) H···S^b	2.58	2.55, 2.68	
E	S···H (NH)^b	2.62, 2.67	2.49	3.24 (S···N)^c
F	M···S	-	-	3.40 - 3.62
G	M···N	-	-	2.99 - 3.05

[a] The H_2O hydrogens were not located so the distances refer to O···S or N contacts.
[b] The N-H groups were located in the structures so these distances refer to H···S contacts.
[c] The N-H groups were not located in this structure so the distance refers to the S···N contact.

Figure 5. Description of the types of contacts present in the structures of **1**−**3**.

fairly consistent for both types of contacts in both structures in a distance range of 2.49−2.68 Å. The contact (E) acts to organize sheets of TMT ligands in the two structures. Although it is remarkable that there are so many contacts, and so many of the same type, for **1** and **2**, the interactions themselves are consistent with known guidelines for hydrogen-bond formation.[10] Furthermore, they fulfill Pauling's early requirement that the hydrogen bonds organize to form aggregates which can be considered as an independent chemical species.[11] That is clearly the case for **1** and **2**. It would appear that the potential for hydrogen bonding is reduced in **3** by the presence of covalent interactions between the Ba atoms and the S and N atoms of the ligand (F and G in Figure 5, respectively). There is, however, one long contact (N···S, 3.24 Å) between the ligands as observed in the structures of **1** and **2**. This is the only common contact shared among **1**−**3**, but it is not observed in the Na_3TMT derivative.[5]

Conclusion

The solubility in water of the three compounds decreases from Ca to Ba. The same trend is observed for the sulfates of these elements.[12] The EPA requires that wastewaters contain less than 2 mg/L of Ba.[1] The solubility of **3** is 4.69 g/L and, thus, is not low enough to achieve this level. As a remediation agent for Ba, the TMT system is not a good choice in the absence of additional reagents. A common feature in the structures of **1**−**3** is an interligand hydrogen-bond contact between an $N{-}H^+$ group and an adjacent S^- ion.

Experimental Section

General Considerations. All manipulations involving N_2 were conducted using Schlenk techniques. $(TMT)Na_3$ was provided by Degussa Corp. and was converted to $TMTH_3$ with HCl. The group 2 hydroxides (98% purity) were obtained from standard sources and used as received. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. X-ray Data for **1**−**3** were collected on a Siemens SMART-CCD unit. Hydrogens that were designated for the sulfur atoms ultimately refined to unrealistically short distances (S−H 0.4 Å). However, they refined suitably when found from difference maps for two nitrogens of each TMT ligand for **1** and **2**. Reasonable hydrogen atoms could not be found in the solution of **3**. (See Table 1 for crystal data and experimental details).

Preparation of $Ca(H_2TMT)_2{\cdot}11H_2O$ (1). $Ca(OH)_2$ (1.07 g, 14.4 mmol) was stirred in deionized water (200 mL) under a nitrogen purge for at least 1 h. $TMTH_3$ (5.18 g, 29.2 mmol) was added and the mixture stirred over the course of 48 h under nitrogen. At this point the solution was filtered (in air) to remove a small amount of undissolved $TMTH_3$ (0.13 g, 0.73 mmol) and the filtrate allowed to evaporate over a period of several days to form colorless crystalline blocks (yield 8.05 g, 95.6%; mp >250 °C). In air, these crystals become opaque with a yellow color. XRD on this material indicates the presence of $TMTH_3$ and $CaCO_3$ (calcite). IR (KBr, cm^{-1}): 3140 m, br, 1626 w, 1555 w, 1476

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[10] Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

[11] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 6.

[12] *CRC Handbook of Chemistry and Physics*, 58th ed.; CRC Press, Inc.: Cleveland, OH, 1977.

s, 1402 s, 1242 s, 1154 s, 797 w, 710 w, 500 w. Anal. Calcd (found): C, 12.20 (12.54); H, 4.44 (3.75); N, 14.23 (14.19). Solubility (H_2O): 187 g/L.

Preparation of $Sr(H_2TMT)_2{\cdot}11H_2O$ (2). $Sr(OH)_2{\cdot}8H_2O$ (1.87 g, 7.00 mmol) was mixed in 1 L of deionized water under a nitrogen purge for 1 h. $TMTH_3$ (2.49 g, 14.0 mmol) was added and the mixture stirred under nitrogen for 48 h until both reagents dissolved. Following filtration (from 0.01 g of undissolved material), the filtrate was allowed to evaporate in air for 4 days, leading to the formation of colorless cubic crystals (yield 3.66 g, 82%; mp >250 °C). IR (KBr, cm^{-1}): 3150 m, 2617 m, 2376 s, br, 2212 m, br, 1244 s, br, 1128 s, br, 873 m, 804 w, 715 m, 463 m. Anal. Calcd (found): C, 11.29 (11.78); H, 4.11 (4.33); N, 13.17 (13.43). Solubility (H_2O): 10.4 g/L.

Preparation of $Ba(H_2TMT)_2{\cdot}4.5H_2O$ (3). $Ba(OH)_2{\cdot}8H_2O$ (3.10 g, 9.83 mmol) was mixed in deionized water (1 L), the solution combined with $TMTH_3$ (3.48 g, 19.6 mmol), and the mixture stirred under nitrogen for 72 h. The solution was filtered (from 0.03 g of undissolved material) and concentrated by boiling to a volume of 200 mL. As the solution cooled to 25 °C, pure, white crystals formed (yield 5.50 g, 98%; mp >250 °C). IR (KBr, cm^{-1}): 3200 m, br, 2410 m, 1550 w, 1504 w, 1402 m, 1359 m, 1234 s, 1145 s, 887 m, 815 m, 756 m, 711 m, 501 m, 455 m. Anal. Calcd (found): C, 12.62 (12.74); H, 2.29 (2.18); N, 14.72 (14.69). Solubility (H_2O): 4.64 g/L.

Acknowledgment. This work was supported by the National Science Foundation (Grant 9452892), the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 31901-AC3), and the Office of Naval Research (Grant N00014-96-1-1271). The receipt of a National Science Foundation CAREER Award (Grant 9625376) is also gratefully acknowledged.

Supporting Information Available: Tables of X-ray experimental details, bond lengths and angles, positional parameters, and anisotropic thermal parameters and figures showing unit cell views (36 pages). Ordering information is given on any current masthead page.

IC970954Z