

Chemistry of 2,4,6-Trimercapto-1,3,5-triazine (TMT): Acid Dissociation Constants and Group 2 Complexes

Kevin R. Henke, Aaron R. Hutchison, Matthew K. Krepps, Sean Parkin, and David A. Atwood*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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The acid dissociation constants of 2,4,6-trimercaptotriazine (H_3TMT , **1**) were determined and now can be employed in the preparation of complexes having specific $M-TMT$ (M = divalent metal; $TMT = 2,4,6$ -trimercapto-1,3,5-triazinide, $C_3N_3S_3^{3-}$) ratios. For example, the combination of H_3TMT (**1**) with $Mg(OH)_2$ at pH 7.1 leads to the crystallization of $Mg(H_2TMT)_2 \cdot 6H_2O$ (**4**). With the appropriate pH adjustment, the contiguous series of compounds $Ba_3(TMT)_2 \cdot 8H_2O$ (**3**), $Ba(H_2TMT)_2 \cdot 7H_2O$ (**5**), and $BaHTMT \cdot 3H_2O$ (**6**) can be isolated. The compounds were characterized by mp, IR, TGA, elemental analysis, and, in the cases of **4**, **5**, and **6**, crystallography. The comparison of **4** with **5** and **6** offers an interesting view of the difference in hard and soft bonding with TMT. In the saltlike Mg structure of **4**, there is extensive hydrogen bonding, but in the Ba structures, **5** and **6**, covalent Ba–S bonding dominates.

Introduction

The compound H_3TMT (**1**) ($TMT = 2,4,6$ -trimercapto-1,3,5-triazinide, $C_3N_3S_3^{3-}$)¹ has been used extensively since its first isolation in the 1880s. It was first prepared by combining methyl thiocyanate and sodium sulfide, forming the sodium thiocyanate. After a warm acidic aqueous workup, the H_3TMT (Figure 1a) precipitates out of solution. It can also be readily and inexpensively prepared by combining 1 molar equiv of cyanuric chloride (1,4,6-trichloro-1,3,5-triazine) with 3 molar equiv of sodium hydrogen sulfide (NaHS) and then lowering the pH to below 4.96 once the NaHS reacts.^{1,2}

The highly water-soluble compound^{3,4} $Na_3TMT \cdot 9H_2O$ (**2**) (Figure 1b) readily forms insoluble precipitates with transition⁵ and main group metals in aqueous solutions. For instance, it can be used to precipitate metal ions such as Ag^+ ,⁶ Zn^{2+} , Cd^{2+} , Hg^+ , Hg^{2+} ,⁷ Tl^+ , and Pb^{2+} from industrial wastewaters and polluted natural waters.^{8,9}

Despite their widespread use, there has been remarkably little definitive or systematic information published about the main group complexes of TMT and its derivatives. For transition

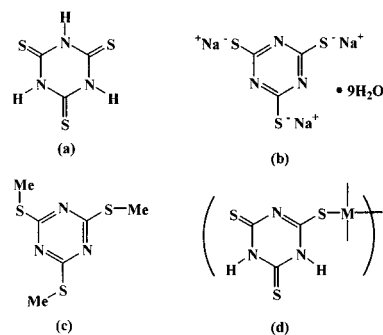


Figure 1. Various forms of TMT units: (a) H_3TMT (**1**) in the thione tautomer, (b) the soluble salt form, $Na_3TMT \cdot 9H_2O$ (**2**), (c) Me_3TMT , demonstrating the thiol form, and (d) idealized structural formula for an $M(H_2TMT)$ complex.

metals, well-defined examples include complexes with osmium ($[Os_3H(CO)_{10}]_3(TMT)$),¹⁰ titanium(III) ($[(\eta^5-MeCp)_2Ti]_3(TMT)$), including a crystal structure incorporating the related 4,6-dithiopyrimidine ligand,¹¹ cobalt(III) ($[Co(en)_2]_2(TMT)X_3$ (where X is I or ClO_4), $Co(en)_2(TMT)$, and $[Co(en)_2(H_2TMT)]-[ClO_4]_2$),¹² copper(I) ($(CuPPh_3)_6(TMT)_2$),¹³ gold(I) ($(AuPPh_3)_3(TMT)$, $(AuPPhMe_2)_3(TMT)$, $[Au(TMT)(AuPPhMe_2)_2]_2$,¹⁴ and $[(AuL)_3TMT]$ (L = base)),¹⁵ and nickel(II) ($NiL(HTMT)$, where L is a multidentate ligand).¹⁶ The most systematically studied

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Table 1. Parameters and Results of 10 Titrations of Na₃TMT·9H₂O (2) with 1 N HCl

titration no.	[Na ₃ TMT·9H ₂ O] (mM)	[K ₂ SO ₄] ^a (mM)	pK _{a1}	pK _{a2}	pK _{a3}
1	6.7	49.8	5.75	8.23	11.35
2	6.8	49.7	5.75	8.32	11.35
3	7.72	49.9	5.60	8.44	11.45
4	8.07	50.1	5.82	8.41	11.44
5	8.38	49.8	5.82	8.35	11.55
6	6.38		5.70	8.44	11.36
7	9.79		5.85	8.35	11.45
8	8.22		5.74	8.35	11.28
9	6.98		5.54	8.36	11.28
10	7.26		5.57	8.31	11.29
ave.			5.71	8.36	11.38
std dev			0.11	0.05	0.09

^a Background electrolyte.

are those of formula M₃(TMT)₂ (M = divalent metal¹⁷ or group 2 element¹⁸). The present work will broaden the potential for synthesizing binary combinations of TMT and main group or transition metals by determining the acid dissociation constants for H₃TMT (1). By knowing the dissociation constants and controlling the pH, specific complexes can be targeted for synthesis. For example, this information can be used to rationalize the formation of the new compounds Ba₃(TMT)₂·8H₂O (3), Mg(H₂TMT)₂·6H₂O (4), Ba(H₂TMT)₂·7H₂O (5), and BaHTMT·3H₂O (6).

Results and Discussion

Acid Dissociation Constants for H₃TMT. Na₃TMT·9H₂O dissolves in water to produce a variety of species whose concentrations are determined by pH. If the pH of the solution is above 12.5, the TMT trianion (C₃N₃S₃³⁻ or TMT³⁻) is the most abundant species. At pH values of about 10 and 7, the most abundant species are the monohydrogen TMT dianion (HTMT²⁻) and the dihydrogen TMT monoanion (H₂TMT⁻), respectively. At pH values below 5, the sparsely water-soluble acid, H₃TMT, is most abundant, and substantial reaction with metal ions is not expected.

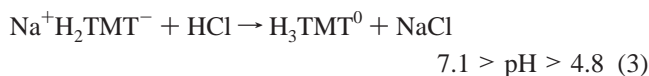
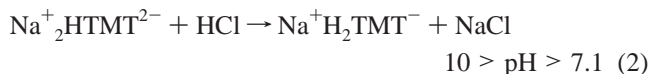
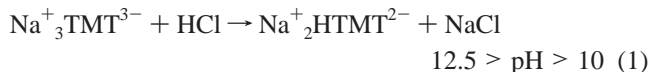
The acid dissociation constants were derived via a rigorous procedure^{19,20} and are given as pK_a values in Table 1. This procedure gave results that are significantly superior to those already listed in the literature.²¹ Not only were these values useful for the preparation of 3–6, but they also make it possible to rationalize some results from other experiments we have performed, which were not consistent with the previous values.²²

The results for pK_{a1} are complicated by the fact that H₃TMT begins to precipitate at pH values of 5.63–6.20. Actually, pK_{a1} represents the pH where [H₂TMT⁻] is equal to the total concentration of H₃TMT, both precipitated and dissolved. Although pK_{a1} is not defined in the classical sense, our successful reactions demonstrate that this number is of practical use.²²

Group 2 Complex Synthesis and Characterization. It is possible to prepare divalent metal complexes containing the series of ligand units TMT³⁻, HTMT²⁻, and H₂TMT⁻ by

controlling the pH of aqueous ligand solutions (eqs 1–3). It should be possible to maximize yields of TMT–metal complexes by adding the appropriate metal stoichiometry.

In aqueous solution,



For the Mg–TMT compound 4, Mg(OH)₂ and the acid form of TMT, H₃TMT (1), were used. This combination was used because the metal hydroxide was basic enough to raise the pH of the H₃TMT/metal hydroxide solution to the target pH of 7.1, where the monoanion, H₂TMT⁻, is the major anion species without any additional adjustment to the pH. When using metal salts at basic pH, Na₃TMT·9H₂O is used in place of the acid form. Three barium complexes were formed, consistent with the pK_a studies, explained previously herein. Two of the compounds, 5 and 6, were structurally characterized by single-crystal X-ray analysis. These two compounds cocrystallized from a solution of BaCl₂ and Na₃TMT at pH 10, which was lowered from an initial pH of 12.5 by the addition of HCl. At pH 10, HTMT²⁻ is the major anion in solution. As the HTMT²⁻ crystallizes with the Ba²⁺, the relative concentration of H₂TMT⁻ increases. This results in the monoanionic species, H₂TMT⁻, becoming prevalent enough to attract Ba²⁺ and crystallize BaHTMT·3H₂O (6). In keeping with the results of the pK_a study, Ba₃TMT₂·8H₂O (3) can easily be synthesized at a pH of about 12.5, where the trianion, TMT³⁻, is the dominating species. The sodium form of TMT is utilized for this reaction, because, in solution, all three Na⁺ ions dissociate, yielding the trianion without any external pH adjustments. Two separate solutions containing BaCl₂ and Na₃TMT·9H₂O were combined and filtered. The combined solution had a pH of 12–12.5. Ethanol was then layered on top of the aqueous solution to encourage crystal growth. All attempts to grow crystals suitable for single-crystal analysis have, thus far, failed.

It was previously suggested that the major bands observed at 1540, 1125, and 745 cm⁻¹ in the IR spectrum of uncoordinated H₃TMT are characteristic of the nonaromatic, trithione form of the TMT ring system (Figure 1a). Specifically, the double bond of the thione peak vibrates at 1150 cm⁻¹.²³ The aromatic, trithiol form of the ring, on the other hand, is characterized by the presence of the corresponding bands around 1490, 1245, and 860 cm⁻¹, as found in the spectrum of (CH₃)₃-TMT (Figure 1c).¹⁷ In a study of mixed ligand nickel complexes, it was observed that, upon coordination, some bands in the original infrared spectrum of the free H₃TMT split, and new bands are also observed, signifying that a complex has formed.²¹ Similar features are also observed in the spectra of complexes 3–6 reported here. These bands can be attributed to the presence of two types of S–C and N–C bonds (as displayed in Figure 1d).

For the three compounds for which crystal structures have been obtained, the IR spectra reinforce the structures. The structures of 4 and 5 are similar, and as expected, the IR spectra

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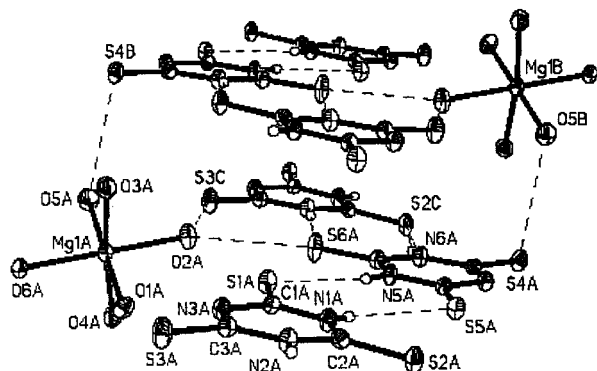


Figure 2. Structure of $\text{Mg}(\text{H}_2\text{TMT})_2 \cdot 6\text{H}_2\text{O}$ (**4**) depicting the extensive hydrogen bonding within the compound.

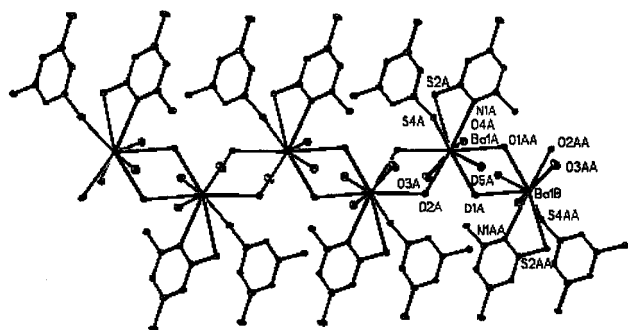


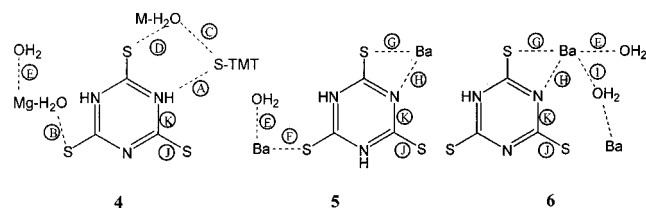
Figure 3. Structure of **5**, $\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 7\text{H}_2\text{O}$, containing the repeating unit $[\text{Ba}(\mu\text{-H}_2\text{O})_2]_n$ with $\text{Ba}-\text{O}$ distances of ~ 2.8 Å.

of these two compounds show almost identical vibrations. For **4** and **5**, both types of $\text{C}-\text{S}$ and $\text{C}-\text{N}$ bonds are evident. Peaks at 1552 and 1489; 1240 and 1147; and 874 and 719 cm^{-1} for **4**, and 1549 and 1489; 1247 and 1147; and 877 and 712 cm^{-1} for **5** demonstrate this. The IR spectra of **6** show that the compound is mainly in the thiol form (1495, 1260, 860 cm^{-1} ; no peak at 1150 cm^{-1}), which the crystal structure and bond lengths confirm. The structure of compound **3** can therefore be expected to be totally in the thiol form, on the basis of the IR data. The thione form of **4** and **5** corresponds to $\text{C}-\text{S}$ bond lengths of 1.657 and 1.659 Å, respectively, while the thiol form in the same two compounds has bond lengths of 1.692 and 1.695 Å, respectively. With $\text{C}-\text{S}$ bond lengths ranging from 1.698 to 1.705 Å, **6** shows no evidence of the thione form. It can be speculated from IR data that **3** would have $\text{C}-\text{S}$ bond lengths of at least 1.698 Å. This demonstrates the extremes that the three $\text{C}-\text{S}$ bonds may adopt in a single TMT molecule. These $\text{C}-\text{S}$ bond lengths are within reported values for $\text{C}-\text{S}$ single bonds (1.712 Å) and $\text{C}-\text{S}$ double bonds (1.66 Å).²⁴

Evidence that the hydrogen atoms of HTMT^{2-} and H_2TMT^- are located on the nitrogen atoms (Figure 1d) is provided by the presence of bands assigned to $\text{N}-\text{H}$ stretching vibrations in the 2880–3200 cm^{-1} range for **4**–**6**. As anticipated, corresponding bands are not observed in the spectra of **3**, further supporting the trithiol structure. The weak, broad peak from 3126 to 3260 cm^{-1} and sharp, jagged peak at 1653 cm^{-1} are indicative of water.²⁵

Structural Characterization. The structure of $\text{Mg}(\text{H}_2\text{TMT})_2 \cdot 6\text{H}_2\text{O}$ (**4**) completes the group 2 series for the formula $\text{M}(\text{H}_2\text{TMT})_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$).¹⁸ Like the Ca and Sr derivatives

Table 2. Description of the Types of Contacts Present in the Structures of **4**, **5**, and **6**



label	contact	distance (Å)		
		4	5	6
A	$\text{S} \cdots \text{N}$	~ 3.3		
B	$\text{S} \cdots \text{O}$	3.27		
C	$\text{S} \cdots \text{O}$	3.15		
D	$\text{S} \cdots \text{O}$	3.19		
E	$\text{M} \cdots \text{O}$	2.036–2.107	2.730–2.990	2.851, 2.863
F	$\text{M} \cdots \text{S}$		3.55	
G	$\text{M} \cdots \text{S}$		3.378	3.269–3.328
H	$\text{M} \cdots \text{N}$		2.946	3.106–3.145
I	$\text{M} \cdots \text{O} \cdots \text{M}$			2.799, 2.907
J	$\text{C}-\text{S}$	1.657–1.692	1.659–1.695	1.698–1.705
K	$\text{C}-\text{N}$	1.337–1.378	1.332–1.383	1.324–1.374

preceding it, **4** has a great deal of hydrogen bonding (Figure 2). These contacts are formed between three adjacent TMT molecules ($\text{S} \cdots \text{N} \sim 3.3$ Å), a common feature in most TMT structures. The $\text{Mg}-\text{H}_2\text{O}$ units form two types of hydrogen bonds to sulfur atoms, one that is to a single S atom ($\text{S4B} \cdots \text{O5A} = 3.27$ Å) and one that is to two S atoms ($\text{S3C} \cdots \text{O2A} = 3.19$ Å and $\text{S6A} \cdots \text{O2A} = 3.15$ Å). These contacts are summarized in Table 2.

Interestingly, the structure of **5**, $\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 7\text{H}_2\text{O}$ (Figure 3), is a polymorph of the previously reported structure, $\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 4.5\text{H}_2\text{O}$. There is very little difference in the primary bonding between the two structures. Both contain the repeating unit $[\text{Ba}(\mu\text{-H}_2\text{O})_2]_n$, forming a chain, with $\text{Ba}-\text{O}$ distances that are comparable for both compounds (~ 2.8 Å). The barium atoms in each structure are covalently bound to the sulfur atom of one TMT molecule (~ 3.550 Å) and the sulfur (~ 3.378 Å) and nitrogen (~ 2.946 Å) atoms of another TMT molecule, with the second TMT molecule acting as a bidentate chelate (Table 2).

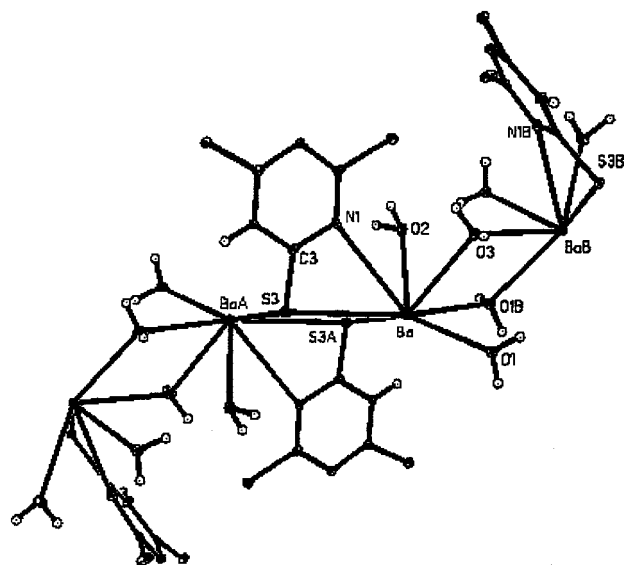


Figure 4. Compound **6**, $\text{BaHTMT} \cdot 3\text{H}_2\text{O}$, in which the seventh coordination site vacated by one TMT is now occupied by an additional water, creating a tetrahydrate.

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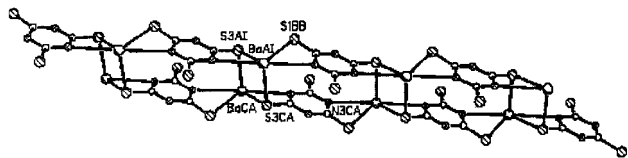


Figure 5. TMT molecules aligned along the length of the one-dimensional array, located essentially between the barium atoms in $\text{BaHTMT}\cdot 3\text{H}_2\text{O}$ (**6**).

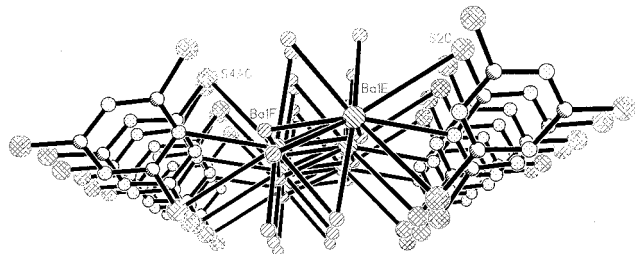


Figure 6. View demonstrating the stacking of the TMT units in **5**.

There are two differences in the structures. The first is that there are free waters in **5**, whereas, for the other, all of the water molecules are coordinated to a barium atom. This leads to an extensive network of hydrogen bonded waters in the 4.5 hydrate structure, with some of the hydrogen bonding occurring between the S atoms and both protons of a water molecule ($\text{S}\cdots\text{O} \sim 3.4$ Å; $\text{S}\cdots\text{H}-\text{O} \sim 2.7$ Å (see figure in Supporting Information)). The second, most significant, difference is that the TMT units in **5** are not connected through intermolecular $\text{S}\cdots\text{N}-\text{H}$ hydrogen bonding, a common feature in TMT structures and one that is found in the 4.5 hydrate structure ($\text{S}\cdots\text{N} = 3.24$ Å). In **5**, apparently, the additional water molecules provide better hydrogen bonding than the ammonium hydrogens on adjacent TMT molecules. In the absence of the intermolecular bonding, the TMT units adopt a coplanar, efficiently packed arrangement. This type of stacking is a second common feature for many TMT structures.

The barium atoms are connected to one less TMT unit in **6**, in comparison to **5**. Thus, the seventh coordination site vacated by the TMT is now occupied by an additional water, making **6** a tetrahydrate (Figure 4). The TMT molecules bond through both a sulfur (~ 3.273 Å) and a nitrogen (~ 3.106 Å) in the same bidentate fashion observed for **5**. Another similarity is the presence of two bridging water molecules ($\text{Ba}-\text{O} \sim 2.85$ Å) which connect all of the barium atoms in a one-dimensional chain (Table 2). The TMT molecules are aligned along the length of the one-dimensional array, located essentially between the barium atoms (Figure 5). In the structure of **5** and the other group 2 structures, by contrast, the TMT units are stacked in a coplanar array and perpendicular to the length of the group 2 H_2O chain (Figure 6).

Experimental Section

All water used was freshly distilled and deionized (DI), with a resistivity > 16 MΩ·cm. The pH measurements were conducted on an Orion model 710A pH/ISE meter and an Orion 8102BN Ross combination electrode. The meters were calibrated with pH 4.01, 7.00, and 10.01 ± 0.01 Orion, Inc., buffers at 20–25 °C. Thermogravimetric analysis (TGA) studies in the range 30–600 °C were carried out using a TA Instruments TGA 2950. Finely powdered samples of approximately 10–25 mg were placed into platinum pans and purged with argon gas at a flow rate of 100 cm^3/min . The samples were heated at a rate of 5 or 10 °C/min. Infrared spectra were recorded as KBr pellets or Nujol mulls on a Nicolet Magna 560 FT-IR spectrometer. Elemental analyses (EA) (C, H, N, S) were performed on an Elementar Americas Vario EL III instrument.

Determination of the Acid Dissociation Constant of H_3TMT . Data points were produced by titrating Aldrich 1.043 N (Lot # 14104EU) or Fluka 1.0 N (Analysis # 380097/1 41698) HCl into 10 6.38–9.79 mM aqueous solutions of purified $\text{Na}_3\text{C}_6\text{N}_6\text{S}_3\cdot 9\text{H}_2\text{O}$ (Table 1) and monitoring the pH. Data from 10 titrations of Na_3TMT with HCl were plotted on graphs of pH versus volume (mL) of 1 N HCl to produce the titration curves. The first five included K_2SO_4 as a background electrolyte. The second five titrations were conducted without the K_2SO_4 electrolyte. The two groups of titrations were consistent with each other, within experimental error. An example of a representative titration curve is given in the Supporting Information.

To determine the dissociation constants, we first divided each of the 10 titration curves into three sections (a total of 30 sections) corresponding to the three areas of greatest slope on the curves. All 30 sections were then individually fitted to polynomial equations using *Tablecurve 2D* or *SigmaPlot* software (Jandel Scientific, San Rafael, CA). The values of the inflection points (titration end points) were determined by taking the second derivative of the fitting equations.²⁶ On each of the 10 titration curves, three crossover points, located halfway between the end points, were found using the curve fit equations and verified by directly measuring them off of the 10 titration curves. Using the generally accepted assumption that only two of the four dissolved TMT species are in significant concentrations at each crossover point, the pH value at each crossover point then corresponds to a $\text{p}K_a$. This is a reasonable assumption with weak acids having $\text{p}K_a$ values separated by 2.5 units or more, including phosphoric and fumaric acids.^{19,20}

Preparation of Na_3TMT . $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ was obtained from Degussa Corporation and then purified by the following method. A solution obtained by dissolving $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ (57 g, 141 mmol) in 100 mL of DI water was filtered using a 0.45 μm membrane filter to remove Na_2S impurities. To the filtrate was carefully added, without stirring, 200 mL of 95% ethanol. Within minutes, white crystals of $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ began to form at the aqueous/organic interface. The mixture was allowed to sit overnight and then filtered (this time using ordinary qualitative filter paper). The crystals were washed with diethyl ether and then air-dried overnight. The typical yield was about 40 g (70%) (mp > 250 °C).

Preparation of H_3TMT . The H_3TMT was obtained by treating the $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ obtained from Degussa with concentrated hydrochloric acid in a 1:3 molar ratio. In a typical reaction, 100 g of $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ was dissolved in 350 mL of DI water and the solution filtered. To the filtrate was added 61 mL of concentrated hydrochloric acid (12.1 N). A yellow precipitate formed immediately. The mixture was stirred briefly, and the precipitate was isolated by filtration, washed with copious amounts of DI water, and dried, first at room temperature and then at 110 °C. The typical yield was about 40 g (91%) (mp 230 °C (dec)). The H_3TMT was characterized by IR, elemental analysis (EA), and a distinctive XRD pattern. All other reagents were purchased new from commercial sources with $> 95\%$ purity and were used as obtained.

Preparation of $\text{Ba}_3\text{TMT}_2\cdot 8\text{H}_2\text{O}$ (3). A 50 mL solution of $\text{Na}_3\text{TMT}\cdot 9\text{H}_2\text{O}$ was made (1.67 g, 4.12 mmol) and stirred for 30 min until completely dissolved. A 50 mL solution of $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ was made (1.50 g, 6.14 mmol) and stirred for 30 min until completely dissolved. The two solutions were then combined and allowed to sit without stirring for 1 min, whereupon the solution became slightly cloudy. The cloudy solution was filtered (0.45 μm paper) to obtain a clear, very pale yellow solution. Ethanol (46 mL) was slowly added down the side of the beaker to form a layer above the water. White precipitate and prickly snowball crystals (a spherical crystal covered with crystallites perpendicular to the surface) formed immediately in the ethanol. Yield: 1.16 g (63%). Mp/decomposition: 325–335 °C, with decomposition to yellow powder (sealed tube). Anal. Calcd for $\text{Ba}_3\text{C}_6\text{S}_6\text{N}_6\text{H}_{16}\text{O}_8$ (905.65): C, 7.95; H, 1.78; N, 9.28; S, 21.18. Found: C, 7.65; H, 1.78; N, 8.07; S, 17.82. TGA revealed eight waters of hydration. IR (Nujol, cm^{-1}): 3258 w, 3126 w, 1653 m, 1635 w, 1506 w, 1437 s, 1253 m, 1234 s, 1219 s, 1122 w, 1052 w, 975 w, 885 w, 847 s, 792 m, 731 m, 693 w.

Preparation of $\text{Mg}(\text{H}_2\text{TMT})_2\cdot 6\text{H}_2\text{O}$ (4). $\text{Mg}(\text{OH})_2$ (0.66 g, 11.3

(26) Harris, D. *Quantitative Chemical Analysis*, 5th ed.; Freeman: New York, 1999; pp 254–256 and 265–305.

mmol) and H_3TMT (4.00 g, 22.6 mmol) were combined and stirred in 200 mL of DI water. The initial solution was slightly yellow and had an approximate pH of 7.1. After 48 h of stirring in air, the solution was filtered. Total yield: 2.86 g (52%). Mp/decomposition: >250 °C. Anal. Calcd for $\text{MgC}_6\text{S}_6\text{N}_6\text{H}_{16}\text{O}_6$ (483.93): C, 14.88; H, 3.33; N, 17.36. Found: C, 14.66; H, 3.29; N, 17.09. TGA revealed six waters lost. IR (KBr, cm^{-1}): 3574.3 w, 3404.6 m, br, 3130 s, 2937.8 w, 2910.8 w, 1552.8 s, 1489.1 s, 1415.8 m, 1354.1 m, 1240.3 s, 1147.7 s, 873.8 w, 719.5 m, 468.7 m.

Preparation of $\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 7\text{H}_2\text{O}$ (5) and $\text{BaHTMT} \cdot 3\text{H}_2\text{O}$ (6). A 50 mL solution of $\text{Na}_3\text{TMT} \cdot 9\text{H}_2\text{O}$ was made (1.67 g, 4.12 mmol) using DI water and stirred for 30 min until completely dissolved. A 50 mL solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was made (1.50 g, 6.14 mmol) with DI water and stirred for 30 min until completely dissolved. The two solutions were then combined and allowed to sit without stirring for 1 min whereupon a very fine white precipitate began to form. The solution was filtered (0.45 μm paper) to obtain a clear, pale yellow solution, pH \sim 12. HCl (12 M) was slowly added dropwise to lower the pH to 10. The solution was then allowed to evaporate in air at room temperature. Two visually and chemically distinct compounds crystallized from the solution. Yellow cubes (\sim 2–4 mm^3) formed at the core of each cluster ($\text{BaHTMT} \cdot 3\text{H}_2\text{O}$ (6)). Off white needles ($\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 7\text{H}_2\text{O}$ (5), \sim 2 mm thick and 4–8 mm long) grew out of the cubes from the central core. Total yield: 0.63 g (16%). The crystals were physically separated before analysis.

Analysis of $\text{Ba}(\text{H}_2\text{TMT})_2 \cdot 7\text{H}_2\text{O}$ (5). Mp/decomposition: crystals turned opaque at 98 °C and melted at 316–8 °C with gas evolution. A dark yellow liquid remained upon cooling (sealed tube). Anal. Calcd for $\text{BaC}_6\text{S}_6\text{N}_6\text{H}_{16}\text{O}_6$ (597.85): C, 12.04; H, 2.70; N, 14.05; S, 32.09. Found: C, 12.01; H, 2.18; N, 13.93; S, 32.35. TGA revealed four waters lost below 225 °C. IR (KBr, cm^{-1}): 3447 s, br, 3083 s, 2902 s, 1549 s, 1490 s, 1419 m, 1355 s, 1275 m, 1247 s, 1147 s, 998 w, 877 m, 806 m, 712 m, 467 m.

Analysis of $\text{BaHTMT} \cdot 3\text{H}_2\text{O}$ (6). Mp/decomposition: crystals turned opaque at 138 °C and very gradually decomposed to a light yellow

solid from \sim 280 to 400 °C (sealed tube). Anal. Calcd for $\text{BaC}_3\text{S}_3\text{N}_3\text{H}_7\text{O}_3$ (366.87): C, 9.81; H, 1.92; N, 11.45; S, 26.14. Found: C, 9.94; H, 1.94; N, 11.31; S, 25.97. TGA revealed three waters lost below 200 °C. IR (KBr, cm^{-1}): 3401 m, br, 3160 s, 2963 s, 1495 s, 1460 s, 1437 s, 1332 m, 1260 m, 1204 s, 1123 m, 963 w, 860 s, 786 m, 751 m, 470 w.

Conclusions

Consistent pK_a values were determined for H_3TMT and are summarized in Table 1. This information was useful in directing the synthesis of various TMT compounds, such as the group 2 M–TMT compounds reported herein. They should prove of general utility in forming other metal complexes, as well.

In the structures of these compounds, it was found that saltlike structures predominate for the group 2 elements Mg, Ca, and Sr, with the presence of extensive hydrogen bonding, including $\text{S} \cdots \text{H}-\text{E}$ (E = O, N). The barium structures, on the other hand, are best described as covalent with no hydrogen bonding.

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Supporting Information Available: Additional figures and a CIF file detailing the crystallographic parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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