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# Transition metal complexes of 2,4,6-trimercapto-1,3,5-triazine (TMT): potential precursors to nanoparticulate metal sulfides

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## Abstract

Although known for over 100 years, complexes of the TMT ligand with transition metals have not, until now, been prepared in a predictable and controlled manner. In the present work, high yield, intentional syntheses of a series of transition metal–TMT combinations are reported. These are of the form $M_3(TMT)_2 \cdot nH_2O$ (M = Co (**1**), Cu (**2**), Cd(**3**)), $M(HTMT) \cdot nH_2O$ (M = Co (**4**), Cu (**5**)) and $M(H_2TMT)_2 \cdot nH_2O$ (M = Co (**6**), Cu (**7**)). They are prepared by carefully controlling the pH of aqueous TMT solutions and metal to ligand stoichiometry. Serving to demonstrate that these transition metal–TMT complexes may be useful as materials precursors, nanoparticulate Greenockite (CdS) was formed by increasing the pH of a solution of **3**. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* TMT ligand; Nanoparticulate metal sulfides; Cadmium sulfide

## 1. Introduction

The highly water–soluble compound [1], $Na_3TMT \cdot 9H_2O$ (TMT = 2,4,6-trimercapto-1,3,5-triazinide, $C_3N_3S_3^{3-}$) [2], readily forms insoluble precipitates with univalent and divalent transition metal ions in aqueous solutions. As a result, it is widely used to precipitate metal ions such as $Ni^{2+}$, $Pd^{2+}$ [3], $Cu^{2+}$, $Ag^+$ [4], $Zn^{2+}$, $Cd^{2+}$, $Hg^+$, $Hg^{2+}$ [5], $Tl^+$ and $Pb^{2+}$, from industrial waste waters and polluted natural waters [6,7]. Another form of TMT is the sparsely water–soluble acid derivative; ($H_3TMT$) (Fig. 1(a)) [8].

An extensive and diverse range of applications have been developed for both $H_3TMT$ and metal–TMT complexes. These include use as silver plating agents, anion exchange resins, flame resistant fabrics with $H_3TMT$ [9–11], vulcanization of rubber with $H_3TMTNa_3TMT \cdot 9H_2O$ and an unspecified barium–TMT compound [12,13], waste water treatment and dyes with $Na_3TMT \cdot 9H_2O$ [14], tarnish proofing agents with $Na_3TMT \cdot 9H_2O$ and $K_3TMT \cdot nH_2O$ [15], electroplating of copper onto polyvinyl chloride with

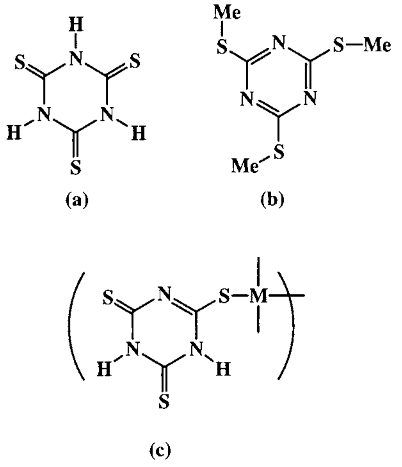

Fig. 1. Various forms of TMT units: (a) $H_3TMT$ in the thione tautomer; (b) $Me_3TMT$ (demonstrating the thiol form) and (c) an idealized structural formula for an $M(H_2TMT)$ complex.

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$NaH_2TMT\cdot3H_2O$ and unspecified tin(II)–TMT compounds [16], and electrodeposition of copper with unspecified TMT compounds [17].

Despite their widespread use, remarkably little definitive information has been published about the chemistry of metal–TMT complexes. Chudy and Dalziel made a seminal contribution in 1975, detailing the rational synthesis of complexes having the general formula $M_3(TMT)_2$ (with M = divalent metal) [18]. This stoichiometry was recently structurally confirmed for the heavier group 2 elements [19]. For transition metals, well-defined examples include complexes with osmium, $[\{Os_3H(CO)_{10}\}_3(TMT)]$ [20], titanium(III), $[\{(\eta^5\text{-}MeCp)_2Ti\}_3](TMT)$ (including a crystal structure incorporating the related 4,6-dithiopyrimidine ligand) [21], cobalt(III), $[\{Co(en)_2\}_2(TMT)]X_3$ (where X is I or $ClO_4$), $Co(en)_2(TMT)$ and $[Co(en)_2(H_2TMT)][ClO_4]_2$ [22], copper(I); $(CuPPh_3)_6(TMT)_2$ [23], gold(I); $(AuPPh_3)_3(TMT)$; $(AuPPhMe_2)_3(TMT)$, $[Au(TMT)(AuPPhMe_2)_2]_2$ [24], $[\{AuL\}_3TMT]$ (L = base) [25], and nickel(II) derivatives of the type NiL(HTMT) (where L is a multidentate ligand) [26].

In order to understand the industrial use of the TMT ligand, we have begun a systematic study of the formation and stability of main group [19,27] and transition metal TMT compounds. While this study is primarily fundamental in nature, there is the possibility that these compounds could be used as precursors to transition metal sulfide solid state materials since we have recently discovered that the TMT ligand can act as a sacrificial sulfide source (results presented herein). It should be noted that the by-product from the materials-formation reaction is cyanuric acid which is non-toxic.

In summary, the goal of the present work will be to prepare fully characterized transition metal–TMT complexes for eventual use as precursors to transition metal sulfide nanomaterials. These compounds are of the formula $M_3(TMT)_2\cdot nH_2O$ (M = Co (**1**), Cu (**2**), Cd(**3**)), $M(HTMT)\cdot nH_2O$ (M = Co (**4**), Cu (**5**)) and $M(H_2TMT)_2\cdot nH_2O$ (M = Co (**6**), Cu (**7**)).

## 2. Results and discussion

### 2.1. Synthesis

$Na_3TMT\cdot9H_2O$ dissolves in water to produce a variety of species whose concentrations are determined by pH [28]. If the pH of the solution is above 12.5, the TMT trianion ($C_3N_3S_3^{3-}$ or $TMT^{3-}$) is the most abundant species. At pH values of about 10 and 7, the most abundant species are the monohydrogen TMT dianion ($HTMT^{2-}$) and the dihydrogen TMT monoanion ($H_2TMT^-$), respectively. At pH values below 5 the sparsely water–soluble acid, $H_3TMT$, is most abundant and substantial reaction with metal ions is not expected. Consistent with these observations, we have prepared divalent metal complexes containing the series of ligand units, $TMT^{3-}$, $HTMT^{2-}$ and $H_2TMT^-$, by controlling the pH of aqueous ligand solutions and metal to ligand stoichiometry (Eqs. (1)–(3)).

$$2Na_3TMT + 3MCl_2 \xrightarrow{pH \sim 12.5} M_3(TMT)_2;$$
$$M = Co(1), Cu(2), Cd(3) \quad (1)$$

$$Na_3TMT + MCl_2 \xrightarrow{pH \sim 10} M(HTMT);$$
$$M = Co(4), Cu(5) \quad (2)$$

$$2H_3TMT + MCl_2 \xrightarrow{pH \sim 7.5} M(H_2TMT)_2;$$
$$M = Co(6), Cu(7) \quad (3)$$

The complexes $M_3(TMT)_2\cdot nH_2O$ (M = Co (**1**), Cu (**2**)) and Cd(**3**)) were obtained at pH values of 12.5 by reacting metal salts and $Na_3TMT$ $9H_2O$ in a 1.5 to 1 stoichiometry, $M(HTMT)\cdot nH_2O$ (M = Co (**4**) and Cu (**5**)) were obtained at pH values of 10 with a metal–ligand stoichiometry of 1:1 and $M(H_2TMT)_2\cdot nH_2O$ (M = Co (**6**) and Cu (**7**)) were isolated at pH values of 7.5 with a metal–ligand ratio of 0.5:1. All of the complexes were isolated as hydrates.

The pH of the ligand solution probably plays a greater role than the metal–ligand ratio in determining the stoichiometry of the complexes formed. The stoichiometry of complexes formed by $H_3TMT$ with transition metals was previously explored using the technique of thermometric titrimetry. In the study, complexes having a formula, $M_3L_2$ predominated (M(II) = Co, Ni, Cu) [29]. The work presented here shows that by careful control of the pH, complexes with three different metal–TMT stoichiometries are accessible for divalent cobalt, copper, and cadmium in aqueous solution.

### 2.2. Thermal analysis

All the compounds were found to decompose without melting when heated to 350°C in sealed capillaries. More detailed information on the thermal properties of the complexes was obtained by thermogravimetric analysis. The onset of decomposition is near 200°C for **1**, **4** and **7** and 300°C for **3**. For all of the complexes, no plateau corresponding to the end of decomposition is observed up to 600°C. Compound **6** undergoes a weight loss of 5% between 150 and 197°C. This figure is in good agreement with the value of 6% calculated for the loss of the water molecules of hydration. A second weight loss of 71% is observed between 238 and 555°C. This second thermal event exhibits a point of inflexion at about 346°C. Compound **2** undergoes a weight loss of 57% from about 190 to 575°C. The thermogram for the complex shows two points of inflexion in this temperature range ( ~ 307 and 427°C). Compound **5** loses 63% of its weight between 192 and 500°C. Points of inflexion are observed at about 368 and 423°C.

The observation of points of inflexion in the thermograms of these compounds indicates that the decomposition processes are complex. The residues obtained from the TGA of $M_3(TMT)_2 \cdot 2H_2O$ (M = Cu, (**2**) and Cd, (**3**)) were examined by IR. The results showed that heating the compounds to 600°C leads to the decomposition of the TMT ring and that MS is present. (The infrared spectra are similar to those observed for MS prepared from traditional routes).

Other than **6**, these complexes decompose before losing waters of hydration. This has precedence in $[Ni(dpta)(HTMT)(H_2O)] \cdot H_2O$ (where dpta is dipropylenetriamine) which has been shown by single crystal X-ray crystallography to contain one coordinated and one uncoordinated water molecule [19]. Only the loss of the uncoordinated water is observed prior to sample decomposition in this complex.

## *2.3. Magnetic properties*

$Co_3(TMT)_2 \cdot 2.5H_2O$ (**1**) and $Co(HTMT) \cdot 1.5H_2O$ (**4**) exhibit room temperature magnetic moments of 3.7 and 3.8 Bohr Magnetons (B.M.) per cobalt(II) ion, respectively. These values are lower than those typically observed for high-spin six-coordinate (4.7–5.2 B.M.) or tetrahedral (4.4–4.8 B.M.) cobalt(II) complexes [30,31] and indicate the presence of magnetic exchange interactions between cobalt ions. Similar low moments have been observed for $Co(Iz)_2Cl_2$ (IzH = imidazole; 4.27 B.M) [31], $Co(Miz)_2Cl_2$ (Miz = 2-methylimidazole; 3.54 B.M.) [32] and $Co(meimt)_2$ (meimtH = 1-methyl-1-3-imidazoline-2(3H)-thione; 4.0 B.M.) [33]. Polymeric structures are proposed for all these complexes and the observed low magnetic moments attributed to superexchange coupling of the cobalt(II) ions. The magnetic moment for **6**, of 4.5 B.M., while significantly higher than those of the other complexes reported here, is nonetheless, indicative of magnetic exchange interactions.

Compounds **2** and **5** are diamagnetic. This is consistent with the previous work which found that the former complex exhibits bulk diamagnetism over the temperature range 93–373 K [28]. Compound **7** has a room temperature magnetic moment of 0.5, indicating the presence of significant antiferromagnetic coupling.

## *2.4. Infrared spectra*

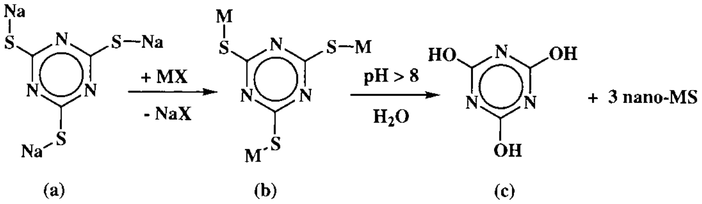
It was previously suggested that the major bands observed at 1540, 1125 and 745 $cm^{-1}$ in the spectrum of uncoordinated $H_3TMT$ are characteristic of the non-aromatic, trithione form of the TMT ring system (Fig. 1(a)) [34]. The aromatic, trithiol form of the ring, on the other hand, is characterized by the presence of the corresponding bands around 1490, 1245 and 860 $cm^{-1}$, as found in the spectrum of $(CH_3)_3TMT$ (Fig. 1(b)) [18]. In a study of mixed ligand nickel complexes, it was observed that upon coordination, some bands in the original infrared spectrum of the free $H_3TMT$ split and new bands are also observed signifying that a complex has formed [19]. Similar features are also observed in the spectra of complexes **4**–**7** reported here. These bands can be attributed to the presence of two types of S–C and N–C bonds (as displayed in Fig. 1(c)).

The spectrum of **1** exhibits only three bands at 1448, 1231, and 872 $cm^{-1}$. The corresponding bands are observed at 1476, 1227 and 850 $cm^{-1}$ in the spectrum of **2** and at 1454, 1223, and 854 $cm^{-1}$ in the spectrum of **3**. Thus in these complexes, the TMT moiety exists in the aromatic form with covalent metal–sulfur bonds.

Compound **6** displays bands at 1481, 1249, and 880 $cm^{-1}$, indicative of the conjugated form of the TMT ring and additional bands at 1563, 1153 and 764 $cm^{-1}$ are indicative of the unconjugated form. Compounds **4**, **5**, and **7** show similar spectral features. The spectrum of $NaH_2TMT \cdot 3H_2O$, whose structure has been determined by single crystal X-ray diffraction [20], exhibits similar bands at 1484, 1241 and 883 $cm^{-1}$, and at 1558, 1151 and 781 $cm^{-1}$. Evidence that the hydrogen atoms of $HTMT^{2-}$ and $H_2TMT^{-}$ are located on the nitrogen atoms (Fig. 1(c)) is provided by the presence of bands assigned to N–H stretching vibrations in the 2880–3090 $cm^{-1}$ range for **4**–**7**. As expected, corresponding bands are not observed in the spectra of **1**–**3** and of $Na_3TMT \cdot 9H_2O$, whose structure is unambiguously known [2].

## *2.5. Materials synthesis*

Compound **3** is insoluble in water. Nevertheless the conversion of **3** to nanoparticulate greenockite in water was effected by maintaining a $pH > 8$ over the course of weeks to months (under nitrogen). The conversion was monitored by XRD which was used to identify the presence of both starting material and CdS. After 2 months only CdS was detectable by this method. Subsequent TEM measurements indicated that the CdS was nanoparticulate with an average size of 10 nm. It is likely that the decomposition proceeds by base attack at the thiol carbon, resulting in displacement of the sulfur atoms as metal sulfide and the formation of cyanuric acid. The replacement of a single TMT sulfur atom by oxygen was observed previously [19]. While this is not an efficient process for the production of CdS on a large scale, it serves to demonstrate that the TMT ligand can be used as a sacrificial source of sulfide with benign by-products [35]. By comparison to traditional separate source routes to CdS and other metal sulfide materials [36] it is possible that the degree of molecular control inherent to the use of well-defined metal–TMT complexes may prove to be advantageous in preparing these materials. Continued work on this project will explore these possibilities. (Scheme 1)



Scheme 1. The $Na_3TMT$ ligand (a), an idealized formula for metal–TMT complexes (b) and nanoparticulate synthesis (c).

## 3. Experimental

### 3.1. Physical measurement

Thermogravimetric studies in the 30–600°C range were carried out using a TA Instruments TGA 2950. Finely powdered samples of approximately 10 to 25 mg were placed into platinum pans and purged with argon gas at a flow rate of 100 $cm^3$ $min^{-1}$. The samples were heated at a rate of 10°C $min^{-1}$. Infrared spectra were recorded as KBr pellets on a Nicolet Magna 560 FT-IR spectrometer. Magnetic measurements were made at 25°C on a Johnson Matthey model MKI magnetic susceptibility balance with $HgCo(NCS)_4$ as the calibration standard. Diamagnetic corrections were calculated using Pascal's constants. Elemental analyses (C, H, N) were performed by Midwest Microlab, Indianapolis, IN. Powder XRD analyses were conducted on a Rigaku unit using Cu–$K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å) at 40 kV and 20 mA. The samples were typically scanned from 5.00 to 60.00 or 90.00° $2\theta$ using 0.02° $2\theta$ steps at one second per step. The patterns were compared with reference patterns in the International Centre for Diffraction Data (ICDD) and mineral, organic and inorganic powder diffraction data (PDF) computer databases. Scanning electron microscopy was conducted on a Hitachi S-3200N instrument. Particle induced X-ray emission (PIXE) data was obtained following a standard method [37]. TEM measurements were obtained on a JEOL JEM-2010F, which operates at 200 kV.

### 3.2. Materials

The sources of TMT used in this study were $Na_3TMT{\cdot}9H_2O$ and $H_3TMT$. $Na_3TMT{\cdot}9H_2O$ was obtained from Degussa corporation and then purified following slight modifications to a previously reported procedure [38]. A solution obtained by dissolving $Na_3TMT{\cdot}9H_2O$ (57 g, 141 mmol) in 100 ml of 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 $Na_3TMT{\cdot}9H_2O$ began to form between the aqueous and alcohol layers. 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 is about 40 g (70%) (m.p. > 250°C).

The $H_3TMT$ was obtained by treating the $Na_3TMT{\cdot}9H_2O$ obtained from Degussa with conc. HCl in a 1:3 molar ratio. In a typical reaction, 100 g of $Na_3TMT{\cdot}9H_2O$ was dissolved in 350 ml of water and the solution filtered. To the filtrate was added 61 ml of conc. HCl (12.1 N). A yellow precipitate formed immediately. The mixture was stirred briefly, the precipitate isolated by filtration, washed with water and dried, first at room temperature (r.t.) and then at 110°C. The typical yield is about 40 g (91%) (m.p. (dec) 230°C). It was characterized by IR, elemental analyses, and a distinctive XRD pattern. The XRD for compounds **1**–**7** indicated that they were amorphous. All other reagents were purchased from commercial sources and were used as obtained.

### 3.3. Preparation of $Co_3(TMT)_2{\cdot}2.5H_2O$ (*1*)

An aqueous solution (20 ml) of $Na_3TMT{\cdot}9H_2O$ (1.15 g, 2.84 mmol) was added to a light red 20 ml aqueous solution of $CoCl_2{\cdot}6H_2O$ (1.00 g, 4.20 mmol). The mixture was stirred for 0.5 h, filtered, the brown precipitate washed thoroughly with water and ethanol and dried, first at r.t. and then in an oven at 130°C for 6 h. Yield: 0.72 g, 90%. Anal. Calc. for $C_6Co_3N_6S_6{\cdot}2.5H_2O$: C, 12.64; H, 0.88; N, 14.74. Found: C, 12.99; H, 0.72; N, 14.32%. IR ($cm^{-1}$): 1624w, 1448 vs, br, 1418 vs sh, 1231 vs, 872 m.

### 3.4. Preparation of $Cu_3(TMT)_2{\cdot}2H_2O$ (*2*)

An aqueous solution (20 ml) of $CuCl_2{\cdot}2H_2O$ (1.04 g, 6.10 mmol) was filtered into a 20 ml aqueous solution of $Na_3TMT{\cdot}9H_2O$ (1.59 g, 3.92 mmol). A reddish brown precipitate formed immediately. The mixture was stirred for 0.5 h, filtered, the precipitate washed thoroughly with water and ethanol and dried, first at r.t. and then in an oven at 130°C for 6 h. Yield: 1.00 g, 88%. Anal. Calc. for $C_6Cu_3N_6S_6{\cdot}2H_2O$: C, 12.53; H, 0.70; N, 14.61. Found: C, 12.94; H, 0.50; N, 14.41%. IR ($cm^{-1}$): 1724 m, 1653m, 1476 vs, br, 1396 s, sh, 1227 vs, 1144 m, sh, 850 m, 771w, 754 w, 668 vw, 618 w, 535 w, 461 w.

### *3.5. Preparation of $Cd_3TMT_2 \cdot 2H_2O$ (**3**)*

A 50 ml solution of $Na_3TMT \cdot 9H_2O$ was made (2.38 g, 5.87 mmol) and stirred for 2 h. until completely dissolved. A 100 ml solution of $CdCl_2 \cdot 2.5H_2O$ was made (2.01 g, 8.80 mmol) and stirred until completely dissolved. The two solutions were mixed and a white precipitate formed. The cloudy solution was filtered (0.45 μm paper) to obtain the precipitate. The precipitate was washed with de-ionized water and air-dried. Yield: 2.03 g, 96%. m.p. (dec) 330°C. TGA: two waters of hydration at 250°C, decomposed to CdS at 300–500°C. Anal. Calc. for $C_6Cd_3N_6S_6 \cdot 2H_2O$: C, 9.985; H, 0.558; N, 11.644; S, 26.653. Found: C, 9.989; H, 0.643; N, 11.512; S, 26.258%. IR ($cm^{-1}$, nujol): 1454 s, 1435 m, 1332 w, 1223 m, 1150 w, 854 m, 769 w, 718 m.

### *3.6. Preparation of $Co(HTMT) \cdot 1.5H_2O$ (**4**)*

The pH of a solution of $Na_3TMT \cdot 9H_2O$ (1.72 g, 4.24 mmol) in 20 ml of water was lowered to 10 using 2 M HCl solution. To the above solution was added a 20 ml aqueous solution of $CoCl_2 \cdot 6H_2O$ (1.00 g, 4.20 mmol). The mixture was stirred for 0.5 h, filtered, and the precipitate washed with water and ethanol. The greenish brown precipitate was first dried at r.t. and then in an oven at 140°C for 4.5 h. Yield: 0.77 g, 70%. Anal. Calc. for $C_3HCoN_3S_3 \cdot 1.5H_2O$: C, 13.79; H, 1.54; N, 16.09. Found: C, 14.09; H, 0.81; N, 15.77%. IR ($cm^{-1}$): 2971m, 1630m, 1561 m, sh, 1474 vs, vbr, 1244 vs, 1176 s, 1150 s, 1041 m, 879s, 756 w, 630 w, 465 m.

### *3.7. Preparation of $Cu(HTMT) \cdot 0.5H_2O$ (**5**)*

The pH of a solution of $Na_3TMT \cdot 9H_2O$ (2.38 g, 5.87 mmol) in 20 ml of water was lowered to 10 using 2 M HCl solution. To the above solution was added a 20 ml aqueous solution of $CuCl_2 \cdot 2H_2O$ (1.00 g, 5.87 mmol). The mixture was stirred for 0.5 h, filtered, and the precipitate washed with water and ethanol. The orange precipitate was first dried at r.t. and then in an oven at 140°C for 4.5 h. Yield: 1.26 g, 87%. Anal. Calc. for $C_3HCuN_3S_3 \cdot 0.5H_2O$: C, 14.54; H, 0.81; N, 16.96. Found: C, 14.63; H, 0.63; N, 16.90%. IR ($cm^{-1}$): 2913w, 1734 w, 1628 m, 1447 vs, br, 1365 s, 1235 s, 1205 s, 1124 s, 983 w, sh, 972 w, 850 s, 784 w, 742 w, 485w, sh, 463 m.

### *3.8. Preparation of $Co(H_2TMT)_2 \cdot 1.5H_2O$ (**6**)*

The pH of a slurry of $H_3TMT$ (0.750 g, 4.23 mmol) in 100 ml of water was raised to about 7.5 using a 2 M NaOH solution. Most of the $H_3TMT$ dissolved. The solution was filtered and a 20 ml aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.510 g, 2.14 mmol) added to the filtrate. The mixture was stirred for 0.5 h and the brown precipitate isolated by filtration and washed thoroughly with water. The precipitate was first dried at r.t. and then in an oven at 140°C for 4.5 h. Yield: 0.56 g, 60%. Anal. Calc. for $C_6H_4CoN_6S_6 \cdot 1.5H_2O$: C, 16.44; H, 1.61; N, 19.17. Found: C, 16.64; H, 1.67; N, 18.91%. IR ($cm^{-1}$): 3087, 2889, 1592 s, 1563 vs, 1481 vs, 1408 vs, 1375 vs, 1315 m, sh, 1290 s, 1249 vs, 1177 vs, 1153 vs, 1045 m, 990 w, 898 m, 880 s, 823 w, 764 m, sp, 708 s, 512 m, 500 w, 465 vs.

### *3.9. Preparation of $Cu(H_2TMT)_2$ (**7**)*

The pH of a slurry of $H_3TMT$ (1.04 g, 5.87 mmol) in 100 ml of water was raised to about 7.5 using a 2 M NaOH solution. Most of the $H_3TMT$ dissolved. The solution was filtered and a 20 ml aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.509 g, 2.96 mmol) added to the filtrate. The mixture was stirred for 0.5 h, filtered and the precipitate washed thoroughly with water. The orange precipitate was first dried at r.t. and then in an oven at 140°C for 4.5 h. Yield: 1.00 g, 81%. Anal. Calc. for $C_6H_4CuN_6S_6$: C, 17.32; H, 0.97; N, 20.20. Found: C, 17.28; H, 1.03; N, 19.95%. IR ($cm^{-1}$): 3041, 2909, 1734 m, 1577 s, sh, 1540 s, 1481 vs, 1362 s, 1298 w, 1258 s, 1231 s, 1205 s, 1127 vs, 971 vw, 850 m, 784 w, 744 m, 668 m, 475 w, 457 s.

### *3.10. Formation of CdS using $Cd_2TMT_3 \cdot 2H_2O$ (**3**)*

A 0.604 mmol KOH solution (1.80 g of KOH dissolved into 53.13 g of distilled water) was added to a $Cd_3TMT_2 \cdot 2H_2O$ (0.17 g in 20 ml water) suspension. After 1 week of stirring under nitrogen, an additional 2.08 g (37.1 mmol) of solid KOH was added to the suspension bringing the pH to 14. The suspension was periodically sampled (0.07 to 0.20 g of dried solids recovered) over several weeks and the dried residues were analyzed by powder XRD to verify the presence of $Cd_3TMT_2 \cdot 2H_2O$ and/or CdS (greenockite). According to the XRD analyses, within 1 week, the crystalline $Cd_3TMT_2 \cdot 2H_2O$ had largely decomposed and was replaced by broad peaks that were generally centered over the most intense peaks for greenockite. Within 2 months after the initial addition of the 0.604 mmol KOH solution to the $Cd_3TMT_2 \cdot 2H_2O$ suspension, the $Cd_3TMT_2 \cdot 2H_2O$ had entirely converted to orange nanocrystalline greenockite (CdS). PIXE analysis Cd–S ratio (found): 0.50 (0.475).

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