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Inorganic Chemistry Communications 10 (2007) 631–635
INORGANIC CHEMISTRY COMMUNICATIONS
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Synthesis, characterization and reactivity of a trinuclear copper(II) thiocyanurate complex: A spin-frustrated molecular propeller

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Received 12 January 2007; accepted 22 February 2007
Available online 28 February 2007

Abstract

1,3-bis{2-(4-methylpyridyl)imino}isoindoline (**4-MeInH**) reacts with copper(II) acetate and 2,4,6-trimercaptotriazine (**H_3TMTA**) to yield [**Cu(4-MeIn)**]$_3$(**TMTA**), a trinuclear propeller complex composed of three Cu(**4-MeIn**) "blades" coordinated to a 2,4,6-trimercaptotriazine (**TMTA**) "hub". Each copper(II) center is coordinated *via* a exocyclic sulfur and a ring nitrogen from **TMTA**. Although the trimer is infinitely stable in the solid state, dark green solutions fade over time to produce a mixture of dinuclear products which are a result of both hydrolysis and desulfurization reactions. Variable temperature magnetic susceptibility measurements on [**Cu(4-MeIn)**]$_3$(**TMTA**) are consistent with a spin-frustrated doublet ground state and show the presence of moderate antiferromagnetic coupling ($-2J = 38.14\ \text{cm}^{-1}$) between the copper(II) centers.

Keywords: Thiocyanuric acid; 2,4,6-Trimercaptotriazine; Copper; Trinuclear; X-ray diffraction; Magnetism

2,4,6-Trimercaptotriazine (**H_3TMTA**) also known as thiocyanuric acid is widely utilized in waste water heavy metal remediation [1]. Although thiocyanuric acid has been known since the mid-1880s [2,3] and its structural chemistry has been extensively studied, there are few descriptions of its coordination chemistry. The majority of the coordination chemistry involves utilizing **H_3TMTA** as a building block in supramolecular arrays and hydrogen-bonded networks [4,5]. The paucity of trimers [6–9,14] among structurally characterized molecular complexes of H_3TMTA [10–12,29,16,33], has been attributed to the decreased solubility of partial metallated forms [10,13] and steric interactions between bulky co-ligands. Thiocyanuric acid is of additional interest, due to its ability to coordinate in both the thiol and thione forms (Fig. 1) [14,15]. Soft metal ions such as Cu(I) [16], Au(I) [17] are normally found as S-bound complexes, whereas hard metal ions such as lithium(I) [18] are found associated with the hetrocyclic nitrogen atom. We hypothesized that the borderline acidic nature of copper(II) could potentially allow for coordination by both the nitrogen and sulfur atoms [19].

To overcome the tendency for H_3TMTA to stabilize copper(I), we decided to use 1,3-bis{2-(4-methylpyridyl)imino}isoindoline (**4-MeInH**) [20] as a co-ligand. 1,3-bis(2-arylimino)isoindoles (**AInHs**), which have recently received increased attention [21–25], are restricted to coordinate in a meridional fashion about the metal center, thus imparting trigonal symmetry on pentacoordinate metal ions. Indeed, when [Cu(4-MeIn)(OAc)] (generated *in situ*) is allowed to react with 2,4,6-trimercaptotriazine (**H_3TMTA**) [26] a equilateral triangular complex,

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doi:10.1016/j.inoche.2007.02.015

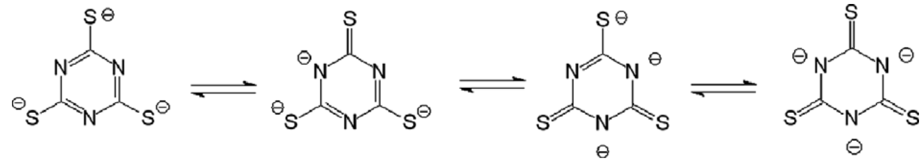

Fig. 1. The tautomeric forms of 2,4,6-trimercaptotriazine (H_3TMTA).

{[**Cu(4-MeIn)**] $_3$(**TMTA**)} equilateral Cu(II) triangular complex, {[**Cu(4-MeIn)**]$_3$(**TMTA**)} precipitates from the reaction mixture [27,28].

X-ray diffraction of a crystal of the chloroform solvate, [**Cu(4-MeIn)**]$_3$(**TMTA**) · **2.5CHCl**$_3$ [29,30] revealed a propeller-like structure composed of three Cu(4-MeIn) ''blades'' coordinated *via* a pair of nitrogen and sulfur donors from a 2,4,6-trimercaptotriazine (TMTA) ''hub''. The three copper centers are coordinated in an almost perfect square pyramidal [31] ($\tau = 0.02$ Cu(1), 0.01 Cu(2) and 0.09 Cu(3)) fashion to the 4-MeIn- ligand and the 2,4,6-trimercaptotriazine bridge. The basal plane of the square pyramid contains the N_3 coordination of a 4-MeIn- ligand and a N-donor from the 2,4,6-trimercaptotriazine moiety, whereas a Cu–S (avg. length 2.787 Å) bonds in the apical direction. The carbon–sulfur bond lengths (in the TMTA unit) are best described as varying in bond order between double (1.656 Å), one-and-half (1.668 Å) and single (1.687 Å) (A typical C–S single bond is 1.681 Å) [32] compared to the C═S (1.641–1.659 Å) bonds [16] in free H_3TMTA. The average C–S length (1.670 Å) is the same as in a monomeric nickel(II) complex with the same N,S-bis-coordination mode [33] which interestingly also shows the same variable C–S bond orders. The bond lengths between the copper(II) and **4-MeIn**$^-$ are similar to those found in the pyridyl-isoindoline copper zwitterionic complex reported by Balogh-Hergovich and co-workers (**Cu**(**I**)(**indH**)(***O*-bs**), **indH**$_2$ = 1,3-bis(2-pyridylimino)isoindoline and ***O*-bs** = *O*-benzoylsalicylate) [34]. It was originally assumed that the copper was in the +1 oxidation state, but Wicholas and co-workers speculated that this complex actually contained a copper(II) center. As the Cu–O(apical) distance (2.557 Å) is well within the accepted distances for Jahn–Teller elongated bonds of this type [35].

The similarities between the Cu-4-MeIn$^-$ bond lengths in {[Cu(4′-MeIn)]$_3$(TMTA)}, Cu–N(isoindoline) (1.905 Å), and the Cu–N(pyridyl)$_{avg}$ (2.007 Å) with those found in Cu(indH)(*O*-bs), [Cu–N(isoindoline) (1.881 Å), and the Cu–N(pyridyl)$_{avg}$ (2.008 Å)] further supports the +2 oxidation state assignment (see Figs. 2 and 3).

[**Cu(4-MeIn)**]$_3$(**TMTA**) is infinitely stable in the solid state, however, when a dark green solution of the complex is allowed to stand for extended periods of time, the solution color fades to a pale yellow to produce a mixture of dinuclear products which are a result of both hydrolysis and desulfurization reactions. Slow vapor diffusion of toluene into a faded chloroform solution of [Cu(4-MeIn)]$_3$(TMTA) resulted in a few single crystals. X-ray diffraction revealed that the crystals [29,36] were a mixture

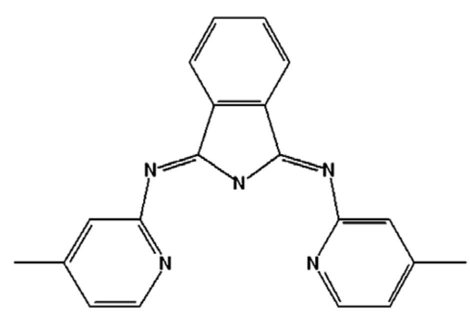

Fig. 2. 1,3-bis{2-(4-methylpyridyl)imino}isoindoline (**4-MeInH**).

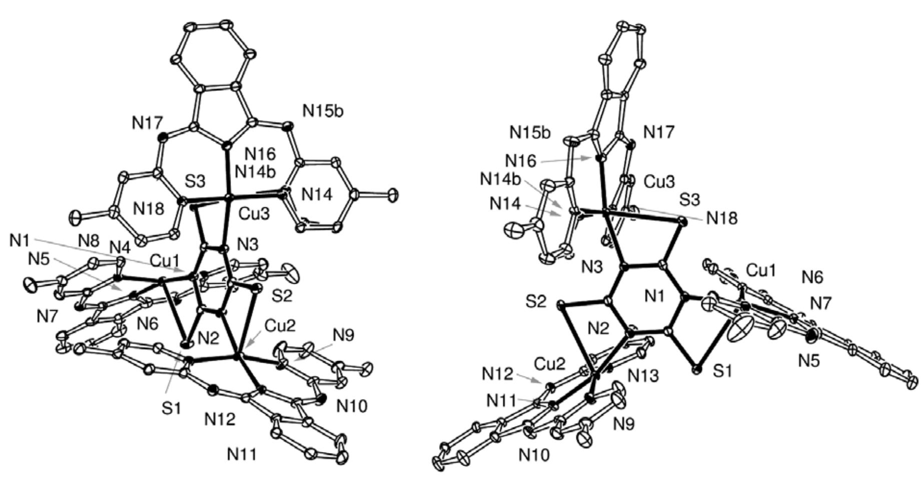

Fig. 3. ORTEP Views (30% ellipsoids) of [Cu(4-MeIn)]$_3$(TMTA) · 2.5 $CHCl_3$ (solvent and hydrogen not shown).

of 63.1% hydrolysis, {**Cu(4-MeIn)**]$_2$(**$C_3HN_3S_3$**)} and 36.9% desulfurized {**Cu(4-MeIn)**]$_2$ (**$C_3HN_3S_2$**)} products (Figs. 4 and 5). A similar reaction has been observed in a cobalt(III) complex of TMTA [37]. Repeated elemental analyses revealed deficiencies in sulfur and copper, however, these results varied widely as the degree of decomposition was variable between samples. The geometry about each copper center can again be described as nearly square pyramidal ($\tau = 0.01$ for Cu(1) and 0.12 for Cu(2)) [31]. Each basal plane is occupied by a **4-MeIn**$^-$ ligand and a triazine nitrogen donor , possessing similar bond lengths to those found in [**Cu(4-MeIn)**]$_3$(**TMTA**) . Each apical site is occupied by a μ_2-exocyclic sulfur donor of thiolate character (C–S length of 1.681 Å) which bridges the two copper centers. Cu(1) and Cu(2) are lifted out of the ligand plane by 0.401 and 0.495 Å, respectively. The remaining, uncoordinated TMTA nitrogen is protonated (the hydrogen was found in density map).

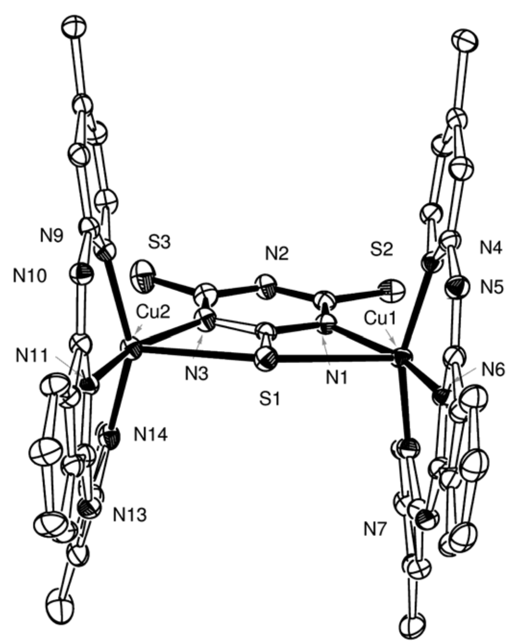

Fig. 4. ORTEP Diagrams (30% ellipsoids) of 0.631{Cu(4$^-$MeIn)]$_2$-($C_3HN_3S_3$)} · 0.369{Cu(4$^-$ MeIn)]$_2$($C_3HN_3S_2$)} · 2($CH_3C_6H_5$) · 0.282(H_2O); only ({Cu(4$^-$MeIn)]$_2$($C_3HN_3S_3$)} is shown (S_2 or S_3 are replaced by hydrogen in {Cu(4$^-$MeIn)]$_2$($C_3HN_3S_2$)}).

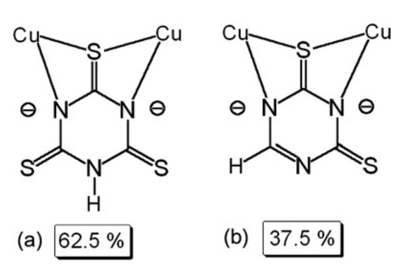

Fig. 5. Diagram of the products of (a) the hydrolysis and (b) the desulfurization reactions.

Spectroscopic Studies [38] (FT-IR and UV–visible) reveal characteristic changes in the IR spectrum indicative of presence of a deprotonated isoindoline ligand and thiocyanurate stretches [39], respectively, (absence of a strong band at 1100 cm^{-1}) absorptions in the range 1600-1660 cm^{-1}). Whereas the UV–visible spectrum of {[Cu(4-MeIn)]$_3$(TMTA)} shows two intense peaks at 421 nm (17154 M^{-1} cm^{-1}) and 441 nm (13411 M^{-1} cm^{-1}, sh), which we assign as Cu $\leftarrow$ S(σ) and Cu $\leftarrow$ S(π) LMCT transitions, respectively, [40,41]. The d–d transitions occur at 663 nm (477 M^{-1} cm^{-1}), and at 798 nm (363 M^{-1} cm^{-1}, broad shoulder) indicative of the presence of copper(II) with pseudo-D_{3h} symmetry [42]. Variable temperature magnetic susceptibility measurements [43] of [Cu(4-MeIn)]$_3$(TMTA) show the presence of moderate antiferromagnetic coupling between the copper(II) centers (Fig. 6). $\chi_m T$ at 300 K is cm^3 mol^{-1} K, which is slightly lower than the value expected for three uncoupled S$\frac{1}{2}$ centers and approaches 0.375 cm^3 mol^{-1} K (the value of a single S$\frac{1}{2}$ center) at 3 K. Such behavior is consistent with a spin-frustrated doublet ground state [44]. The variable temperature magnetic behavior of {[Cu(4-MeIn)]$_3$(TMTA)} was fit by applying the isotropic Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian $\left(\mathscr{H} = -2J\left[\widehat{S}_1 \cdot \widehat{S}_2 + \widehat{S}_2 \cdot \widehat{S}_3 + \widehat{S}_3 \cdot \widehat{S}_1\right]\right)$ to an equilaterial triangle (C_{3v}) model of spin $\frac{1}{2}$ centers. The energy, $E(S_T)$ of each state is determined from

$$E(S_T) = -J\left[S_T(S_T+1) - \sum_i S_i(S_i+1)\right] \tag{1}$$

where S_T = and where S_T is the total spin ($S_1 + S_2 + S_3$) and $S_i(i = 1,2,3)$ *is the spin of each ion.*

Since, S_T can take values $\frac{1}{2}(\uparrow\uparrow\downarrow)$, $\frac{1}{2}(\uparrow\downarrow\uparrow)$ or $\frac{3}{2}(\uparrow\uparrow\uparrow)$, the S_T $\frac{1}{2}$ state is thus doubly degenerate, with an energy $\frac{-3J}{2}$, while $S_T = \frac{3}{2}$ state has an energy of $\frac{3J}{2}$. Substitution of these $E(S_T)$ values into the Van Vleck equation [45], and including the terms for paramagnetic impurity (ρ) yields the expression for the molar magnetic susceptibility given in Eq. (2).

$$\chi_m = (1-\rho)\left[\frac{Ng^2\beta^2}{3kT}\,\frac{3+15e^{3J/kT}}{4+4e^{3J/kT}}\right] + \rho\frac{Ng^2\beta^2}{4kT} \tag{2}$$

where N is the Avogadro number, g the Landé g-factor, β the Bohr magneton, k the Boltzmann constant and T the Kelvin temperature.

The experimental $\chi_m T$ data of [Cu(4-MeIn)]$_3$(TMTA) was fit using Eq. (2). A Least-squares fit ($R^2 = 2.23 \times 10^{-4}$) produced $g = 2.00$, $J = -19.07$, $\rho = 3.50\%$. The negative sign of J indicates the presence of antiferromagnetic interactions between the copper(II) centers and therefore, the complex has a doubly degenerate $S_T\frac{1}{2}$ is the ground spin state, with the $S_T\frac{3}{2}$ state 57.21 cm^{-1} higher in energy (Fig. 5b). There are no indications of *antisymmetric exchange* interactions [46,47], as are sometimes seen in triangular complexes with nearly degenerate $S\frac{1}{2}$ states. Such behavior manifests generally as a decrease below the $\chi_m T$ value of

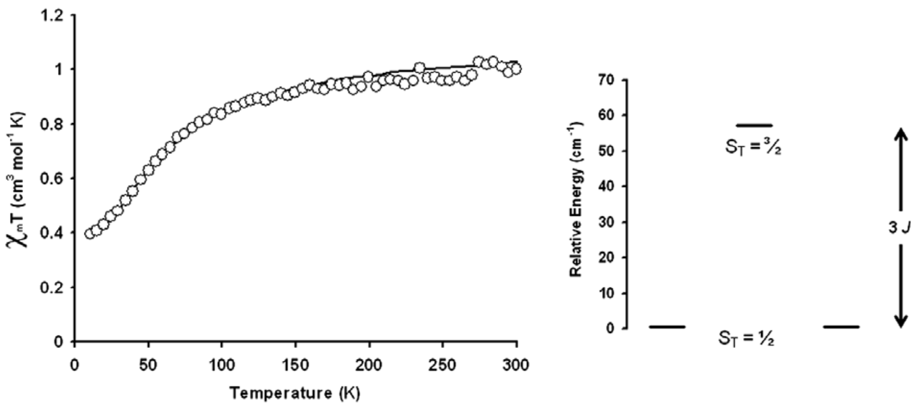

Fig. 6. (a) χ_mT *vs.* Temperature plot of [**Cu(4-MeIn)**]$_3$(**TMTA**) · **2.5CHCl$_3$**, the solid line is the best fit to the data as described in the text (b) the corresponding spin ladder.

$0.375\ \mathrm{cm^3\ mol^{-1}\ K}$ (one unpaired electron) at low temperature.

Acknowledgements

M.J.P. and N.K.P. thank La Salle University for support. The Smart Apex diffractometer was funded by NSF grant 0087210, by Ohio Board of Regents grant CAP-491, and by YSU. S.L. acknowledges support from NSF grants MRSEC DMR 0520471 and DMR 0603644.

Appendix A. Supplementary material

CCDC 627205 and 627206 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.02.015.

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[26] 2,4,6-Trimercaptotriazine (**H$_3$TMTA**) was purchased from *TCI* America.
[27] [**Cu(4-MeIn)**]$_3$(**TMTA**) · 2.5 **CHCl$_3$**. A methanolic solution (15 mL) of thiocyanuric acid (59 mg, 0.33 mmol) was added to a stirring solution of 1,3-bis{2-(4methylpyridyl)imino}isoindoline (**4-MeInH**), (0.33 g, 1 mmol in 30 mL MeOH) and Cu(OAc)$_2$ · H$_2$O (30 mg, 1 mmol in 10 mL 50:50 MeOH/H$_2$O). The resulting olive green suspension was stirred for 30 min. The precipitate was collected *via* vacuum filtration, washed with MeOH (3 × 10 mL) and dried in air. Recrystallization from hot chloroform afforded emerald green crystals (0.41 g, 81% yield). Calcd.: C 47.90, H 3.10, N 15.35 Found: C 47.63, H 3.08, N 15.24. ESI-MS: M+: 1343 (<5%); +805 (15%).
[28] Elemental microanalysis was performed by Robertson-Microlit (Madison, NJ). Electrospray mass spectra were obtained on a Micromass LC Platform with ESI mass analyzer at the Mass Spectrometry Laboratory at the University of Pennsylvania.
[29] (a) X-ray crystallographic data was collected with graphite-monochromatized Mo Kα X-ray radiation (fine-focus sealed tube) using a Brüker SMART CCD Diffractometer at 100(2) K. The weighted *R*-factor *wR* and goodness of fit are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F2 > 2\sigma(F^2)$ is used only for calculating *R*-factors. (b) Molecular structures were created using Ortep 3 (version 1.08) (L.J. Farrugia, J. Appl. Cryst. 30 (1997) 556).

[30] X-ray data on a $0.315 \times 0.19 \times 0.15$ mm olive-green crystal of $[Cu(4\text{-}MeIn)]_3(TMTA) \cdot 2.5\ CHCl_3$ were collected. Twenty-one percent of the unit cell volume consisted of chloroform filled voids. The solvent molecules were severely disordered and have been "squeezed" out using the program Platon for Windows (A.L. Spek, Acta Cryst. (1990) A46, C34, A.L. Spek, Platon – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (2000)). One of the *p*-Me-pyridine substituents is disordered over two positions with an occupancy ratio of 0.698(3)–0.302(3). The disordered six membered rings were restraint to resemble ideal hexagons and equivalent atoms were restraint to have identical anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom. Crystal data: $M = 1343.99$, Triclinic, $P\bar{1}$, $a = 14.9345(14)$ Å, $b = 15.7229(14)$ Å, $c = 17.0048(16)$ Å, $\alpha = 94.161(2)°$, $\beta = 111.924(2)°$, $\gamma = 106.300(2)°$, $V = 3484.1(6)$ Å^3, $Z = 2$, $F(000) = 1374$, GOF = 1.060, $R_1 = 0.0486$, $wR_2 = 0.1397$ $[I > 2\sigma(I)]$.

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[36] X-ray data on a $0.303 \times 0.17 \times 0.166$ mm green block of $0.631\{Cu(4^{-}MeIn)]_2(C_3HN_3S_3)\} \cdot 0.369\{Cu(4^{-}MeIn)]_2(C_3HN_3S_2)\} \cdot 2(CH_3C_6H_5) \cdot 0.282(H_2O)$ were collected at 100(2) K. All hydrogen atoms placed in calculated positions and were refined with isotropic displacement parameters 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom. Hydrogen atoms of the disordered water molecule were omitted. Crystal data: $M = 1131.32$, Triclinic, $P\bar{1}$, $a = 11.518(2)$ Å, $b = 14.944(3)$ Å, $c = 16.115(3)$ Å, $\alpha = 72.669(3)°$, $\beta = 75.519(3)°$, $\gamma = 83.297(4)°$, $V = 2561.1(8)$ Å^3, $Z = 2$, F (000) = 1168.7, GOF = 1.041, $R_1 = = 0.0563$, $wR_2 = 0.1491$ $[I > 2\sigma(I)]$.

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