Inorg. Chem. **2008**, *47*, 10565−10574

Inorganic Chemistry
Article

Stabilization of Copper(II) Thiosulfonate Coordination Complexes Through Cooperative Hydrogen Bonding Interactions

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Received July 3, 2008

A series of copper(II) thiosulfonate complexes have been prepared via the reaction of [Cu(Me$_3$tren)(OH$_2$)](ClO$_4$)$_2$ (Me$_3$tren = tris(2-methylaminoethyl)amine) with three thiosulfonate ligands (RSO$_2$S$^-$, where R = Me, Ph, and MePh) and characterized by microanalysis, FTIR spectroscopy, and X-ray crystallography. In these complexes, the distorted trigonal bipyramidal copper(II) coordination sphere is occupied by four amine nitrogen atoms from the tripodal tetramine ligand and an apically bound sulfur atom from the thiosulfonate ligand. By using the tripodal tetramine ligand the oxidation of the thiosulfonate has been restricted, allowing the isolation of the complexes. The Cu−S distances were found to be similar to those in related thiosulfate complexes, indicating coordinative interactions of similar strength. Two types of intramolecular hydrogen bonding interactions were evident which enhance the binding of the thiosulfonate to the copper(II) center. These interactions, which involve two amine N−H groups and either one or two thiosulfonate oxygens, were found to be weaker than in the corresponding thiosulfate complexes. The complex formation constants for the thiosulfonate complexes (log K_f = 0.3−0.7) were found to be two orders of magnitude lower than compared to the thiosulfate analogues. This correlates well with a lower strength of intramolecular hydrogen bonding.

Introduction

The rapid oxidation of thiosulfate by copper(II) ions is a well-known reaction, and it is generally accepted that a copper(II)−thiosulfate complex is a reactive intermediate that promotes this reaction. As a direct consequence of this reactivity, there have been few reported examples of stable copper(II)−thiosulfate coordination complexes.[1−3] In each of these examples, the copper(II) ion was five-coordinate and the thiosulfate anion was coordinated in a monodentate fashion via the terminal sulfur atom. The coordination sphere of the copper(II) center was completed by four nitrogen donor atoms, either from two ethylenediamine (en) ligands[1,2] or from a tripodal tetraamine ligand (e.g., tren, tris(2-aminoethyl)amine, and derivatives thereof).[3]

Further insights into the structure and properties of these reactive copper(II) thiosulfate complexes can be gained via the study of the coordination chemistry of thiosulfonates (RS$_2$O$_2^-$), organic derivatives of thiosulfate in which one of the oxygen atoms is formally replaced by an organic group (Figure 1). (We note that both thiosulfonate esters (Figure 1c) and thiosulfonate anions (Figure 1b) have been referred to as thiosulfonates; herein, “thiosulfonate” refers to the anion). The bond angles around the central sulfur atom are close to tetrahedral (thiosulfate possesses C_{3v} symmetry whereas thiosulfonates are at most C_s). As is the case for thiosulfate, the common coordination mode for thiosulfonates is via the terminal sulfur atom.

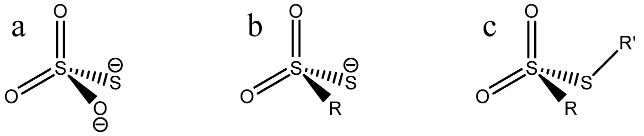

Figure 1. Structures of (a) thiosulfate, (b) thiosulfonates, and (c) thiosulfonate esters.

Most previous research on thiosulfonates has had a biological emphasis. Thiosulfonate salts have been investigated as more effective antidotes for cyanide poisoning than thiosulfate, in combination with the enzyme rhodanese

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10.1021/ic801234c CCC: $40.75

(thiosulfate:cyanide sulfur transferase).[4−6] Biological formation of thiosulfonate compounds, such as thiotaurine (2-aminoethanethiosulfonate)[7] and alaninethiosulfonate,[8] has also been established. Some deep-sea invertebrates that live near hydrothermal vents produce thiotaurine from hypotaurine (2-aminoethanesulfinate), to detoxify the high concentrations of H_2S.[6,9] Thiotaurine has been used as a pretreatment for sulfur mustard (mustard gas) poisoning[10] while thiosulfonic acids (and their S-esters) are biologically active as fungicides and bactericides.[11]

The coordination chemistry of thiosulfonates has not been extensively studied. The limited examples of thiosulfonate−metal complexes include Au(I),[12−17] Cu(I),[18,19] Fe(II),[20] Ru(II),[21,22] Ag(I),[23] Hg(II),[23] Pt(II),[24,25] and Ir(III)[26] complexes. To our knowledge there have not been any quantitative studies on the formation of Cu(II) thiosulfonates complexes. The monothiosulfonato−Cu(I) complexes ($CuMeS_2O_2$, $CuEtS_2O_2$, and $CuPrS_2O_2$) were, however, obtained via reduction of copper(II) by thiosulfonates.[18,19]

In an extension of our previous work, in which a series of thiosulfate complexes were stabilized through the use of the tripodal tetradentate ligand tris(2-aminoethyl)amine (tren) and several N-functionalized derivatives of tren,[3] we present herein the first detailed investigation of copper(II) thiosulfonate complexes. We report the syntheses, characterization, and X-ray crystal structures of three copper(II) complexes of composition $[Cu(Me_3tren)(RS_2O_2)](ClO_4)$, where Me_3tren = tris(2-methylaminoethyl)amine and R = Me, Ph, and MePh, and compare structural features of these complexes, for example, intramolecular hydrogen bonding, with those of thiosulfate copper(II) complexes bearing these tripodal polyamine ligands.[3] Taking advantage of the fact that, as was the case for thiosulfate, coordination of thiosulfonate to copper(II) is characterized by an intense L → Cu(II) charge transfer transition in the 300−400 nm spectral region, constants for binding of methanethiosulfonate ($MeS_2O_2^-$) to the tren and Me_3tren copper(II) complexes have been determined and are compared to those reported previously for the corresponding thiosulfate complexes.[3]

Experimental Section

Materials and Reagents. Me_6tren, Bz_3tren, $[Cu(tren)(H_2O)](ClO_4)_2$, $[Cu(Me_6tren)(H_2O)](ClO_4)_2$, $[Cu(Me_3tren)(H_2O)](ClO_4)_2$, and $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ were synthesized as described previously (tren = tris(2-aminoethyl)amine, Me_3tren = tris(2-methylaminoethyl)amine, and Me_6tren = tris(2,2-dimethylaminoethyl)amine).[3] The syntheses of $NaMeS_2O_2\cdot H_2O$,[7] $NaPhS_2O_2$,[8] and $NaMePhS_2O_2$[8] were based on literature procedures. Other chemicals were used as received from commercial suppliers. Deoxygenated water was prepared by boiling freshly distilled water under nitrogen for 2 h.

Instrumentation. UV−visible−NIR spectra were recorded on a Varian Cary 5G spectrophotometer fitted with a water-jacketed cell holder. An externally circulating water bath (Varian) maintained the temperature to a precision of ±0.1 °C. FTIR spectra were recorded using either a Perkin-Elmer 1600 FTIR or a Bruker Equinox IFS 55 FTIR to a resolution of 4 cm^{-1}. A Bruker Equinox IFS 55 FTIR fitted with a Specac Goldengate ATR stage was used for recording ATR-IR spectra. The pH of stock solutions for spectrophotometric studies was fixed using a Titrando autoburette, fitted with a Metrohm electrode. Elemental analyses were performed by Campbell Microanalytical Services, University of Otago, New Zealand.

$[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$. $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (9 mg, 0.02 mmol) was dissolved in a minimum amount of MeCN to give a blue solution, and $NaMePhS_2O_2$ (10 mg, 0.050 mmol) was added. The mixture was filtered, yielding a green solution. Slow diffusion of Et_2O into the filtrate resulted in crystallization of green plates after several days. Analysis via single crystal X-ray crystallography confirmed the formation of $[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$. Yield: 1 mg (11%).

A better yielding synthesis of this compound was developed as follows. $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (0.18 g, 0.40 mmol) was dissolved in 15 mL of hot ^{i}PrOH, and $NaMePhS_2O_2$ (0.083 g, 0.40 mmol) was added in portions while stirring. Upon addition of the first portion of the thiosulfonate salt, an immediate blue to green color change occurred. At the completion of the addition of the thiosulfonate salt, the solution was dark green and clear. Stirring was continued for a few minutes, and a green solid was found to precipitate. The solid was collected by filtration of the solution after it had been allowed to stand at room temperature (RT) for a few minutes. The microcrystalline green product was dried at the pump and washed with Et_2O. Yield: 0.12 g (56%). Characterization. Microanalyses: Found (%): C, 35.8; H, 5.8; N, 10.4. Calculated for $C_{16}H_{31}ClCuN_4O_6S_2$ (%): C, 35.7; H, 5.8; N, 10.4. Selected IR bands [KBr disk: ν (cm^{-1})]: 3254 s, 2883 m, 1251 m, 1124 s, 1102 s, 1066 s, 988 m, 856 m, 825 m, 708 m, 662 s, 624 m.

$[Cu(Me_3tren)(PhS_2O_2)]ClO_4$. $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (9 mg, 0.02 mmol) was dissolved in minimum MeCN to give a blue solution, and $NaPhS_2O_2$ (10 mg, 0.05 mmol) was added. Slow diffusion of Et_2O into the green filtrate obtained following filtration of this mixture caused green blocks of the desired product to crystallize after several days, along with white/colorless needles, which were assumed to be $NaPhS_2O_2$. Analysis of the green blocks

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Table 1. Crystal Data for $[CuL(MePhS_2O_2)]ClO_4$ (I), $[CuL(PhS_2O_2)]ClO_4$ (II), and $[CuL(MeS_2O_2)]ClO_4$ (III) (L = Me_3tren)

crystal data	I	II	III
empirical formula	$C_{16}H_{31}ClCuN_4O_6S_2$	$C_{15}H_{29}ClCuN_4O_6S_2$	$C_{10}H_{27}ClCuN_4O_6S_2$
formula weight	538.56	524.53	462.27
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	11.302(1)	7.9481(5)	10.5593(8)
b (Å)	8.598(1)	21.598(1)	23.073(2)
c (Å)	24.084(3)	12.8819(8)	16.117(1)
β (deg)	96.490(3)	106.872(3)	107.938(2)
V (Å^3)	2325.2(5)	2116.2(2)	3735.8(5)
Z	4	4	8
ρ_{calcd} (g cm^{-3})	1.538	1.646	1.643
μ Mo Kα (mm^{-1})	1.273	1.396	1.569
$2\theta_{max}$ (deg)	55.4	60.0	55.0
reflections collected	23438	28997	39905
unique reflections (R_{int})	5426 (0.0563)	7145 (0.0291)	8573 (0.0555)
“observed” [$I > 2\sigma(I)$] reflections	5117	6774	7720
GOF on F^2	1.394	1.313	1.349
$R1$,[a] w$R2$[b] [$I > 2\sigma(I)$]	0.0808, 0.1378	0.0494, 0.0894	0.0841, 0.1498
maximum difference peak, hole (e Å^{-3})	0.566, −0.728	0.748, −0.528	1.099, −0.975

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

by X-ray diffraction confirmed that the compound was $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$. Insufficient compound was obtained to permit further characterization.

A slightly higher yielding synthesis was based on the preparation of $[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$. $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (0.10 g, 0.21 mmol) and 1 equiv of $NaPhS_2O_2$ (0.042 g, 0.20 mmol) were dissolved in a minimal amount of hot ^{i}PrOH, and the solution was heated at ~80 °C for 5 min. The solution was then filtered while hot, allowed to slowly cool to RT, and then stored overnight at 4 °C. Small green crystals formed after one week, which were collected by vacuum filtration and washed with Et_2O. The green color of the filtrate indicated that significant amounts of the compound remained in solution. Yield: 10 mg (9%). Characterization. Microanalyses: Found (%): C, 34.3; H, 5.5; N, 10.5. Calculated for $C_{15}H_{29}ClCuN_4O_6S_2$ (%): C, 34.4; H, 5.6; N, 10.7. Selected IR bands [KBr disk: ν (cm^{-1})]: 3286 (m), 3255 (m), 2969 (m), 2926 (m), 2886 (m), 1250 (s), 1124 (s), 1102 (s), 1065 (s), 986 (m), 964 (m), 856 (m), 824 (m), 761 (m), 718 (m), 691 (m), 618 (s), 610 (m).

$[Cu(Me_3tren)(MeS_2O_2)]ClO_4$. $NaMeS_2O_2 \cdot H_2O$ (28 mg, 0.18 mmol) was dissolved, with gentle heating, in 5 mL of 95% EtOH. To this solution was added 1 mL of a 25 mM MeOH solution of $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (0.025 mmol). The solution was taken to dryness by rotary evaporation and the residue dissolved in ~1 mL of ^{i}PrOH to give a green solution (after gentle heating). A further 1 mL of ^{i}PrOH was added, and slow diffusion of Et_2O into this solution yielded small green crystals after a few hours. One crystal was analyzed by X-ray diffraction and found to be $[Cu(Me_3tren)(MeS_2O_2)]ClO_4$. Insufficient compound was obtained for further characterization.

A larger batch was prepared by dissolving $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (10 mg, 0.21 mmol) and $NaMeS_2O_2 \cdot H_2O$ (31 mg, 0.20 mmol) in a minimum amount of hot ^{i}PrOH. The solution was filtered while hot, slowly cooled to RT, and then stored at 4 °C for several hours. Green crystals formed which were collected by filtration and washed with Et_2O. Yield: 7 mg (7%). Characterization. Microanalyses: Found (%): C, 26.2; H, 5.8; N, 12.1. Calculated for $C_{10}H_{27}ClCuN_4O_6S_2$ (%): C, 26.0; H, 5.9; N, 12.1. Selected IR bands [KBr disk: ν (cm^{-1})]: 3257 s, 2966 m, 2926 m, 2881 m, 1459 m, 1257 m, 1206 m, 1076 br s, 990 m, 958 m, 859 m, 829 m, 747 m, 624 m.

Spectrophotometric Studies. Due to the slow decomposition of the thiosulfonate solutions, all solutions for spectrophotometric measurements were prepared immediately prior to use. For the $[Cu(tren)(H_2O)]^{2+}$-$MeS_2O_2^-$ binding studies, four stock solutions were prepared from deoxygenated water: (i) a buffer solution prepared from the free acid of MOPS (0.140 M) and sufficient $NaClO_4 \cdot H_2O$ to obtain an ionic strength (I) of 0.150 M after titration to pH 7.5 with ~2 M NaOH; (ii) a CuL^{2+} solution containing 1.20 mM $[Cu(tren)(H_2O)](ClO_4)_2$ (I = 3.60 mM); (iii) a $MeS_2O_2^-$ solution consisting of 0.200 M $NaMeS_2O_2 \cdot H_2O$ (I = 0.200 M), which was filtered through a 0.22 μm Millipore membrane to remove traces of suspended solids, such as elemental sulfur, prior to use; and (iv) a 0.200 M $NaClO_4 \cdot H_2O$ solution. Solutions with different $MeS_2O_2^-$ concentrations (I = 0.200 M) were prepared by mixing appropriate volumes of the $MeS_2O_2^-$ and ClO_4^- stock solutions. The buffer, CuL^{2+}, and $MeS_2O_2^-$ solutions were then mixed in the ratio $^1/_3$:$^1/_6$:$^1/_2$, which resulted in a final ionic strength of 0.15 M. Prior to mixing the three solutions, the $MeS_2O_2^-$ solution was equilibrated at 25 °C in the thermostatted spectrophotometer cell block, and the CuL^{2+} and MOPS solutions were mixed and equilibrated at 25 °C in a thermostatted water bath. For the $[Cu(Me_3tren)(H_2O)]^{2+}$-$MeS_2O_2^-$ and $[Cu(Me_6tren)(H_2O)]^{2+}$-$MeS_2O_2^-$ systems, the stock solutions and samples were prepared as described for $[Cu(tren)(H_2O)](ClO_4)_2$ but using $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ and $[Cu(Me_6tren)(H_2O)](ClO_4)_2$ with a few minor differences as outlined below. The concentration of the $Cu(Me_3tren)^{2+}$ stock solution was 2.99 mM rather than 1.20 mM to achieve a sufficient change in the spectrum with increasing $[MeS_2O_2^-]$ to allow measurement of the binding constant.

Crystallography. Single-crystal X-ray data were collected on a Bruker X8 Apex diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å) at 123(2) K using φ and/or ω scans (Table 1). Data were corrected for Lorentz and polarization effects, and absorption corrections were applied using SADABS.[27] The structures were solved by conventional methods and refined using the full-matrix least-squares method using the SHELXS-97[28] and SHELXL-97[29] programs, respectively. The program X-Seed[30] was used as an interface to the SHELX programs and to prepare the

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Table 2. Position of $\nu(SO_2)$ Vibrations in Thiosulfonate Compounds

ligand	compound	$\nu(SO_2)$ (cm^{-1})	ref
$MeS_2O_2^-$	$NaL \cdot H_2O$	1196, 1084	this work
	NaL	1220−1180 (br), 1100−1075 (br)	32
	$[Cu(Me_3tren)(L)]ClO_4$	1257, 1206, 1076	this work
	[Ru(Cp)(dppe)(L)]	1266^a	21
$MePhS_2O_2^-$	NaL	1190, 1120, 1070	33
	$[Cu(Me_3tren)(L)]ClO_4$	1251, 1122, 1089	this work
	$[Ru(Cp)(Ph_3P)(CO)(L)]$	1266^a	22
$PhS_2O_2^-$	NaL	1225, 1191, 1121, 1067	this work
	NaL	1220, 1120, 1070 1190, 1117, 1063	33, 34
	$[Cu(Me_3tren)(L)]ClO_4$	1250, 1123, 1065	this work
	[Ru(Cp)(dppe)(L)]	1253^a	21

[a] Some stretches obscured by other ligand vibrations.

figures. Non-hydrogen atoms were refined with anisotropic thermal parameter forms. Hydrogen atoms attached to carbon were placed in calculated positions using a riding model and with $U_{iso}(H) = 1.2-1.5U_{iso}(C)$; otherwise, they were located on Fourier difference maps and refined with isotropic thermal parameters (N−H distances were restrained to reasonable values in III, while for I the amine hydrogen atoms, H(1), H(2), and H(3), were constrained to have identical thermal motion). In the structure of III, one SO_2Me group was modeled as disordered, with the methyl carbon and one oxygen atom occupying two alternate positions, having refined occupancies of 0.88:0.12. The anisotropic refinement of the minor disordered component was restrained to be the same as that of the major component. The data for I and II showed several significant systematic absence violations for the space group $P2_1/n$; however, refinement in lower symmetry space groups was less satisfactory.

Results and Discussion

Synthesis and Characterization. Generally, copper(II) thiosulfonate complexes were prepared by dissolving the precursor copper(II) tripodal amine complex and the sodium thiosulfonate salt in hot ^{i}PrOH, and allowing the resulting green solution to slowly cool to RT. Isolated product yields were relatively low due to the low stability of the thiosulfonate complexes (vide infra) and the fact that significant amounts of the product remained in solution. The complexes were characterized by IR spectroscopy, elemental analysis, and X-ray crystallography.

The thiosulfonate complexes exhibited significant shifts of the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibrations on coordination to Cu(II) when compared with those of the sodium salts of these ligands (Table 2). The antisymmetric stretch, $\nu_{as}(SO_2)$, is particularly sensitive to metal ion coordination,[21] generally shifting to higher energy on coordination via the terminal sulfur. As for thiosulfate compounds, the $\nu_s(SO_2)$ mode shows only minor changes.[31] The ν(SR) is less diagnostic, apart from being difficult to assign in the aromatic thiosulfonates, although it seems to shift to lower energy in thiosulfonate complexes. For example, the band at 768 cm^{-1} in $NaMeS_2O_2 \cdot H_2O$ shifts to 747 cm^{-1} in $[Cu(Me_3tren)(MeS_2O_2)]ClO_4$.

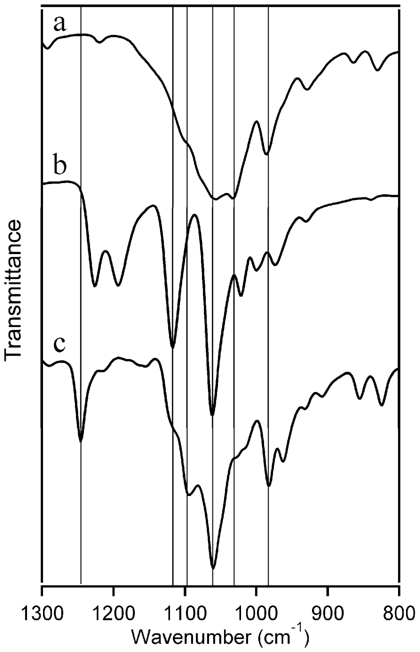

Figure 2. Section of FT IR spectra of (a) $[Cu(Me_3tren)(H_2O)](ClO_4)_2$; (b) $NaPhS_2O_2$; and (c) $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$.

The comparison of IR spectra in Figure 2 illustrates the changes that occur on coordination of thiosulfonates to Cu(II). The two bands associated with the split $\nu_{as}(SO_2)$ mode at 1225 and 1191 cm^{-1} ($NaPhS_2O_2$, spectrum b) combine and shift to 1251 cm^{-1} for $Cu(Me_3tren)(PhS_2O_2)]ClO_4$ (spectrum c). This band is absent in the spectrum of $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (spectrum a), whereas a number of other vibrations in the spectrum of $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$ are common to $NaPhS_2O_2$ (1121 and 1067 cm^{-1}) or $[Cu(Me_3tren)(H_2O)](ClO_4)_2$ (988, 963, 858, and 829 cm^{-1}) The broad perchlorate bands in $[Cu(Me_3tren)(PhS_2O_2)](ClO_4)$ (1000−1100 cm^{-1} region) are less intense than the $\nu_s(SO_2)$ bands.

X-ray Crystal Structures. The molecular structures of the copper(II)−thiosulfonate complexes $[Cu(Me_3tren)(RS_2O_2)]ClO_4$, determined by X-ray crystallography (Figures 3, 4, and 5 for R = Ph, MePh, and Me, respectively), confirmed that the thiosulfonate ligands coordinate to the copper(II) center via the terminal sulfur atom. For the $MeS_2O_2^-$ complex, two independent $[Cu(Me_3tren)(MeS_2O_2)]ClO_4$ units were found within the unit cell. The Cu(II) geometry in each complex is slightly distorted trigonal bipyramidal; τ values[35] lie in the 83−93% range. Two of the amine protons are aligned with the SO_2R group, thereby facilitating intramolecular N−H···O hydrogen bonding, which is discussed further below.

Bond distances and angles (Table 3) around the Cu(II) centers are comparable to those in $[Cu(Me_3tren)(MeCN)](ClO_4)_2$ (Cu−N$_{ax}$ 2.030(2) Å; Cu−N$_{eq}$ 2.080(2), 2.093(2), and 2.111(3) Å; N$_{eq}$−Cu−N$_{eq}$ 123.2(1), 124.1(1), and 110.2(1)°; N$_{ax}$−Cu−N$_{eq}$ 85.3(1), 84.72(9), and 84.0(1)°).[3]

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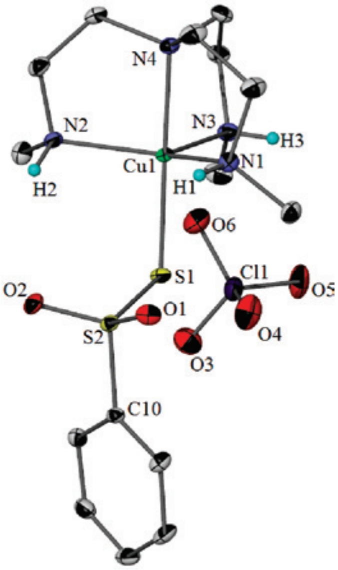

Figure 3. Molecular structure of [Cu(Me_3tren)(PhS_2O_2)]ClO_4 (thermal ellipsoids drawn at 50% level, non-amine hydrogen atoms omitted for clarity).

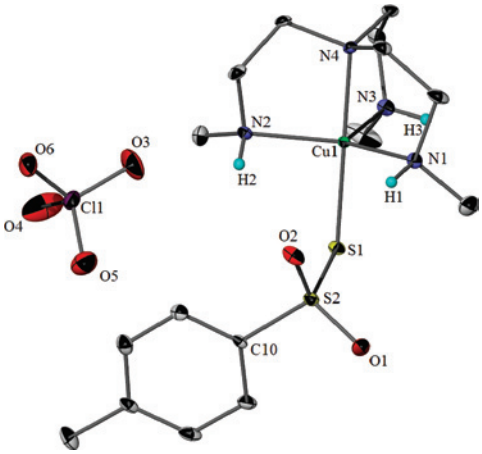

Figure 4. Molecular structure of [Cu(Me_3tren)($MePhS_2O_2$)]ClO_4 (thermal ellipsoids drawn at 50% level, non-amine hydrogens omitted for clarity).

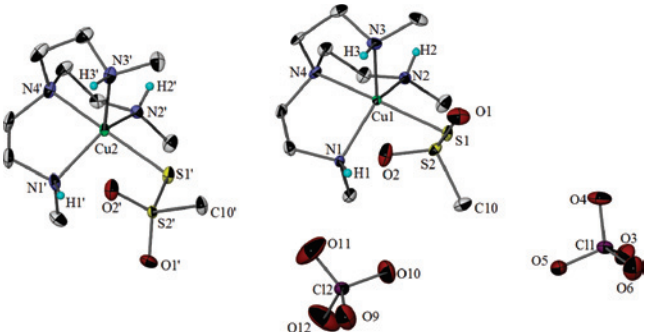

Figure 5. Molecular structure of the two independent complexes in [Cu(Me_3tren)(MeS_2O_2)]ClO_4 (thermal ellipsoids drawn at 50% level, non-amine hydrogen atoms omitted for clarity, major (88%) disorder component of O1′, S2′, and C10′ shown).

The Cu−N_{ax} bonds are the shortest of the four Cu−Me_3tren bonds in all cases, as for [Cu(Me_3tren)(MeCN)]$(ClO_4)_2$. All of the N_{ax}−Cu−N_{eq} angles are less than 90° and as a consequence the Cu(II) center is displaced out of the equatorial plane away from the bridge-head nitrogen by 0.195(2), 0.195(1), 0.205(3), and 0.213(3) Å for the $MePhS_2O_2^-$, $PhS_2O_2^-$, and the two independent $MeS_2O_2^-$ complexes, respectively. The displacements are in excellent agreement with that observed for the copper(II) ion in the MeCN complex (0.194(2) Å).

Relative to the corresponding thiosulfonate salts (Table 4), the S−S distances show the greatest change upon coordination to Cu(II), increasing by 0.070 Å for the $MePhS_2O_2^-$ complex and 0.033 Å for the $PhS_2O_2^-$ complex. There is therefore significant donation of electron density onto the Cu(II) center. The S−O distances are essentially unchanged from the respective salts, despite the increase in the energy of the $\nu_a(SO_2)$ vibration evidenced by the IR spectra.

The Cu−S distances for the thiosulfonate complexes are the same (within 3σ) as for the thiosulfate complexes (Table 4), despite the lesser negative charge of the thiosulfonates compared to the doubly charged thiosulfate. Table 5 summarizes some key geometric parameters for known X-ray structures of thiosulfonate complexes. The S−S and M−S distances for the [Cu(Me_3tren)(RS_2O_2)]ClO_4 complexes are the same as those found in the Au(I), Ru(II), Fe(II), and Pt(II) complexes (corresponding distances are 2.03 ± 0.01 and 2.33 ± 0.04 Å, respectively). The greatest variation is found among the M−S−S angles, suggesting that thiosulfonate complexes can adopt a range of M−S−S angles; the small angle for the Pt(II) complex arises because the SO_2R moiety is part of a six-membered chelate ring.

Intramolecular Hydrogen Bonding Interactions. In the thiosulfonate complexes and the previously reported thiosulfate complexes,[3] the proximity of amine hydrogen atoms on the tren-based ligands to the thiosulfonate/thiosulfate oxygen atoms accommodates the formation of moderate to weak intramolecular hydrogen bonds (Table 6). In the discussion that follows we use the classification of hydrogen bonding proposed by Jeffrey,[38] which defines strong, moderate, and weak hydrogen bonds based on measurable physical properties, such as shifts in IR and ^{1}H NMR spectra, in addition to bond lengths and angles. Analysis of the available structures indicates that two hydrogen bonding modes are adopted (Figure 6), for simplicity designated type I and type II. In both cases, two N−H···O hydrogen bonds are present, but in type I two different oxygen atoms on the oxoanion act as acceptors while in type II one oxygen atom accepts both hydrogen bonds.

The two hydrogen bonding interactions can be classified in terms of the alignment of the SO_2R moiety relative to the CuSSO/R plane (designated type I and type II; Figure 7). Ideally, type I would be characterized by two Cu−S−S−O torsion angles of ± 60° (i.e., the two S−O bonds are at ±60° to the Cu−S bond for the oxygens that point up toward the Cu) and type II by one torsion angle close to 0° (i.e., one of the S−O bonds is aligned with the Cu−S bond, and this oxygen atom points up toward the Cu). For the thiosulfonate complexes, [Cu(Me_3tren)(PhS_2O_2)]ClO_4 exhibits the type I hydrogen bonding mode whereas the type II mode is found in [Cu(Me_3tren)($MePhS_2O_2$)]ClO_4 (Figure 6b, Table 6). For

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(38) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997; p 303.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Cu(Me_3tren)(RS_2O_2)]ClO_4$ Complexes[a]

		MePh	Ph	Me	Me[b]
$Cu-N_{ax}$	Cu−N(4)	2.049(4)	2.0416(2)	2.063(4)	2.064(5)
$Cu-N_{eq}$	Cu−N(1)	2.138(4)	2.116(2)	2.051(4)	2.064(5)
	Cu−N(2)	2.093(4)	2.079(2)	2.132(5)	2.131(5)
	Cu−N(3)	2.082(4)	2.136(2)	2.120(5)	2.129(5)
Cu−S	Cu−S(1)	2.317(1)	2.2989(6)	2.324(2)	2.317(2)
S−S	S(2)−S(1)	2.020(2)	2.0108(7)	2.010(2)	2.014(2)
S−O	S(2)−O(1)	1.451(4)	1.447(2)	1.454(4)	1.449(5)
	S(2)−O(2)	1.459(4)	1.452(2)	1.445(4)	1.473(5)
S−C	S(2)−C(10)	1.773(4)	1.772(2)	1.760(6)	1.760(6)
$N_{eq}-Cu-N_{ax}$	N(1)−Cu−N(4)	84.5(2)	85.60(7)	84.5(2)	84.8(2)
	N(2)−Cu−N(4)	84.6(2)	84.67(7)	84.4(2)	84.0(2)
	N(3)−Cu−N(4)	84.9(2)	83.86(7)	84.3(2)	83.8(2)
$N_{eq}-Cu-N_{eq}$	N(1)−Cu−N(2)	120.4(2)	121.72(7)	120.0(2)	123.7(2)
	N(1)−Cu−N(3)	112.7(2)	112.13(8)	126.7(2)	121.0(2)
	N(2)−Cu−N(3)	124.3(2)	123.60(8)	110.4(2)	112.2(2)
$N_{eq}-Cu-S$	N(1)−Cu−S(1)	96.9(1)	98.40(5)	94.8(1)	96.8(1)
	N(2)−Cu−S(1)	95.8(1)	96.11(5)	92.6(1)	90.0(1)
	N(3)−Cu−S(1)	93.3(1)	91.35(5)	99.2(1)	100.5(1)
$N_{ax}-Cu-S$	N(4)−Cu−S(1)	178.1(1)	174.67(5)	176.0(1)	173.7(1)
Cu−S−S	S(2)−S(1)−Cu	103.02(6)	105.54(3)	102.26(7)	107.97(7)

[a] N_{ax} = axial nitrogen; N_{eq} = equatorial nitrogen. [b] Data for major conformation of second complex.

Table 4. Comparison of Geometric Parameters in Cu(II)−Thiosulfonate and Cu(II)−Thiosulfate Complexes and Thiosulfonate Salts

	Cu−S (Å)	S−S (Å)	Cu−S−S (deg)
Thiosulfonate Complexes			
$[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$	2.317(1)	2.020(2)	103.02(6)
$[Cu(Me_3tren)(PhS_2O_2)]ClO_4$	2.2989(6)	2.0108(7)	105.54(3)
$[Cu(Me_3tren)(MeS_2O_2)]ClO_4$	2.324(2)	2.010(2)	102.26(7)
	2.317(2)	2.014(2)[a]	107.97(7)[a]
Thiosulfate Complexes			
$[Cu(tren)(S_2O_3)]\cdot H_2O$	2.3158(8)	2.0513(8)	103.28(3)
$(H_3Me_3tren)[Cu(Me_3tren)(S_2O_3)]_2(ClO_4)_3$	2.330(3)	2.042(3)	97.1(1)
	2.280(3)	2.014(3)	109.5(1)
$[Cu(Bz_3tren)(S_2O_3)]\cdot MeOH$	2.301(1)	2.061(2)	102.52(6)
Thiosulfonate Salts			
$NaMeS_2O_2\cdot H_2O$[b]		1.979(6)	
$NH_4MeS_2O_2$[c]		1.954(1)	

[a] 1.96(1) Å and 98.8(4)° in the minor conformation. [b] Reference 36. [c] Reference 37.

Table 5. Geometric Parameters for Non-Cu(II) Thiosulfonate Complexes

complex	M−S (Å)	S−S (Å)	<M−S−S (deg)	ref
$[Au(Me_3P)(MePhS_2O_2)]$	2.340(1)	2.033(2)	99.73(7)	13
	2.332(1)	2.039(2)	103.15(6)	
$[Au(Ph_3P)(MePhS_2O_2)]$	2.3286(7)	2.043(1)	103.35	13
$[Au(Me_3CNC)(MePhS_2O_2)]$	2.288(1)	2.045(1)	102.80(5)	13
$[Ru(Cp)(PPh_3)(CO)(MePhS_2O_2)]$	2.383(2)	2.023(3)	110.0(1)	22
$[Ru(Cp)(dppe)(ClPhS_2O_2)]$	2.393(2)	2.032(2)	104.23(8)	21
$[Fe(Cp)(CO)_2(CCl_3PhS_2O_2)]$	2.280(1)	2.022(2)	109.43(6)	20
$[PtL(PPh_3)_2]$[a]	2.362(2)	2.034(2)	92.6	24, 25

[a] L is a cyclic thiosulfonate (no esd reported for Pt−S−S angle); Cp = cyclopentadienyl; dppe = 1,2-bis(diphenylphosphino)ethane; $(CH_2)_3tu$ = trimethylenethiourea; Me_4tu = *N,N,N′,N′*-tetramethylthiourea; $(CH_2)_2tu$ = dimethylenethiourea.

$[Cu(Me_3tren)(MeS_2O_2)]ClO_4$, the Cu−S−S−O torsion angles lie between the type I and type II ranges, resulting in an intermediate intramolecular hydrogen bonding geometry.

Analogous but slightly stronger hydrogen bonding interactions are evident in the structures of the previously reported copper(II)−thiosulfate complexes.[3] These particular combinations of coordination and hydrogen bonding are otherwise unprecedented. No other trigonal bipyramidal transition metal complexes with a tren-based ligand and a coordinated tetrahedral $XY(O)_2Z$ anion were found in the Cambridge Structural Database. The most closely related compound in the CSD is $[Zn(tren)(BNPP)]ClO_4$ (BNPP = bis(*p*-nitrophenyl)phosphate).[39] However, no hydrogen bonding is evident in this compound, because the Zn−O−P angle is too large to bring the oxygen atom(s) close enough to allow hydrogen bonding with the amine protons. The closest nontrigonal bipyramidal analogues are *cis*-$NH_4[Co(en)_2(SO_3)(S_2O_3)]\cdot 3H_2O$,[40] $[Cu(en)_2(S_2O_3)]$,[2] and [*trans*-$Co(en)_2Cl_2$][[*trans*-$Co(en)_2(S_2O_3)_2$].[41] Although two of these complexes are octahedral and the other square pyramidal, all three exhibit hydrogen bonding interactions to the thiosulfate SO_3 group that can be described as type I (shown in Figure 8 for two of the complexes). In each case, these interactions appear to contribute to the conformation adopted by the molecule.

A common feature of all these complexes is a tight M−X−Y angle (ca. 100°). This is necessary for the oxygen atoms to be close enough to accept a hydrogen bond from the amine ligands. Figure 9 plots the distribution of M−X−Y angles for $XY(O)_2Z$ anions (and esters) in the CSD and shows that if X = oxygen, the majority of oxoanion coordination complexes have an M−X−Y angle >120°, whereas the corresponding angle in SXO_3^{n-} compounds (X = sulfur) is smaller. The larger M−X−Y angle, typically found when X = oxygen, would leave the uncoordinated oxygen atoms too far from the tren ligand amine hydrogen atoms to act as hydrogen bond acceptors (see Figure S1, Supporting Information). On the other hand, *S*-coordinated monothio−arsenate, −silicate, −phosphate, and −selenate complexes of $[Cu(R_3tren)(H_2O)]^{2+}$, R = H, Me, Bz, would be expected to form intramolecular hydrogen bonds with the amine co-ligand.

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Table 6. Intramolecular Hydrogen Bonding in Cu(II)-$Me_3tren-RS_2O_2^-$ Complexes[a]

bond	N−H (Å)	H···O (Å)	N···O (Å)	<(NHO) (deg)	torsion(s)	H-bonding mode
$[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$						
N(1)−H(1)···O(2)	0.95(5)	2.52(5)	3.171(5)	126(4)	+10	type II
N(2)−H(2)···O(2)	0.84(6)	2.37(6)	3.072(6)	142(5)	+10	
$[Cu(Me_3tren)(PhS_2O_2)]ClO_4$						
N(1)−H(1)···O(1)	0.84(3)	2.75(3)	3.227(3)	118(2)	−62	type I
N(2)−H(2)···O(2)	0.84(3)	2.52(3)	3.203(2)	140(3)	+69	
$[Cu(Me_3tren)(MeS_2O_2)]ClO_4$						
N(1)−H(1)···O(2)	0.83(2)	2.30(4)	3.010(6)	143(6)	+25	intermediate
N(1′)-H(1′)···O(2′)	0.84(2)	2.44(5)	3.149(6)	142(6)	−18[b]	
$[Cu(tren)(S_2O_3)]$[c]						
N(3)−H(18)···O(3)	0.83(2)	2.69(2)	2.969(2)	101(2)	−67	type II
N(4)−H(8)···O(2)	0.87(3)	2.34(3)	3.077(3)	143(2)	+54	
$[Cu(Bz_3tren)(S_2O_3)]$[c]						
N(2)−H(2)···O(1)	0.83(4)	2.06(4)	2.866(5)	163(3)	−59	type II
N(3)−H(3)···O(2)	0.80(3)	2.62(4)	3.178(5)	129(3)	+61	
$[Cu(Me_3tren)(S_2O_3)]$ (a)[c]						
N(3)−H(3)···O(1)	0.93	2.29	2.95(1)	128	+6	type I
N(2)−H(2)···O(1)	0.93	2.56	3.07(1)	115		
$[Cu(Me_3tren)(S_2O_3)]$ (b)[c]						
N(3′)−H(3′)···O(1′)	0.93	2.34	3.09(1)	137	−16	type I

[a] Torsion(s) = Cu−S−S−O angle. [b] Major conformation (34.0° for the minor conformation). [c] Reference 3.

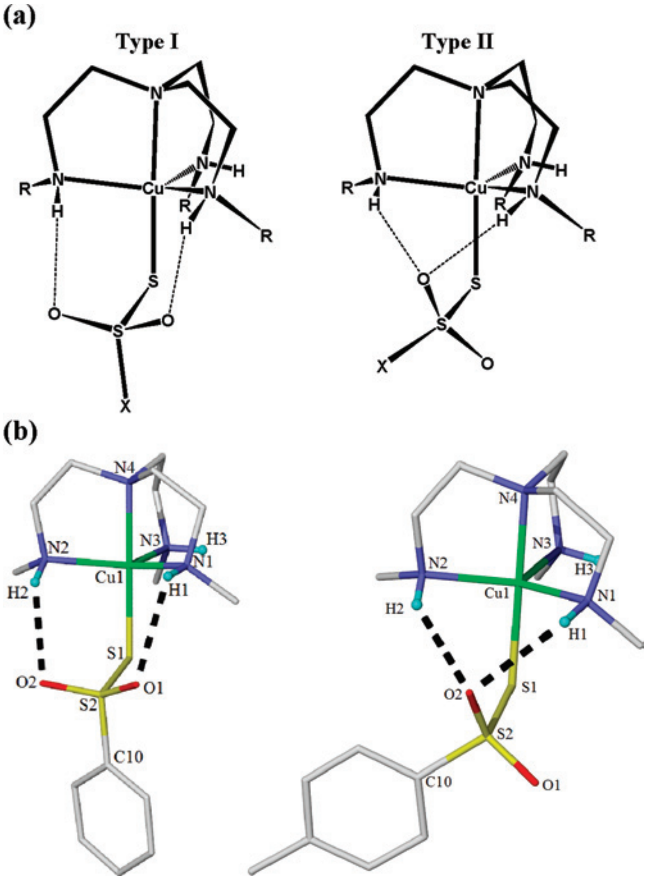

Figure 6. (a) Intramolecular hydrogen bonding modes (broken lines) observed in thiosulfate complexes, $[CuL(S_2O_3)]$ (R = H, Me, and Bz and X = O), and thiosulfonate complexes, $[CuL(S_2O_3R')]$ (R = Me and X = Me, Ph, and MePh). (b) Examples of type I and type II hydrogen bonding modes found in $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$ and $[Cu(Me_3tren)(MePhS_2O_2)]$-$ClO_4$, respectively.

The closest analogues of thiosulfate, monothioselenate and selenoselenate, are unfortunately not stable.[42] Selenosulfate, however, can be prepared from elemental selenium and sulfite[42] and has been used to prepare $[Cu(en)_2(SeSO_3)]$, the only literature example of a selenosulfate−copper(II) complex. The X-ray crystal structure[1] shows that $SeSO_3^{2-}$ coordinates weakly to Cu(II) in the apical position of a square pyramid. The Cu−Se distance (2.89 Å) is within the range of covalent radii overlap defined by the CSD as a bonding

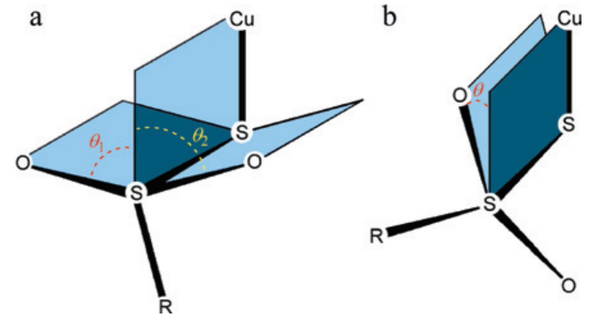

Figure 7. Torsion angles describing the orientation of the SO_2R group relative to the Cu−S bond: (a) type I ($-50° < \theta_1 < -70°$, $50° < \theta_2 < 70°$) and (b) type II ($-10° < \theta < 10°$).

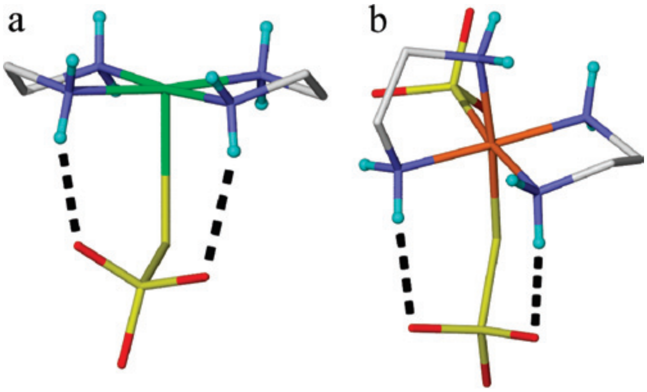

Figure 8. Intramolecular amine−thiosulfate hydrogen bonding in (a) $[Cu(en)_2(S_2O_3)]^2$ and (b) $NH_4[Co(en)_2(SO_3)(S_2O_3)]\cdot 3H_2O$;[40] non-amine protons, counterions, and water omitted for clarity.

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(42) Ball, S.; Milne, J. *Can. J. Chem.* **1995**, *73*, 716–724.

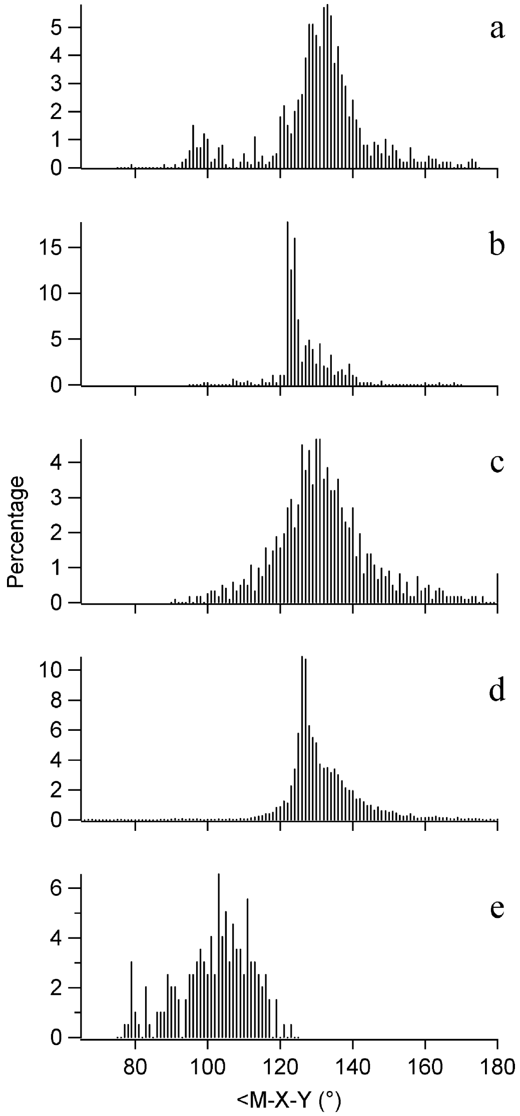

Figure 9. Distribution of M−X−Y angles for oxoanion coordination complexes (number of structures) of (a) sulfate (999); (b) arsenate (495); (c) perchlorate (1223); (d) phosphate (6502); and (e) SXO_3^{n-} (198) (X = S, P, Si, and esters thereof).

interaction.[43] The Cu−Se−S angle in this compound (100°) is favorable for the formation of intramolecular N−H···O hydrogen bonds, leading to an N···O close contact of 2.81 Å.[1] The Cu−Se−S−O torsion angles (+46° and −82°) mean that the hydrogen bonding interaction is best described as distorted type I, but with the formation of only one of the two possible hydrogen bonds.

Intermolecular Interactions. The three complexes exhibit a variety of CH/π interactions that have a significant influence on crystal packing of $[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$ (see Figures S2−S7 and Tables S1−S3 in Supporting Information).

Thiosulfonate Binding Constants. In previous studies, we reported that the addition of thiosulfate to copper(II)−tren complexes in aqueous and nonaqueous solution caused a color change, from blue to green,[3] arising from a new S → Cu(II) LMCT centered at ∼350 nm. This intense transition was useful for determining the strength of the interaction between the copper(II) center and the thiosulfate anion. In aqueous solution, the coordination of $MeS_2O_2^-$ to some Cu(II)−tren complexes was sufficiently strong to allow determination of the formation constants, whereas $PhS_2O_2^-$ and $MePhS_2O_2^-$ coordinated more weakly and the complex formation could not quantified.

The spectrophotometric data for the Cu(II)-L-$MeS_2O_2^-$ system (L = tren and Me_3tren, Figure 10) show the appearance of the LMCT in the same region as for the corresponding thiosulfate complexes.[3] The similar energy of the LMCT for the two classes of complexes provides evidence that the chromophores are similar, namely, S → Cu(II). The complex formation constants were determined as described in our previous study;[3] additionally, the formation constant for $[Cu(tmpa)(S_2O_3)]$ was measured (tmpa = tris(pyridin-2-ylmethyl)amine, see Supporting Information, Figure S8). The concentration of the $[Cu(L)(H_2O)]^{2+}$ present in solution was corrected for the effect of hydrolysis to $[Cu(L)(OH)]^+$ at the pH of study using the acid dissociation constant for each complex (pK_a = 9.08(2) for $[Cu(Me_3tren)(H_2O)]^{2+}$,[44] 9.40(5) for $[Cu(tren)(H_2O)]^{2+}$,[45] and 8.51(1) for $[Cu(Bz_3tren)(H_2O)]^{2+}$; note that this p$K_a$ value was previously reported incorrectly[3] as 7.10(9)). The values for the thiosulfate complexes[3] were also recalculated to account for partial deprotonation of the complex and are compared with the thiosulfonates in Table 7.

Coordination of $MeS_2O_2^-$ to $[Cu(Me_6tren)(H_2O)]^{2+}$ and $[Cu(tmpa)(H_2O)]^{2+}$ was also examined. While a LMCT was observed for the Cu(II)-tmpa-$MeS_2O_2^-$ system (see Supporting Information, Figure S9) the change in intensity of this band with $[MeS_2O_2^-]$ was linear over the accessible ranges of $MeS_2O_2^-$ concentration. For the Cu(II)-Me_6tren-$MeS_2O_2^-$ system no spectral change was evident. Consequently, the binding of $MeS_2O_2^-$ was too weak to be quantifiable for either system.

The complex formation constants for the thiosulfonate complexes are two orders of magnitude smaller than those for corresponding thiosulfates, and in the case of $MeS_2O_2^-$, coordination to the Me_6tren complex could not be detected. The weaker binding affinity of thiosulfonate for Cu(II) when compared with thiosulfate implies that less electron density is available on the terminal sulfur of thiosulfonates for ligation. It would therefore be expected that the S−S and Cu−S distances in the X-ray crystal structures would reflect this; however, this was not the case. The lower strength of intramolecular N−H···O hydrogen bonding of the thiosulfonate complexes when compared with the thiosulfate complexes, which is clearly evident in the solid state compounds, is postulated to be responsible for the variation in the complex formation constants. The strength of the hydrogen bonding is influenced by the polarization

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(43) Cambridge Crystallographic Data Centre, Radii & Bond Lengths, 2004.http://www.ccdc.cam.ac.uk/products/csd/radii/table.php (accessed July 2006).

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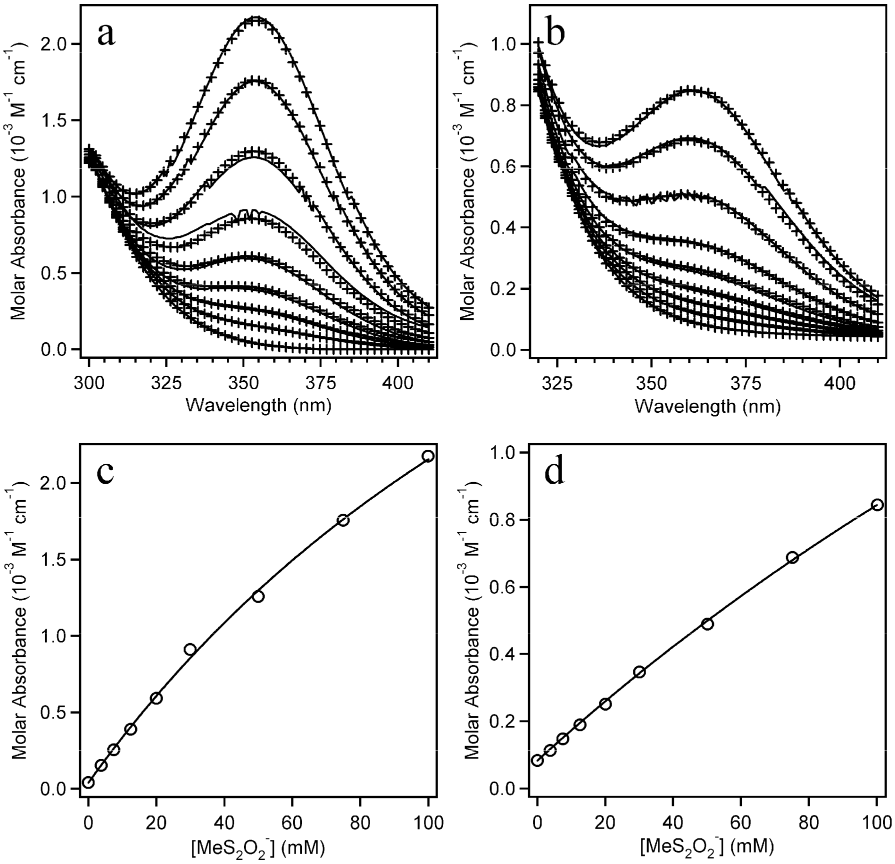

Figure 10. Changes in the UV spectrum with $MeS_2O_2^-$ concentration for $[Cu(L)(H_2O)]^{2+}$ complexes: measured (+) and calculated (−) spectra for (a) L = tren; (b) L = Me_3tren; measured (○) and calculated (—) data at λ_{max} for (c) L = tren, λ_{max} = 354 nm, and (d) *L* = Me_3tren, λ_{max} = 363 nm. The spectra were recorded in aqueous solution at pH 7.5 and $T = 25$ °C.

Table 7. Stability Constants and Spectral Data for the $[CuL]^{2+}$−$MeS_2O_2^-$/$S_2O_3^{2-}$ Systems Measured in Water at pH 7.5 and 25 °C[a]

	$MeS_2O_2^-$			$S_2O_3^{2-}$		
ligand	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	log K_f	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	log K_f
tren	354	6700	0.68 (±0.06)	356	7050	2.74 (±0.02)[b]
Me_3tren	363	4500	0.3 (±0.1)	364	6450	2.77 (0.01)[b]
Me_6tren				410	5780	1.2 (±0.1)[b]
Bz_3tren				367	5600	4.29 (±0.03)[b]
tmpa	385			388	5500	2.65 (±0.02)

[a] Values in parentheses are two standard deviations; $K_f = K_{app}(1 + (K_a/[H^+]))$. [b] Values recalculated from previous study to account for hydrolysis of the complex and converted from an activity to a concentration scale;[3] see Supporting Information.

Table 8. Measures of N−H Polarization for Tripodal Tetraamine Ligands

ligand	pK_a[a]	δ(NH)
tren	10.42(1), 9.88(1), 8.915(5)	1.36
Me_3tren	10.93(1), 10.24(1), 9.17(1)	1.30
Bz_3tren	9.16(1), 8.56(2), 7.17(3)	1.64

[a] For the protonated ligand at 25 °C; $I = 1.0$ M ($NaClO_4$) for tren[45] and Me_3tren;[44] $I = 0.1$ M (KNO_3) for Bz_3tren.[3]

of both the N−H bond of the amine ligand (the donor) and of the S−O bond of the thiosulfate/thiosulfonate anion (the acceptor).

The polarization of the N−H bond can be approximated by the chemical shifts of the amino hydrogen atoms in the ^{1}H NMR spectra of the neutral ligands (in $CDCl_3$) and by the pK_a values of the protonated ligands (in water). Lower pK_a and higher δ(NH) indicate greater polarization; accordingly, Bz_3tren has a larger δ(NH) and lower pK_a values than tren and Me_3tren (Table 8) and forms a significantly more stable thiosulfate complex with the shortest N···O intramolecular hydrogen bonding distance. For tmpa and Me_6tren, the low stability of the corresponding thiosulfate and thiosulfonate complexes can be attributed to the fact that neither tripodal ligand possesses amine protons that can engage in intramolecular hydrogen bonding with the SO_3/SO_2R moiety.

Conclusions

We have carried out the first detailed investigation of copper(II) thiosulfonate complexes. Through the application of an *N*-substituted derivative of the tripodal tetramine ligand, tris(2-aminoethyl)amine ligand, we have been able to stabilize and synthesize three copper(II) thiosulfonate complexes. The choice of ligands is critical since, as was the case of a series of thiosulfate copper(II) complexes reported recently by our group,[3] tripodal tetramine ligands are able to minimize oxidation of these oxoanions, thereby allowing their isolation and characterization. The structures of these complexes revealed that the Cu−S distances were similar to those in the related thiosulfate complexes, indicating a coordinative interaction of similar strength. In these thiosulfonate and thiosulfate complexes, two types of intramolecular hydrogen bonding interactions are evident, involving two amine N−H groups and one or two thiosulfonate oxygens. These interactions appear to be stronger in the thiosulfate complexes, and we postulate that this could be responsible for the generally higher affinity of thiosulfate, cf., thiosulfonates, for copper(II) centers. The variation in the thiosulfonate binding constant with the amine ligand was also the same as was observed for the thiosulfonate complexes. In both cases, intramolecular hydrogen bonding is proposed to tune the strength of the Cu(II)−S coordination and results in the following trend for K_f: Bz_3tren ≫ Me_3tren = tren > tmpa > Me_6tren.

Acknowledgment. We are grateful to the Australian Postgraduate Award Scheme (A.J.F) and the Australian Institute for Nuclear Science and Engineering (AINSE) for financial support.

Supporting Information Available: Crystallographic data for $[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$, $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$, and $[Cu(Me_3tren)(MeS_2O_2)]ClO_4$ in CIF format. Figure S1 (effect of the size of <MXY on intramolecular hydrogen bonding); Figures S2−S7, and Tables S1−S3 (CH/π interactions, intermolecular hydrogen bonding interactions, and crystal packing diagrams for $[Cu(Me_3tren)(MePhS_2O_2)]ClO_4$, $[Cu(Me_3tren)(PhS_2O_2)]ClO_4$, and $[Cu(Me_3tren)(MeS_2O_2)]ClO_4$. Experimental details of spectrophotometric titrations for the $[Cu(tmpa)(H_2O)]^{2+}$-$S_2O_3^{2-}$ and $[Cu(tmpa)(H_2O)]^{2+}$-$MeS_2O_3^{-}$ systems and the resultant data (Figures S8 and S9). This material is available free of charge via the Internet at http://pubs.acs.org.

IC801234C