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# Chemistry of copper trimercaptotriazine (TMT) compounds and removal of copper from copper-ammine species by TMT

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**The acid dissociation constants of 2,4,6-trimercaptotriazine ($H_3TMT$) were determined by acid-base titration and now can be employed in the preparation of complexes having specific Cu−TMT ratios. IR, EA and TGA characterized the compounds. We analyzed the relevant IR spectra and attribute 2910–2925, 3030–3250 and 3430 cm$^{-1}$ to triazine ring overtone, N−H stretching vibrations and water in the TMT complexes, respectively. The solubility of Cu−TMT complexes was determined with ICP-AES. The results indicate that $Cu_3(TMT)_2 \cdot 2H_2O$ (3) is much more insoluble and more stable than $Cu(H_2TMT)_2$ (1), $Cu(HTMT) \cdot 0.5H_2O$ (2) and CuS. The extremely small value of $K_{SP}$ for compound 3 ($2.11 \times 10^{-46}$) indicates that $Na_3TMT$ is a very advantageous chelating agent in precipitating complex copper (e.g. copper-ammine species) from industrial wastewaters. The influences of ammonia concentration, pH and settling time on the effectiveness of copper precipitation were investigated. Also, a 'real world' printed circuit board factory effluent initially containing 350.9 ppm of Cu was treated and it was found that more than 99.9% of the copper was removed from the solution as an insoluble compound 3. Copyright © 2006 John Wiley & Sons, Ltd.**

**KEYWORDS:** TMT; copper; chemical precipitation; water treatment; copper-ammine species

## INTRODUCTION

Toxic heavy metals in air, soil and water is a global problem that is a growing threat to the environment. Numerous metal contaminants, such as Cd, Cu, Pb, Hg, Cr, Ag and Zn, may cause a great deal of harm in the biosphere. Consider copper, for example; it is used in printed circuit board manufacturing, electroplating, metal processing, paper pulp manufacturing and wood preservation. When ingested excessively, humans will suffer from Wilson's disease.[1] Furthermore, such metals often undergo biomagnification and become potentially hazardous to humans. During the past few decades, the Chinese government has instituted the integrated wastewater discharge standard (a 0.5 mg/l limit on copper) to protect the quality of surface and ground water from heavy metal pollutants.[2] In response to the regulatory requirements, numerous companies have developed and marketed chemical products to precipitate heavy metals from wastewaters.

One particular chemical reagent for precipitating divalent and univalent heavy metals from water is TMT-55 (manufactured by Degussa Corporation), which is 2,4,6-trimercaptotriazine, trisodium salt, nonahydrate [$Na_3TMT \cdot 9H_2O$; Fig. 1(a)]. In the solid, the planar $C_3$ symmetry is obvious with each of the sodium atoms associated with the sulfurs.[3] Degussa Corporation and some papers suggest that $Na_3TMT \cdot 9H_2O$ exhibits high affinity for the cupric ion. They **have** discussed industrial wastewater treatment applications to remove copper with TMT-55.[4–6]

Despite the widespread use of TMT-55, only recently have systematic investigations of the formation and stability of main group and transition metal TMT compounds been undertaken;[7,8] however, thermodynamic data have not yet been published for transition metal−TMT compounds. In our study, laboratory experiments and analyses were performed to further confirm the acid dissociation constants of 2,4,6-trimercaptotriazine [$H_3TMT$, seen in Fig. 1(b)], reported by K.R. Henke.[9] By knowing the dissociation constants and

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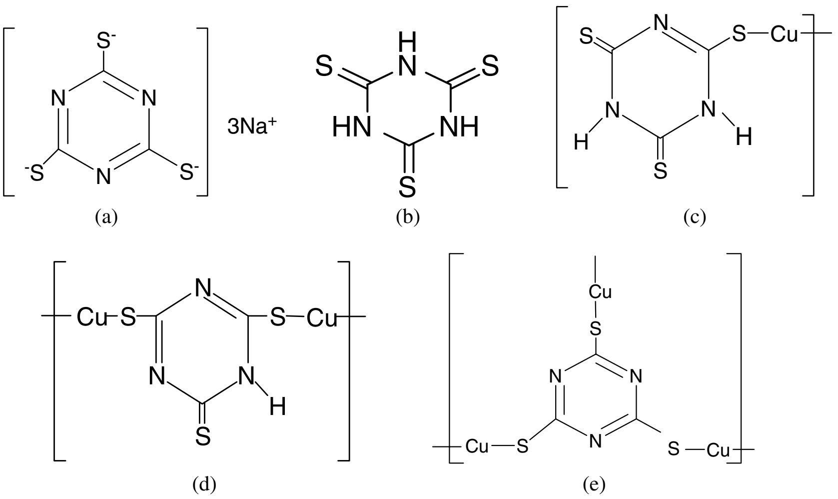

**Figure 1.** Various forms of TMT units: (a) the soluble sodium salt form, $Na_3TMT$ (TMT-55); (b) $H_3TMT$ in the thione tautomer; (c) Cu $(H_2TMT)_2$ (**1**), (d) CuHTMT (**2**), and (e) $Cu_3$ $(TMT)_2$ (**3**) (demonstrating the thiol form). For clarity, the structural waters are all omitted.

controlling the pH, complexes having specific Cu–TMT ratios can be targeted for synthesis and relevant IR spectra analyzed. Our paper also summarizes the solubility of Cu–TMT compounds and calculates respective solubility product constants ($K_{SP}$) by leaching the TMT compounds in deionized water (pH 6). The solubility data will provide some indication of the likely stability of these compounds if they come into contact with clean rainwater or low total dissolved solids (TDS) natural waters. The solubility product constants ($K_{SP}$) for Cu–TMT compounds will provide useful insights into the successful water treatment applications with TMT-55. Taking copper-ammine species as an example, which are mainly present in waste ammonia etchant solutions and rinse water from the etching machine discharged by printed circuit board factories, we investigated the influence of ammonia concentration, pH and settling time on the effectiveness of copper precipitation by TMT-55 and characteristics of the obtained precipitate.

## EXPERIMENTAL

### Analytical methods

The pH measurements were conducted on a Hanna pH 211 meter and an E-201-C-6 combination electrode. The meter was calibrated with pH 4.01, 6.86 and 9.18 Shanghai REX Inc. buffers. Thermogravimetric analysis (TGA) studies in the range 30–600 °C were carried out using a Setaram Setsys-16 TA instrument. Finely powdered samples of approximately 20 mg were placed into platinum pans and purged with $N_2$ gas at a flow rate of 100 $cm^3/min$. The samples were heated at a rate of 10 °C/min. Infrared data were recorded as KBr pellets on a Nicolet-Nexus 670 FT-IR spectrometer and are reported in $cm^{-1}$. Carbon, sulfur, nitrogen and hydrogen analyses on the solid compounds were measured with an Elementar Vario EL III CHNS analyzer using a sulfanilic acid ($C_6H_7NO_3S$) standard. Copper analyses were performed with Iris Interpid II XSP inductively coupled plasma-atomic emission spectrometer (ICP-AES).

### 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 Aldrich and then purified following a previously reported procedure.[10] $H_3TMT$ was also prepared as previously reported.[10] TMT-15, a 15% aqueous solution of the trisodium salt of 2,4,6-trimercaptotriazine, was prepared by dissolving 33.32 g of purified $Na_3TMT \cdot 9H_2O$ in 100 g of deionized water; its pH value was 12.5 and the density at 20 °C was 1.12 g/ml. All other chemicals were commercial reagent grade. All water was freshly deionized, with a conductivity $<0.7$ μS/cm.

### Titration of $Na_3TMT \cdot 9H_2O$ with 0.5188 M $H_2SO_4$

Titrations of $Na_3TMT \cdot 9H_2O$ were performed with a ZD-2 automatic potentio-titration meter. Data points were produced and plotted on graphs by titrating 0.5188 M $H_2SO_4$ into five aliquots of 100 ml 32.88 mmol/l aqueous solutions of $Na_3TMT \cdot 9H_2O$ and monitoring the pH with a pH electrode.

### Syntheses

#### *Synthesis of Cu $(H_2TMT)_2$ (**1**)*

The pH of a slurry of $H_3TMT$ (2.62 g, 14.8 mmol) in 250 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 50 ml aqueous solution of $CuCl_2 \cdot 2H_2O$ (1.27 g, 7.4 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., then in an oven at 140 °C for 4.5 h. Yield: 2.53 g, 83%. Anal. calcd for $CuC_6N_6S_6H_4$ (416.11):

C, 17.32; H, 0.97; N, 20.20; S, 46.24. Found: C, 17.25; H, 1.05; N, 19.97; S, 46.28%. IR ($cm^{-1}$): 3434 m, 3162 m, 3039 m, 2911 m, 1735m, 1575 s, sh, 1540 s, 1481 vs, 1364 s, 1299 w, 1254 s, 1232 s, 1205 s, 1125 vs, 972 vw, 849 m, 783 w, 746 m, 667 m, 474 w, 458 s.

### *Synthesis of Cu (HTMT)·0.5$H_2O$ (**2**)*

The pH of a solution of $Na_3TMT \cdot 9H_2O$ (5.95g, 14.68mmol) in 50 ml of water was lowered to 10 using 2 M HCl solution. To the above solution was added a 50 ml aqueous solution of $CuCl_2 \cdot 2H_2O$ (2.50 g, 14.68 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., then in an oven at 140 °C for 4.5 h. Yield: 3.08 g, 85%. Anal. calcd For $CuC_3N_3S_3H \cdot 0.5H_2O$(247.83): C, 14.54; H, 0.81; N, 16.96; S, 38.82. Found: C, 14.67; H, 0.65; N, 16.92; S, 38.52%. IR ($cm^{-1}$): 3429 m, 3243 m, 2924 m, 1734 w, 1629 m, 1452 vs, br, 1369 m, sh, 1237 s, 1207 s, 1127 s, 972 w, 851 s, 785 w, 742 w, 485 w, 466 m.

### *Synthesis of $Cu_3$ $(TMT)_2 \cdot 2H_2O$ (**3**)*

An aqueous solution (50 ml) of $CuCl_2 \cdot 2H_2O$ (2.51 g, 14.7 mmol) was filtered into a 50 ml aqueous solution of $Na_3TMT \cdot 9H_2O$ (3.98 g, 9.8 mmol). A reddish brown precipitate immediately resulted and the mixture was heated on a steam bath with intermittent stirring for 0.5 h, the precipitated material filtered off, washed thoroughly with hot (70 °C) water and ethanol and dried, first at room temperature and then in an oven at 130 °C for 6 h. Yield: 1.29 g, 90%. Anal. calcd for $Cu_3C_6N_6S_6 \cdot 2H_2O$(575.20): C, 12.53; H, 0.70; N, 14.61; S, 33.45. Found: C, 12.89; H, 0.48; N, 14.42; S, 33.21%. TGA also revealed two waters of hydration. IR ($cm^{-1}$): 3424 m, 2925 m, 1721 m, 1656 m, 1470vs, br, 1397 s, sh, 1228vs, 1147 m, sh, 853 m, 771w, 752 w, 670 vw, 615 w, 537 w, 462 w.

## Analytical procedures for copper ICP analyses

All experiments were run a minimum of three times at room temperature and under normal atmospheric pressure. The averaged results have been reported herein.

### *Determination of the solubility and solubility product constants ($K_{SP}$) for compounds **1–3***

In order to obtain the constants of solubility products ($K_{SP}$) for compounds 1, 2 and 3, their solubility in deionized water at room temperature was measured with the apparatus of ICP-AES. Dry samples of compounds 1–3 were weighed out to the nearest 0.05 g on a Mettler Toledo AB204-E balance and placed with 50 ml deionized water in 50 ml volumetric flasks. The flasks and their contents were thoroughly mixed for four days on end-over-end tumblers until saturation. Deionized water blanks were also included in the four day dissolving tests. After mixing, the leachates were filtered at 0.45 μm. The copper concentration analyses of the Cu–TMT leachates were performed with an Iris Interpid II XSP inductively coupled plasma-atomic emission spectrometer (ICP-AES).

### *Determination of the residual copper contents after precipitating copper from copper-ammine species*

A series of 100 ml $CuCl_2$ samples containing different amounts of $Cu^{2+}$ and $NH_3$ were prepared. To each solution the certain amount of TMT-15, the coagulant (aluminum sulfate) and flocculant (polyacrylamide) were added. The residual copper contents in the top aqueous solution after settling were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES).

# RESULTS AND DISCUSSION

## Results of IR data

The spectrum of **3** exhibits only three bands at 1470, 1228 and 853 $cm^{-1}$, which suggests that the TMT moiety exists in the aromatic, trithiol form with covalent metal–sulfur bonds [Fig. 1(e)].

Compound 1 displays bands at 1481, 1232 and 849 $cm^{-1}$, indicative of the conjugated, trithiol form of the TMT ring and additional bands at 1540, 1125 and 746 $cm^{-1}$ are indicative of the unconjugated, trithione form [Fig. 1(c)]. The corresponding bands are observed at 1452, 1237 and 851, and 1629, 1127 and 785 $cm^{-1}$ in the spectrum of **2** [Fig. 1(d)].

Evidence that the hydrogen atoms of $H_2TMT^-$ and $HTMT^{2-}$ are located on the nitrogen atoms [Fig. 1(c) and (d)] is provided by the presence of bands assigned to N–H stretching vibrations at 3162 and 3039 $cm^{-1}$ for **1** and at 3243 $cm^{-1}$ for **2**. $H_3TMT$ also show similar spectral features around 3163–3041 $cm^{-1}$. Therefore we can conclude that it is the range of 3030–3250 $cm^{-1}$ rather than 2880–3090 $cm^{-1}$, as reported by Bailey[10] that is assigned to N–H stretching vibrations in the series of TMT complexes. At the same time, the bands around 2910–2925 $cm^{-1}$ are found in all the TMT complexes involved in our work, including $H_3TMT$ (2910 $cm^{-1}$) and $Na_3TMT \cdot 9H_2O$(2920 $cm^{-1}$).[11] It consequently seems necessary to attribute 2910–2925 $cm^{-1}$ to triazine ring overtone similar to the band assigned previously as an overtone in the spectrum of cyanuric acid.[12,13] Therefore, our conclusion that the bands near 2910–2925 $cm^{-1}$ should not be due to N–H stretching vibrations will help us avoid improper judgment of IR spectra for different Cu–TMT complexes. For example, there is the band at 2925 $cm^{-1}$ (triazine ring overtone) and no band around 3030–3250 $cm^{-1}$ (N–H stretching vibrations) in the spectrum of **3**, which is consistent with our conclusion. The broad peak near 3430 $cm^{-1}$ is indicative of water in compounds 1–3, which is also supported by the collected IR spectroscopy data of the baked KBr pellets.

## Determination of the acid dissociation constants of $H_3TMT$ and synthesis of Cu–TMT complexes

As a tribasic acid, $H_3TMT$ dissolves in water to produce four species —$H_3TMT$, $H_2TMT^-$, $HTMT^{2-}$ and $TMT^{3-}$ through

**Table 1.** The comparison of the three acid dissociation constants of $H_3TMT$

| | $pK_{a1}$ | $pK_{a2}$ | $pK_{a3}$ |
|---|---|---|---|
| Value from Hirt | 4.96 | 8.0 | — |
| Value from Henke | 5.71 | 8.36 | 11.38 |
| Value from our studies | 5.72 | 8.28 | 11.46 |

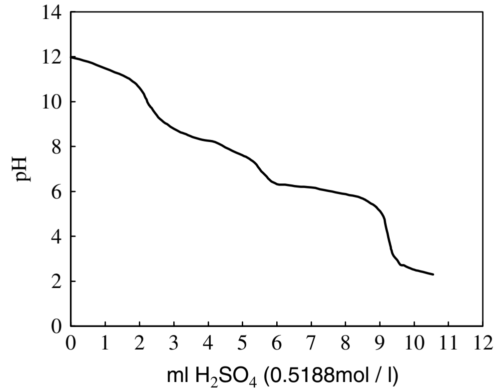

**Figure 2.** Titration curve of $Na_3TMT$ with $H_2SO_4$.

the three dissociation equilibriums:

$$H_3TMT \Leftrightarrow H^+ + H_2TMT^- \quad K_{a1} = \frac{[H^+][H_2TMT^-]}{[H_3TMT]} \tag{1}$$

$$H_2TMT^- \Leftrightarrow H^+ + HTMT^{2-} \quad K_{a2} = \frac{[H^+][HTMT^{2-}]}{[H_2TMT^-]} \tag{2}$$

$$HTMT^{2-} \Leftrightarrow H^+ + TMT^{3-} \quad K_{a3} = \frac{[H^+][TMT^{3-}]}{[HTMT^{2-}]} \tag{3}$$

Note: $[H_3TMT]$ is the total concentration of $H_3TMT$, both precipitated and dissolved.

Hirt *et al.* first published the acid dissociation constants of $H_3TMT$ in 1961.[14] Afterwards, Henke *et al.* also derived the acid dissociation constants via a rigorous procedure.[9] Their calculated values are listed in Table 1.

Data from our five titrations of $Na_3TMT$ with $H_2SO_4$ were plotted on graphs of pH vs volume (ml) of 0.5188 M $H_2SO_4$ to produce the titration curves. An example of a representative titration curve is shown in Fig. 2. When we take the first derivative ($\Delta pH/\Delta ml$) of the data on the titration curves, three points of greatest slope on the curves are found (Fig. 3). The average values of three points that possess the greatest slope in five titration curves are pH = 9.87, 7 and 3.62, respectively. The three inflection points represent the converse titration end points of equilibria (3), (2) and (1). At pH values of 9.87, 7 and 3.62, the most abundant species are $HTMT^{2-}$, $H_2TMT^-$ and $H_3TMT$, respectively. The three acid dissociation constants of $H_3TMT$ can be calculated as follows:

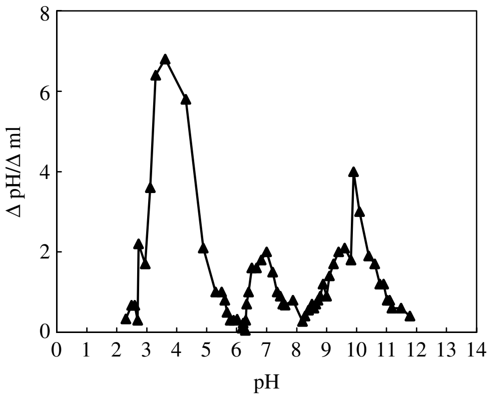

**Figure 3.** Curve of $\Delta pH/\Delta ml$ vs pH.

(1) During titration, at pH values of 3.62, the most abundant species was $H_3TMT$. After dilution with 8.5ml $H_2SO_4$, the total concentration of TMT ($C_T$) was decreased from 0.03288 to 0.03030 mol/l. Taking $H_3TMT$ and $H_2O$ as the frames of reference, we have the proton balance:

$$[H_2TMT^-] + 2[HTMT^{2-}] + 3[TMT^{3-}] + [OH^-] = [H^+]$$

Considering that $[HTMT^{2-}]$, $[TMT^{3-}]$ and $[OH^-]$ are small enough to be negligible, we simplify the proton balance to: $[H_2TMT^-] = [H^+]$. We can substitute equation (1) for $[H_2TMT^-]$ in the above equation:

$$[H^+]^2 = K_{a1}[H_3TMT] \tag{4}$$

In addition, we have the material balance:

$$[H_3TMT] = C_T - [H_2TMT^-] = C_T - [H^+] \tag{5}$$

Substitution of equation (5) into equation (4) yields:

$$K_{a1} = \frac{[H^+]^2}{C_T - [H^+]}$$

where $[H^+] = 10^{-3.62}$ and $C_T = 0.03\,030$ mol/l. Thus, $K_{a1} = 10^{-5.72}$.

(2) During titration, at pH values of 7, the most abundant species is $H_2TMT^-$. Taking $H_2TMT^-$ and $H_2O$ as the frames of reference, we have the proton balance:

$$[H_3TMT] + [H^+] = [HTMT^{2-}] + 2[TMT^{3-}] + [OH^-]$$

Considering $[TMT^{3-}]$ is small enough to be negligible, we simplify the proton balance to:

$$[H_3TMT] + [H^+] = [HTMT^{2-}] + [OH^-]$$

We can substitute equation (1) for $[H_3TMT]$, equation (2) for $[HTMT^{2-}]$ and $[OH^-] = K_w/[H^+]$ into the above equation:

$$[H^+]^2 = \frac{K_{a1}(K_{a2}[H_2TMT^-] + K_w)}{[H_2TMT^-] + K_{a1}}$$

In many cases, $[H_2TMT^-] \gg K_{a1}$, $K_{a2}[H_2TMT^-] \gg K_w$. Therefore, the equation simplifies to: $[H^+]^2 = K_{a1}K_{a2}$ where $[H^+] = 10^{-7}$ and $K_{a1} = 10^{-5.72}$. Thus, $K_{a2} = 10^{-8.28}$.

(3) During titration, at pH values of 9.87, the most abundant species is $HTMT^{2-}$. Taking $HTMT^{2-}$ and $H_2O$ as the frames of reference, we have the proton balance:

$$[H_2TMT^-] + 2[H_3TMT] + [H^+] = [TMT^{3-}] + [OH^-]$$

Considering $[H_3TMT]$ is small enough to be negligible, we simplify the proton balance to:

$$[H_2TMT^-] + [H^+] = [TMT^{3-}] + [OH^-]$$

We can substitute equation (2) for $[H_2TMT^-]$, equation (3) for $[TMT^{3-}]$ and $[OH^-] = K_w/[H^+]$ into the above equation:

$$[H^+]^2 = \frac{K_{a2}(K_{a3}[HTMT^{2-}] + K_w)}{[HTMT^{2-}] + K_{a2}}$$

In many cases, $[HTMT^{2-}] \gg K_{a2}$, $K_{a3}[HTMT^{2-}] \gg K_w$. Therefore, the equation simplifies to: $[H^+]^2 = K_{a2}K_{a3}$ where $[H^+] = 10^{-9.87}$ and $K_{a2} = 10^{-8.28}$. Thus, $K_{a3} = 10^{-11.46}$

The above-calculated values are also listed in Table 1. The data in Table 1 indicates that our values are basically consistent with those of Henke.

Using the values of K. R. Henke and the equations listed below, we calculated the each fraction ($\alpha$) of four dissolved TMT species—$TMT^{3-}$, $HTMT^{2-}$, $H_2TMT^-$ and $H_3TMT$ in the TMT total concentration ($C_T$) at any given pH and plotted the calculated data in Fig. 4 of pH vs the fraction $\alpha$.

$$D_n = [H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3} \quad (6)$$

$$\alpha_0 = \frac{[H_3TMT]}{C_T} = \frac{[H^+]^3}{D_n} \quad (7)$$

$$\alpha_1 = \frac{[H_2TMT^-]}{C_T} = \frac{K_{a1}[H^+]^2}{D_n} \quad (8)$$

$$\alpha_2 = \frac{[HTMT^{2-}]}{C_T} = \frac{K_{a1}K_{a2}[H^+]}{D_n} \quad (9)$$

$$\alpha_3 = \frac{[TMT^{3-}]}{C_T} = \frac{K_{a1}K_{a2}K_{a3}}{D_n} \quad (10)$$

From the calculated values and Fig. 4, we can find that, if the pH of the solution is above 12.5, $TMT^{3-}$ is the most abundant species ($\alpha_3 \geq 92.95$). Therefore, the complex $Cu_3(TMT)_2$ was obtained at pH values of 12.5 by reacting metal salts and $Na_3TMT \cdot 9H_2O$ in a 1.5 stoichiometry. At pH values of 9.9, the percentage of the monohydrogen TMT dianion ($HTMT^{2-}$) is the greatest ($\alpha_{2\,\max} = 94.17$). Therefore Cu (HTMT) was obtained at pH values of about 10 with a metal–ligand stoichiometry of 1:1. At pH values of 7, the maximum percentage of the dihydrogen TMT monoanion ($H_2TMT^-$) is 91.33% ($\alpha_{1\,\max} = 91.33$). Consistent with the result, we prepared Cu $(H_2TMT)_2$ at pH values of about 7.5 with a metal–ligand ratio of 0.5:1. At pH values below 5 the sparsely water-soluble acid, $H_3TMT$, is most abundant($\alpha_0 \geq 83.68$) and a substantial reaction with metal ions was not expected. The work presented here shows that it is possible to prepare Cu–TMT complexes containing the series of ligand units $TMT^{3-}$, $HTMT^{2-}$ and $H_2TMT^-$ by careful control of the pH [equations (11)–(13)]. The pH of the ligand solution probably plays a greater role than the metal–ligand ratio in determining the stoichiometry of the complexes formed.[10]

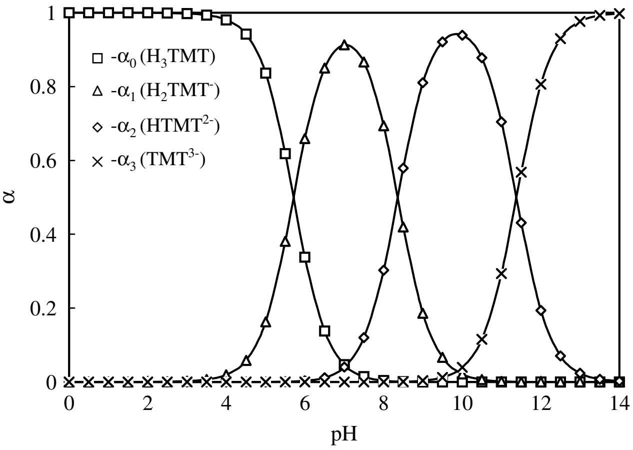

**Figure 4.** Fraction of $H_3TMT$ species as a function of pH.

$$\text{pH} \approx 12.5 \quad 2Na_3TMT + 3CuCl_2 \longrightarrow Cu_3(TMT)_2\downarrow \quad (11)$$

$$\text{pH} \approx 10 \quad Na_2HTMT + CuCl_2 \longrightarrow Cu(HTMT)\downarrow \quad (12)$$

$$\text{pH} \approx 7.5 \quad 2NaH_2TMT + CuCl_2 \longrightarrow Cu(H_2TMT)_2\downarrow \quad (13)$$

## Determination of the solubility and solubility product constants ($K_{SP}$) for compounds 1–3

For Cu–TMT complexes, there are the following solubility equilibria in the aqueous solutions:

$$\begin{matrix} Cu(H_2TMT)_2(s) \Leftrightarrow Cu(H_2TMT)_2(aq) \\ \Leftrightarrow Cu^{2+} + 2H_2TMT^-\ Ksp_{(1)} \end{matrix} = [Cu^{2+}]\cdot[H_2TMT^-]^2 \quad (14)$$

$$\begin{matrix} CuHTMT(s) \Leftrightarrow CuHTMT(aq) \\ \Leftrightarrow Cu^{2+} + HTMT^{2-}\ Ksp_{(2)} \end{matrix} = [Cu^{2+}]\cdot[HTMT^{2-}] \quad (15)$$

$$\begin{matrix} Cu_3(TMT)_2(s) \Leftrightarrow Cu_3(TMT)_2(aq) \\ \Leftrightarrow 3Cu^{2+} + 2TMT^{3-}\ Ksp_{(3)} \end{matrix} = [Cu^{2+}]^3\cdot[TMT^{3-}]^2 \quad (16)$$

In these equations, [Cu-TMT] (aq) is called the intrinsic solubility ($S^0$) of the Cu–TMT complexes. Because the intrinsic solubility $S^0$ of many insoluble salts, including metallic sulfides, is low enough to be omitted, we assume that the dissolved Cu–TMT complexes are highly ionized in water following the above equations.[15] Hence, the solubility

**Table 2.** The aqueous solubility data and $K_{SP}$ for the compounds

| | Copper concentration $C$ (mg/l)[a] | Solubility (mol/l) | $K_{SP}$ |
|---|---|---|---|
| Cu $(H_2TMT)_2$ (**1**) | 1.234 | $1.94 \times 10^{-5}$ | $1.27 \times 10^{-14}$ |
| Cu (HTMT)$\cdot 0.5H_2O$ (**2**) | 6.271 | $9.87 \times 10^{-5}$ | $2.81 \times 10^{-11}$ |
| $Cu_3$ $(TMT)_2 \cdot 2H_2O$ (**3**) | 0.0807 | $4.23 \times 10^{-7}$ | $2.11 \times 10^{-46}$ |
| CuS | 0.219[b] | $3.45 \times 10^{-6}$[c] | $6.3 \times 10^{-36}$[d] |

[a] These are the mean values of the same six experiments, subtracting the blanks.

[b] This value is calculated by $c$, ignoring intrinsic solubility ($S^0$) of CuS.

[c] This value is taken from Lide.[16]

[d] This value is from Dean.[17]

for compounds **1–3** is determined only by the amount of dissolved copper in the solution, which has already been measured with ICP-AES and is listed in Table 2. By knowing the copper concentration and the Cu–TMT complex stoichiometry, aqueous solubilities can be calculated. The results are also listed in Table 2.

The pH of fresh deionized water, which was used to dissolve the Cu-TMT complexes, is 6. At a pH value of 6, with equations (6)–(10) and (14)–(16), we can calculate each fraction[a] () of $TMT^{3-}$, $HTMT^{2-}$ and $H_2TMT^-$ and deduce the relation between their concentrations and copper concentrations ($C$ mol/l):

$$\alpha_1 = \frac{[H_2TMT^-]}{C_T} = \frac{K_{a1}[H^+]^2}{D_n} = 0.659$$

$$[H_2TMT^-] = \alpha_1 \cdot C_T = 2\alpha_1 C_1 \tag{17}$$

$$\alpha_2 = \frac{[HTMT^{2-}]}{C_T} = \frac{K_{a1}K_{a2}[H^+]}{D_n} = 2.88 \times 10^{-3}$$

$$[HTMT^{2-}] = \alpha_2 \cdot C_T = \alpha_2 C_2 \tag{18}$$

$$\alpha_3 = \frac{[TMT^{3-}]}{C_T} = \frac{K_{a1}K_{a2}K_{a3}}{D_n} = 1.20 \times 10^{-8}$$

$$[TMT^{3-}] = \alpha_3 \cdot C_T = \frac{2}{3}\alpha_3 C_3 \tag{19}$$

(1) For Cu $(H_2TMT)_2$(1): $Ksp_{(1)} = [Cu^{2+}] \cdot [H_2TMT^-]^2 = C_1 \cdot (2\alpha_1 C_1)^2$. From the data in Table 2 and equation (17), $C_1 = 1.94 \times 10^{-5}$ $mol/L$ $\alpha_1 = 0.659$. The solubility product constant ($K_{SP}$) for compound **1** is: $K_{SP(1)} = 1.27 \times 10^{-14}$.

(2) For Cu (HTMT) $\cdot$ $0.5H_2O$(2): $Ksp_{(2)} = [Cu^{2+}] \cdot [HT-MT^{2-}] = C_2 \cdot (\alpha_2 C_2)$. From the data in Table 2 and equation (18), $C_2 = 9.87 \times 10^{-5}$ mol/l, $\alpha_2 = 2.88 \times 10^{-3}$. The solubility product constant ($K_{SP}$) for compound **2** is: $K_{SP(2)} = 2.81 \times 10^{-11}$.

(3) For $Cu_3$ $(TMT)_2 \cdot 2H_2O$(3): $Ksp_{(3)} = [Cu^{2+}]^3 \cdot [TMT^{3-}]^2 = {C_3}^3 \cdot (\frac{2}{3}\alpha_3 C_3)^2$. From the data in Table 2 and equation (19), $C_3 = 1.27 \times 10^{-6}$ mol/l, $\alpha_3 = 1.20 \times 10^{-8}$. The solubility product constant ($K_{SP}$) for compound **3** is: $Ksp_{(3)} = 2.11 \times 10^{-46}$.

The above values are also listed in Table 2. As shown in Table 2, the copper concentration of the leachate, the solubility and $K_{SP}$ of compound **3** are much less than those of **1** and **2**, which indicates that **3** is much more insoluble and more stable than **1** and **2**. Hence, when $Na_3TMT$ is used to remedy heavy metal pollution, the pH control for TMT precipitating agent is important. However, all of these Cu–TMT structures rearrange towards compound **3**, slowly at room temperature, more rapidly on heating.[18]

Table 2 also compares the amount of the copper released by compound **3** in water with aqueous solubility data for analogous sulfides (CuS). Since clean rainwater generally also has a pH-value near 6 at 25 °C because of carbonic acid produced from interactions between the water and carbon dioxide in air,[19] the deionized water leaching tests may be useful in predicting whether substantial copper may leach out of compound **3** and CuS if the compounds come into contact with uncontaminated rainwater or low total dissolved solids (TDS) ground water. Obviously, compared with CuS, compound **3** is significantly insoluble and stable, which approximately accords with the claims of Degussa Corporation.[4]

The solubility product constant ($K_{SP}$) for compound **3** is extremely small ($2.11 \times 10^{-46}$) and indicates that TMT is very effective in irreversibly binding the highly thermodynamic stable copper in complex state as insoluble precipitates from industrial wastewaters. For example, copper present as ammonia complexes in waste ammonia etchant solutions and rinse water discharged by printed circuit board factories has been difficult to remove to meet discharge limits. If we add TMT-15 to the solution containing $[Cu(NH_3)_4]^{2+}$, which is the most stable form (the cumulative formation constant $\beta_4 = 10^{12.59}$)[20] among four complex-ion species: $[Cu(NH_3)]^{2+}$, $[Cu(NH_3)_2]^{2+}$, $[Cu(NH_3)_3]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, the following reaction will take place:

$$3[Cu(NH_3)_4]^{2+} + 2TMT^{3-} \Leftrightarrow Cu_3(TMT)_2(s) + 12NH_3$$

The equilibrium constant for the above reaction is:

$$\begin{aligned} K &= \frac{[NH_3]^{12}}{\{[Cu(NH_3)_4]^{2+}\}^3 \cdot [TMT^{3-}]^2} \\ &= \frac{[NH_3]^{12}}{\{[Cu(NH_3)_4]^{2+}\}^3 \cdot [TMT^{3-}]^2} \cdot \frac{[Cu^{2+}]^3}{[Cu^{2+}]^3} \\ &= \frac{1}{{\beta_4}^3 \cdot K_{SP,Cu_3(TMT)_2}} = \frac{1}{(10^{12.59})^3 \times 2.11 \times 10^{-46}} = 10^{7.906} \end{aligned}$$

The equilibrium constant $K$ is so great (>$10^6$) that the forward reaction can go a long way towards completion.[21] Hence, the addition of TMT-15 can convert the stable complex ion $[Cu(NH_3)_4]^{2+}$ into three-dimensional agglomerate precipitate $Cu_3$ $(TMT)_2$, which is a coarse, easily filtered floc,

**Table 3.** Effect of ammonia concentrations on the Cu removal

| Initial copper concentration (ppm) | $NH_3$ concentration (ppm) | TMT-15 dosage | Final copper concentration (ppm) |
|---|---|---|---|
| 500 | 0 | Stoichiometric | 0.084 |
| 500 | 50 | Stoichiometric | 0.12 |
| 500 | 500 | Stoichiometric | 0.96 |
| 500 | 500 | 5% dose increase | 0.15 |
| 500 | 5000 | Stoichiometric | 1.92 |
| 500 | 5000 | 15% dose increase | 0.20 |

as suggested by Degussa Corporation.[4] In the final section, we will investigate the influences of ammonia concentration, pH and settling time on the effectiveness of copper precipitation and characteristics of the obtained precipitate.

## Results of copper removal from ammonia complexes by using TMT-15

### *Ammonia concentration effects*

This part of the study was designed to investigate the removal of copper as a function of ammonia concentration. A series of four 100 ml $CuCl_2$ solutions containing 500 ppm Cu and 0, 50, 500 and 5000 ppm ammonia, respectively, were prepared. To each solution the stoichiometric molar amount of TMT-15 ($Na_3TMT$:Cu molar ratio of 2:3) were added. The residual copper concentrations in the top solution after settling for 30 min are shown in Table 3. As expected, higher $NH_3$ levels decrease Cu-removal. The obvious conclusion that can be drawn from these experiments is that, in order to reduce copper concentrations from the solutions containing high ammonia levels to meet a 0.5 mg/l discharge limit,[2] the doses of the precipitating reagent had to be increased to maintain a significant dynamic exchange of $NH_3$ and TMT in effect. As may be seen from Table 3, when a 5 or 15% molar increase in TMT dosage was added, respectively for the solutions containing 500 or 5000 ppm $NH_3$, the amount of Cu remaining in the solution fell below 0.5ppm.

### *pH effects*

Figure 5 summarizes the residual copper concentration as a function of initial pH. All solutions contained 500 ppm Cu, 5000 ppm ammonia and a 15% molar excess dose of TMT; 2 M NaOH and HCl solutions were used to adjust the pH of the corresponding solutions. As may be seen from Fig. 5, at pH 7–10, which is the usual pH value range in the printed circuit board factory tailing solutions, the residual copper levels in the aqueous solution have no remarkable difference. With respect to the removal of Cu, TMT provided the same good results at pH values of between 7 and 10.

### *Time Effects*

Figure 6 presents the dependence of copper removal on time. All solutions contained 500 ppm Cu, 5000 ppm ammonia (initial pH = 8), a 15% molar excess dose of TMT. The concentrations of Cu in the filtrate were determined at intervals of 0.5, 1, 6, 12 and 24 h following reagent addition. Figure 6 shows that, within 30 min settling, the Cu was completely precipitated from the corresponding ammonia complexes by TMT. Analysis of the sample after settling for 24 h gave essentially the same Cu levels, indicating a relatively rapid precipitation and no redissolution of copper.

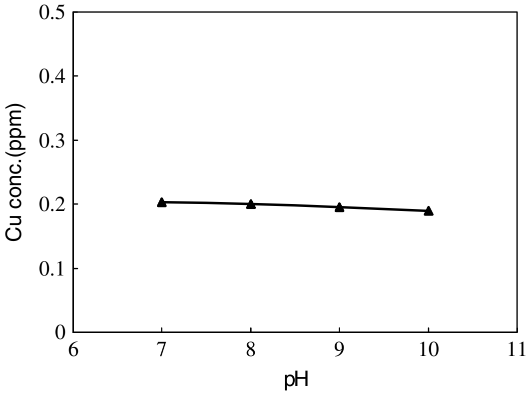

**Figure 5.** pH effect on the residual Cu level.

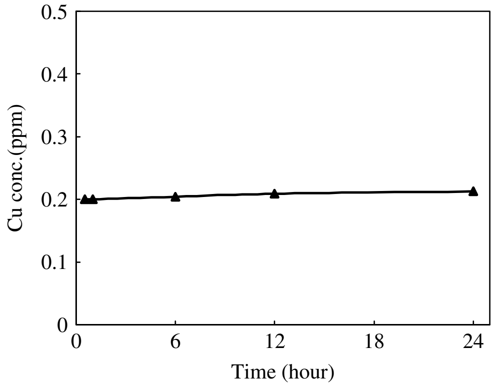

**Figure 6.** Time effect on the residual Cu level.

### *Removal of Cu from real factory effluent*

The effluent tested was obtained from a printed circuit board factory located in Jiangshu Province. The initial copper concentration was 350.9 ppm. Since 349.4 ppm of ammonia were found in the sample, the copper exists mainly as $[Cu(NH_3)_4]^{2+}$. The pH of the effluent tested was ~8. Based on the above experimental results, to two 500 ml aliquots of the effluent, 2.8 ml TMT-15 (5% molar dose increase) were added and to one of two the coagulant and flocculant were also added. Analysis of one sample that had the coagulant and flocculant after settling for 30 min showed that only 0.10 ppm Cu remained in the solution. This corresponds to 99.97% copper removal. Taken from the other sample of no coagulant and flocculant, the reddish brown precipitate was also characterized by IR (1470s, 1228s and 853 m $cm^{-1}$), EA and TGA, indicating that it is in good agreement with compound **3** [$Cu_3$ (TMT)$_2 \cdot 2H_2O$]. The copper concentration (0.0807 mg/l shown in Table 2) of the leachate for compound **3** in deionized water for 96 h indicates that little copper may leach out of the obtained sludge if the sludge comes into contact with uncontaminated rainwater or low-TDS ground water.

## CONCLUSIONS

The following conclusions have been derived from our study:

(1) The spectral features of compounds **1** and **2** show both the conjugated, trithiol form and the unconjugated, trithione form of the TMT rings. The spectrum of compound **3** suggests that the TMT moiety exists only in the aromatic, trithiol form with covalent metal–sulfur bonds. In addition, the bands around 2910–2925, 3030–3250 and 3430 $cm^{-1}$ may be due to triazine ring overtone, N–H stretching vibrations and water in the TMT complexes, respectively.

(2) Our laboratory acid–base titration studies indicate that $pK_{a1}$, $pK_{a2}$ and $pK_{a3}$ of $H_3$TMT are respectively 5.72, 8.28 and 11.46. The three acid dissociation constants of $H_3$TMT are guidelines for the preparation of compounds **1**– **3**.

(3) We report the copper concentration of the leachate, the solubility and the solubility product constants ($K_{SP}$) for compounds **1**–**3** in deionized water (Table 2). The data show that compound **3** is much more insoluble and more stable than **1, 2** and CuS. The extremely small value of $K_{SP}$ for 3($2.11 \times 10^{-46}$) indicates that TMT is very advantageous in precipitating complex copper from industrial wastewaters.

(4) We investigated the effectiveness of copper removal from ammonia containing wastes using TMT-15. Our studies indicate that TMT can relatively rapidly precipitate copper as insoluble compound **3** from the corresponding ammine complexes and the precipitate has no redissolution after settling for 24 h. TMT also provides the same high removal level of Cu at pH values of between 7 and 10. At the same time, since higher $NH_3$ levels decrease Cu removal, the doses of TMT-15 have to be increased to reduce copper concentrations from the solutions containing high ammonia levels to meet a 0.5 mg/l discharge limit.

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