



A pyridine-thiol ligand with multiple bonding sites for heavy metal precipitation

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Abstract

There are immediate concerns with current commercial ligands that are used for heavy metal precipitation, especially the limited arrays of bonding sites. Previous research has indicated that not only do commercial reagents lack sufficient bonding criteria, but they also fail to provide long-term stability as ligand–metal complexes. For this reason, we have developed a pyridine-based thiol ligand (DTPY) which not only offers multiple bonding sites for heavy metals but also should form stable metal–ligand precipitates. In this study, we used the divalent metals cadmium and copper to model the reactivity and pH stability of divalent metal complexes with the DTPY ligand. Using inductively-coupled plasma spectrometry (ICP), results indicate that a 50.00 ppm (parts per million) copper solution, pH of 4.5, can be reduced to below the ICP detection limits of 0.00093 ppm (>99.99% removal), and a 50.00 ppm cadmium solution, pH of 6.0, can be reduced to 0.06 ppm (99.88%). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heavy metal pollution is an existing and growing worldwide problem. During the past few decades, federal and state governments have instituted environmental regulations to protect the quality of surface and ground water from heavy metal pollutants, such as Cd, Cu, Pb, Hg, and Zn [1]. In response to the regulatory requirements, numerous companies have developed and marketed chemical products to precipitate heavy metals from wastewaters [2,3]. Additionally, some of the products have been used to remove heavy metals from already contaminated surface and ground waters. One product is supposedly so innocuous

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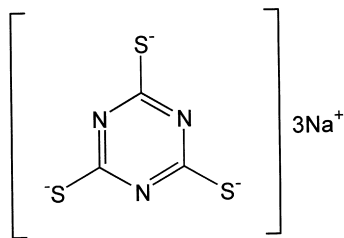


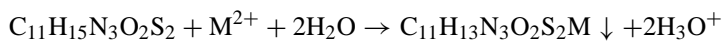
Fig. 1. The chemical structure of TMT-55 or 2,4,6-mercaptotriazine, trisodium salt nonahydrate ($\text{Na}_3\text{C}_3\text{N}_3\text{S}_3 \cdot 9\text{H}_2\text{O}$) (modified after Degussa Corporation, 1993).

that it may be pumped into the subsurface for relatively economical in situ remediation [2,4]. In such cases, the product and precipitates would be left in the subsurface.

One chemical reagent for precipitating divalent heavy metals from water is Thio-Red[®] [2]. The product is a complex aqueous solution of sodium (with or without potassium) thiocarbonate ($[\text{Na},\text{K}]_2\text{CS}_3 \cdot n\text{H}_2\text{O}$, where $n \geq 0$), sulfides, and other sulfur species [4]. Previous laboratory studies summarized by Henke [4] demonstrated that Thio-Red[®] ultimately removes Cu, Hg, Pb, and Zn from aqueous solutions through the formation of stable metal sulfides (that is CuS, HgS, PbS, and ZnS) rather than metal thiocarbonates (that is CuCS_3 , HgCS_3 , PbCS_3 , and ZnCS_3) as claimed in ETUS, Inc., 1994 [2].

A second chemical reagent for precipitating divalent and univalent heavy metals from water is TMT-55, or 2,4,6-mercaptotriazine, trisodium salt nonahydrate $\text{Na}_3\text{C}_3\text{N}_3\text{S}_3 \cdot 9\text{H}_2\text{O}$ (Fig. 1), which is manufactured and distributed by Degussa Corporation USA of Allendale and Ridgefield Park, NJ [3]. Despite the widespread use of TMT-55, only limited information is available on how the product reacts with heavy metals in aqueous solutions, and the chemistry and stability of the resulting heavy metal trimercaptotriazine (TMT) precipitates.

Immediate concerns with ligands, such as the TMT-55, includes the weak non-specific binding abilities for heavy metals (Fig. 1). Ligands with alkyl-thio chains that lack either chain length or sufficient bonding sites may produce precipitates that are unstable over time and under certain pH conditions. For this reason, it has been the focus of our research to design and synthesize sulfur-containing ligands, which not only bind heavy metals, but also produce stable precipitates. Stabilizing metal complexes is accomplished through multiple interactions between a divalent metal cation and the sulfur and nitrogen atoms on the ligand. The ligand under investigation is a pyridine-based thiol compound (DTPY), which utilizes two chains at the 2,6-position, consisting of three carbons, one nitrogen, and two sulfur end groups (Fig. 2). Computer modeling suggests that the designed ligand has a sufficient length for interactions between the metal and each terminal sulfur group. An additional interaction may occur in the form of dative bonds associated with the nitrogen atoms. The theoretical reaction, which produces the precipitate shown in Fig. 3, is as follows:



where $\text{M}^{2+} = \text{Cd}, \text{Pb}, \text{Hg}, \text{Ni}, \text{Zn}$, etc.

The DTPY ligand has been characterized using proton nuclear magnetic resonance (¹H NMR), infra-red (IR), carbon-13 NMR, mass spectroscopy, X-ray diffraction (XRD), and



Molecular Mass (grams): 285.06

Ideal Chemical Analysis (%): C, 46.29; H, 5.30; N, 14.72; O, 11.21; S, 22.47

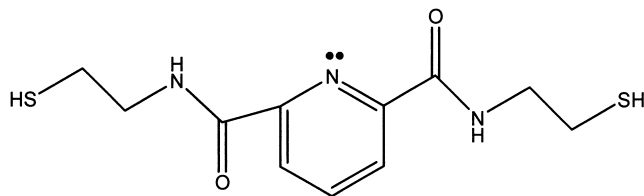


Fig. 2. Structure and chemical information of the pyridine-thio ligand.

single crystal XRD. Fig. 3 illustrates the type of complex, which results in a likely stable DTPY ligand and a divalent metal. A ligand of this type should allow for more robust precipitation of heavy metals through use of a tetrahedral bonding arrangement around a central metal (Hg, Pb, Cd, etc.) atom. Current research emphasizes interactions between the DTPY ligand and mercury, cadmium, copper, and lead. As a precursor for the mercury and lead studies, complexes of Cd^{2+} and Cu^{2+} have been studied. This paper outlines the reactivity and pH stability of the DTPY ligand with Cd^{2+} and Cu^{2+} . Future articles will report on results with Hg^{2+} and Pb^{2+} .

2. Materials and methods

2.1. Materials

The following reagent-grade materials were used in the proprietary synthesis of the DTPY ligand, which was recovered as a white precipitate: 2,6-pyridine dicarboxylic acid ($\text{C}_7\text{H}_5\text{N}_3\text{O}_2$, Aldrich, lot # 07529TS), cysteamine ($\text{C}_2\text{H}_7\text{NS}$, Fluka, lot # 49087/1), and

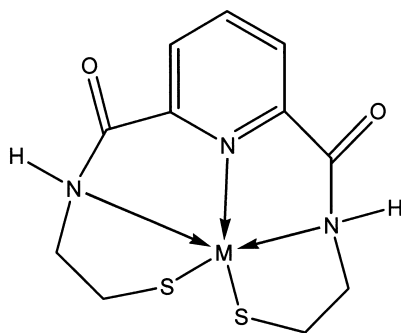


Fig. 3. Theoretical molecular structure of pyridine-thio ligand metal complex. M = divalent heavy metal such as Cd^{2+} or Cu^{2+} .

dry chloroform (CHCl_3 , Mallinckrodt, lot # 4443N13H27). For the pyridine-thio ligand metal reactions, reagent-grade materials were used, including hydrated cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, J.T. Baker Inc., lot # 45062). Homogeneous dark brown anhydrous copper (II) chloride was prepared by heating several grams of bluish-green copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Aldrich, lot # 17923CS) in an oven at 120°C for several days. For reactions carried out in an acetate buffer solution, the acetate buffer was prepared at a pH 6.0 using sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, J.T. Baker Inc., lot # 744103), glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, Mallinckrodt, lot # V193N08H38), anhydrous ethanol ($\text{C}_2\text{H}_6\text{O}$, AAPER Alcohol, lot # 990204), and deionized water. All DTPY ligand metal reactions and inductively-coupled plasma spectrometry (ICP) measurements were performed in a 39% ethanol/61% deionized water solution (by volume) to maximize the solubility of the DTPY ligand in its most pure state. Unless stated otherwise, all reactions with the metal salts were prepared at room temperature and normal atmospheric pressure.

2.2. Analytical methods

Cadmium and copper analyses were performed with a 1999 Duo HR Iris advanced inductive coupled plasma (ICP) spectrometer. For powder XRD analyses, the samples were mounted on glass slides with ethanol and analyzed with a Rigaku unit at 40 kV and 20 mA using $\text{Cu K}\alpha_1$ ($\lambda = 1.540598 \text{ \AA}$) radiation. No pattern matches were obtained for the ligand or metal–ligand complexes, which were compared with organic and inorganic databases from the International Center for Diffraction Data (ICDD) (Newton Square, PA). Single crystal XRD on the DTPY ligand was run on a Nonius-Kappa CCD instrument. ^1H NMR and carbon-13 NMR analyses were performed on a Varian-Gemini-200 instrument, and the samples were run in deuterated chloroform (CDCl_3 , Cambridge Isotope Laboratories, Inc., lot # 01810-5413). IR spectroscopy data on DTPY ligand and metal–ligand complexes were collected using potassium bromide (KBr, Mallinckrodt, lot # 0505 KXXR) pellets and a Nicolet-Avatar 320 FT-IR series spectrometer. All masses were determined using a Sartorius BP2100S balance or a Mettler AE 240 balance.

2.3. Analytical procedures for ICP analyses

2.3.1. Cadmium ICP analyses

A series of 100 ml 50.00 ppm (parts per million) Cd^{2+} samples were prepared, in 39% ethanol/61% water solutions. A total of 12.68 mg of solid DTPY ligand was added immediately to each Cd^{2+} solution, based on a one to one molar ratio. The reaction produced a pH 4.0 solution. Aliquots (10 ml) were collected and filtered at $0.2 \mu\text{m}$ (Nalgene[®] syringe filters lot # 322238) after 1 and 4 h (Table 1). The experiment was repeated for a 50.00 ppm Cd^{2+} solution, except an acetic acid/sodium acetate buffer (5.0 ml) was used to maintain a pH of 6.0. In addition to the one to one molar ratio, an 8.32% increase in DTPY ligand dose was used. The 8.32% increase was based on the amount of DTPY ligand needed to treat the 4.40 ppm Cd^{2+} remaining in the 50.00 ppm Cd^{2+} pH 6.0 solution after 1 h. All experiments were run a minimum of three times. The averaged results have been tabulated in Table 1. A series of dose increases above the one to one molar ratio were also performed on the pH of 4.0 cadmium solutions.

Table 1
ICP results of DTPY and Cd²⁺

Metal	Initial concentration (ppm)	Ligand dosage (mg)	Dosage increase (%)	Volume of buffer ^a (ml)	Solution pH	Time sample removed (h)	Final concentration ^b (ppm)	Maximum cadmium removed ^b (%)
Cadmium	50.00	12.68	None	0.00	4.0	1	15.74	68.53
Cadmium	50.00	12.68	None	0.00	4.0	4	15.05	69.90
Cadmium	50.00	16.50	30.10	0.00	4.0	1	10.66	78.69
Cadmium	50.00	16.50	30.10	0.00	4.0	4	8.22	83.55
Cadmium	50.00	18.58	46.53	0.00	4.0	1	2.29	95.42
Cadmium	50.00	18.58	46.53	0.00	4.0	4	0.94	98.12
Cadmium	50.00	12.68	None	5.00	6.0	1	4.40	91.20
Cadmium	50.00	12.68	None	5.00	6.0	4	4.16	91.68
Cadmium	50.00	13.74	8.32	5.00	6.0	1	0.15	99.70
Cadmium	50.00	13.74	8.32	5.00	6.0	4	0.06	99.88

^a Buffer solution created from acetic acid and sodium acetate.

^b Results are based on the average of triplicate runs.

2.3.2. Copper ICP analyses

Two 100 ml 50.00 ppm Cu^{2+} samples were prepared in 39% ethanol/61% water solutions, and 22.43 mg of solid DTPY ligand, based on one to one molar ratio, was added immediately. Two additional samples were prepared with an additional 8.25% dose increase of DTPY ligand. To one sample of the one to one molar ratio and the 8.25% dose increase, 5.0 ml of acetic acid/sodium acetate buffer was added to maintain a pH of 6.0. Samples of 10 ml were collected and filtered at 0.2 μm (Nalgene[®] syringe filters lot # 322238) after 1 and 4 h.

3. Results and discussion

3.1. Results of Cd^{2+} and Cu^{2+} stoichiometry and metal removal

The ICP data indicate a maximum Cd^{2+} removal using a 46.53% dose increase after 4 h at pH 4.0 of 98.12% (Table 1). At a pH of 6.0, a maximum Cd^{2+} removal of 99.88% was observed within 1 h for the 8.32% increased dose solution (Table 1). A maximum removal of Cu^{2+} for the pH of 4.5 solution occurred within 4 h using an 8.25% increase in DTPY dose, >99.98% (Table 2). At a pH of 6.0, maximum copper removal was seen using a 2.10% dose increase in DTPY, >99.98% (Table 2).

3.2. Results of IR data

The IR data confirmed the presence of the DTPY's (Fig. 2) major functional groups. The confirmed wavelengths of the functional groups included: secondary amine ($-\text{NH}-$) 3275.28 cm^{-1} , aromatic (CHs) on the pyridine ring 2965.46 cm^{-1} , sulfur–hydrogen (S–H) 2525.08 cm^{-1} , carbonyl (CO) 1668.68 cm^{-1} , and the carbon–sulfur bond (C–S) 680.46 cm^{-1} (Fig. 4) [5]. IR data on both of the metal complexes (Cd^{2+} and Cu^{2+}) confirm the carbonyl, the C–S bond, the aromatic CHs on the pyridine ring, and the secondary amine peak [5]. The only missing peak, in both complexes, was the sulfur–hydrogen bond, which was replaced by the expected metal–sulfur. The metal–sulfur bond should be located at wavelengths below the Nicolet-Avatar 320 FT-IR series spectrometer's detection limit of 500 cm^{-1} [6,7].

3.3. Results of proton nuclear magnetic resonance

The ^1H NMR spectrum for the DTPY ligand yielded: ^1H NMR (CDCl_3): δ 1.50 (t, 2H), δ 2.80 (dd, 4H), 3.71 (dd, 4H), 8.05 (t, 3H), 8.39 (d, 1H) (Fig. 5). For the ligand–metal complexes, two comparative ^1H NMRs were obtained in deuterated DMSO (dimethylsulfoxide) acidified with one drop of HNO_3 , and a second sample in deuterated DMSO acidified with one drop of HCl . Acidified DMSO was used because of the insolubility of the ligand–metal complexes in organic and water solutions. Acidifying the DMSO–ligand–metal solution allowed for enough solubility to create a suitable solution for the ^1H NMR analyses. Peak splitting could not be identified due to the low concentration of the ligand–metal complexes; however, the spectrum did yield strong broad peaks that confirmed the presence of aromatic and alkane protons. The protons on the terminal thiol groups were absent indicating the bonding scheme predicted in Fig. 3.

Table 2
ICP results of DTPY and Cu²⁺

Metal	Initial concentration (ppm)	Ligand dosage (mg)	Dosage increase (%)	Volume of buffer ^a (ml)	Solution pH	Time sample removed (h)	Final concentration ^b (ppm)	Maximum copper removed ^b (%)
Copper	50.00	22.43	None	0.00	4.5	1	37.72	75.44
Copper	50.00	22.43	None	0.00	4.5	4	4.13	91.74
Copper	50.00	24.28	8.25	0.00	4.5	1	0.92	98.16
Copper	50.00	24.28	8.25	0.00	4.5	4	<0.0093 ^c	>99.98
Copper	50.00	22.43	None	5.00	6.0	1	1.56	96.88
Copper	50.00	22.43	None	5.00	6.0	4	1.05	97.80
Copper	50.00	22.90	2.10	5.00	6.0	1	1.34	97.32
Copper	50.00	22.90	2.10	5.00	6.0	4	<0.0093 ^c	>99.98

^a Buffer solution created from acetic acid and sodium acetate.

^b Maximum percentage results are based on the average of triplicate runs.

^c Results were below the detection limit for the ICP spectrometer.

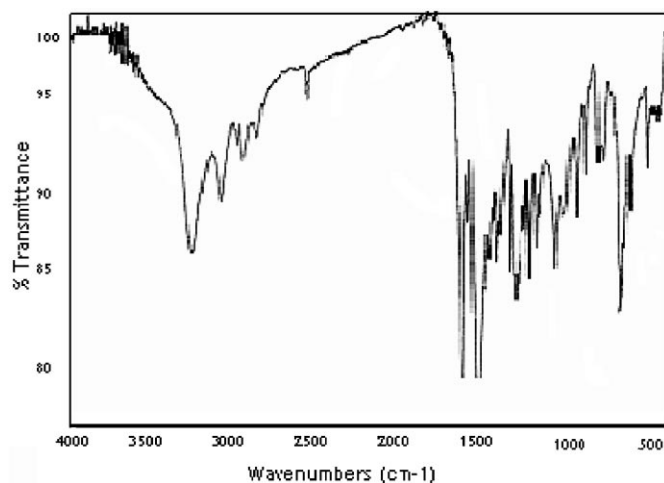
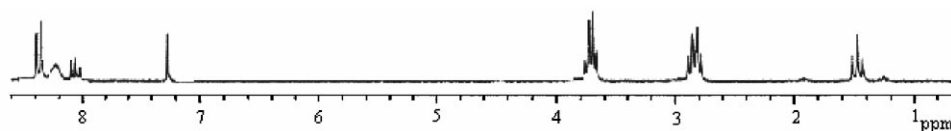


Fig. 4. The IR spectrum of DTPY of Fig. 2.

Fig. 5. ^1H NMR of DTPY ligand.

4. Conclusions

There is a definite need for more stable ligands to meet site remediation, water treatment, and regulatory requirements. Previous studies indicate that commercial remediation reagents may lack sufficient bonding criteria to produce precipitates that have long-term stability. The DTPY ligand promises to provide the required long-term stability. Early results look extremely promising using Cd^{2+} and Cu^{2+} . The results indicate 99.70% removal of cadmium from a 50.00 ppm aqueous solution may be accomplished using the DTPY ligand at an 8.32% dose increase within 1 h at a pH of 6.0. For a 50.00 ppm copper solution, >99.98% removal can be observed within 1 h at a pH of 4.5. IR and ^1H NMR spectroscopy indicates that the precipitate is a metal–DTPY ligand complex bonding at the terminal sulfur ends as depicted in Fig. 3. Future work will focus on the precipitation of Hg^{2+} and Pb^{2+} with the DTPY ligand.

Acknowledgements

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