

A molecular pinwheel multicopper(I) cluster, $[(L^{S^-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ with μ_4 -sulfido, μ_3 -thiolato and nitrogen ligands

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Received (in Cambridge, UK) 29th September 2005, Accepted 28th November 2005

First published as an Advance Article on the web 21st December 2005

DOI: 10.1039/b513768c

A copper(I) complex with new N_2S thiol ligand transforms to a multicopper(I) cluster, $[(L^{S^-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (**1**); its X-ray structure exhibiting μ_4 -sulfido and μ_3 -thiolato coordination is presented and compared to other cuprous thiolato/sulfido clusters including that observed in the copper enzyme nitrous oxide reductase.

From the perspective of copper protein bioinorganic chemistry, copper–sulfur interactions are widespread and of considerable current interest. A recent discovery is that a copper–sulfide cluster, $Cu_4(S)(Im)_7$ (Im = imidazole N-donor from a histidine residue), occurs at the so-called Cu_Z active site of nitrous-oxide reductase (N_2OR).¹ This is the first biological example of copper occurring together with an inorganic sulfide ion. Yet, cysteine (Cys) thiolato-copper coordination occurs in chaperone proteins and electron-transfer centers such as “blue” cupredoxins (type 1 (T1), with additional nitrogen bis-histidine (His) and methionine (thioether) coordination), and the $Cu_2(\mu_2-Cys)_2(His)_2$ cores (“ Cu_A ”) in cytochrome *c* oxidases and N_2OR 's.² Larger copper(I)–thiolate clusters, proposed as $Cu_4(\mu_2-S_{cys})_6$ moieties, are found in copper transcription factors and transporter proteins.³ A recent structure reveals that a yeast copper thionein contains a $Cu^{I}_8(Cys)_{10}$ cluster with both Cys- μ_2 and Cys- μ_3 -copper ligation.⁴

Metal–chalcogenides, including copper–sulfide materials, are also of great interest and importance in solid-state chemistry.⁵ There is also a considerable coordination chemistry of Cu–thiolate compounds, from synthetic models for mono (T1) or binuclear (“ Cu_A ”) (see above) electron-transfer protein centers,^{2,6} to an extensive gas-phase or synthetic/structural coordination chemistry with thiolate copper cluster compounds.⁷ Utilizing thiolates, polysulfide and certain ligands such as phosphanes, clusters

including $\mu_{3,4,6}$ or μ_8 -sulfido and/or μ_1 , μ_2 or μ_3 -thiolato copper compounds have been generated and structurally identified.⁸

With the copper enzyme structures described above and other chemistry involving thiolates and copper protein active sites,[†] our own interests have evolved to further study copper ion chemistry with ligands containing a thiolate and additional nitrogen donor. Here, we report the synthesis of a new tridentate N_2S thiol ligand, $L^{SH,\ddagger}$ and the generation of a cuprous cluster compound $[(L^{S^-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (**1**), possessing μ_4 -sulfido and μ_3 -thiolato coordination (Fig. 1). A copper(I) complex of L^{SH} , $[(L^{SH})Cu^I]ClO_4$,§ was dissolved in a 1 : 1 mixture of acetonitrile and dimethylformamide in a N_2 -filled glove-box, and layered with

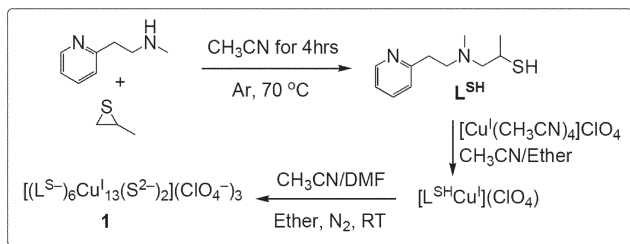


Fig. 1 Synthetic scheme for the title compound **1**, the μ_4 -Sulfido μ_3 -Thiolato- Cu_{13} cluster.

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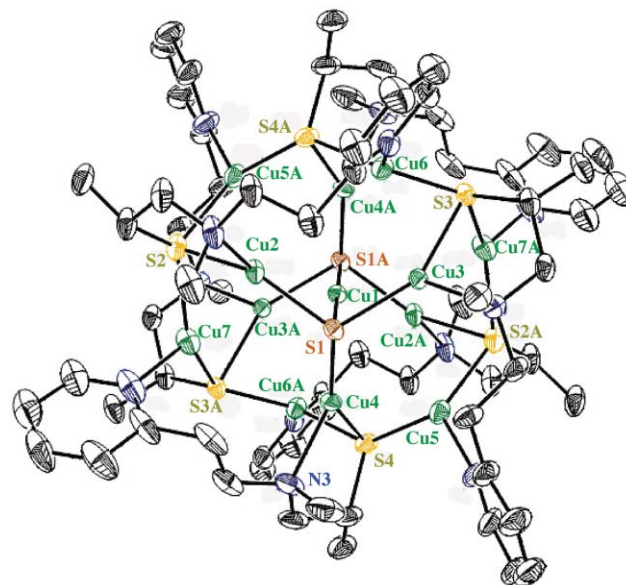


Fig. 2 ORTEP view (50% probability ellipsoids) of the cluster complex $[(L^{S^-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (**1**). Perchlorate counter anions and hydrogen atoms are omitted for clarity. Cu = green; Sulfido = orange; Sthiolate = yellow; N = blue; C = black.

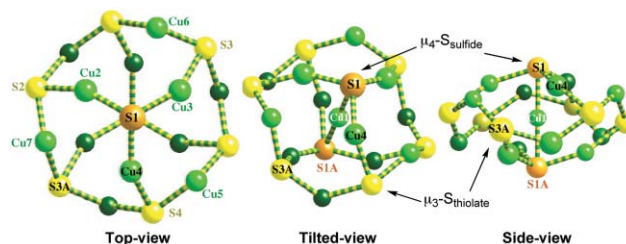
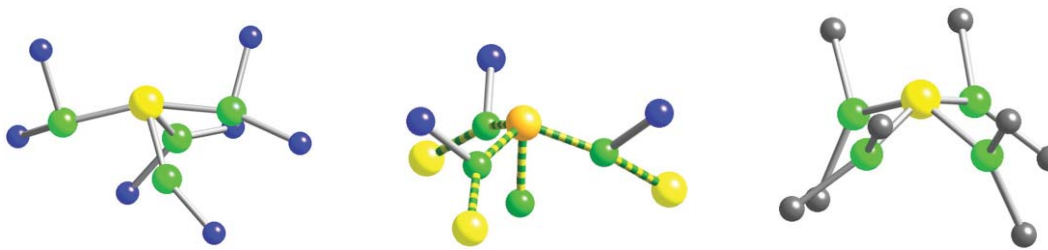


Fig. 3 Three different views of the core structure of the cluster.

Table 1 Comparison of μ_4 -sulfide copper(I) cluster core structures within N_2OR , complex **1** and $[Cu_4(\mu-dppm)_4(\mu_4-S)]^{2+}$ 

Cluster	N_2OR	Complex 1	$[Cu_4(\mu-dppm)_4(\mu_4-S)]^{2+}$ ⁹
Ave Cu–S distance	2.246	2.247, 2.182 (axial)	2.268 (Å)
Geometry	Seesaw	Distorted pyramid	Distorted square pyramid

diethylether. From that solution, yellow crystals formed slowly (over a few weeks). The molecular structure of **1** was determined by X-ray crystallography.[¶] The trication, $[(L^{S-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (Fig. 2) is comprised by thirteen copper(I) ions, six thiolate L^{S-} ligands, two sulfide anions along with three perchlorate counter anions. The two sulfide anions must derive from the thiol ligand (L^{SH}), with associated C–S bond cleavage chemistry occurring during the crystallization process. Nevertheless, the synthetic procedure to produce crystalline complex **1** is reproducible.^{||}

At the center of the cluster, with overall ‘pinwheel’ macrostructure, there is a linear (imposed by crystal symmetry) two-coordinate copper(I) ion ($\angle S1-Cu1-S1A = 180^\circ$) (Fig. 2); this $S1-Cu1-S1A$ vector constitutes the ‘pin’ axis of the cluster. Sulfide $S1$ also bonds to three Cu(I) ions Cu_2 , Cu_3 and Cu_4 (average Cu–S distance = 2.247 Å), which are arranged trigonally, and which constitute a plane found “in front” of the $S1-Cu1-S1A$ vector as viewed in Fig. 2 and 3; in fact, the $S1$ sulfide lies outside (further ‘in front’) of the $Cu_2Cu_3Cu_4$ plane. Similarly, Cu_2A , Cu_3A and Cu_4A are behind that same vector (Fig. 2 and 3), all bonded to $S1A$. The $Cu-S1-Cu'$ angles (Cu, Cu' are Cu_2, Cu_3 or Cu_4) and symmetry related $Cu-S1A-Cu'$ (Cu_2A, Cu_3A, Cu_4A) angles are not equivalent, and range from 110.0° to 112.2° . The six copper ions (Cu_2-Cu_4, Cu_2A-Cu_4A) constitute an inner layer of the macro pinwheel cluster, all having similar distances to $Cu1$ ($Cu-Cu1 = 2.62$ (ave.) Å), see also the views shown in Fig. 3.

These same inner six Cu(I) ions possess trigonally distorted coordination geometries, since two of the donors are the $N_{alkylamino}$ and thiolato atoms of a given L^{S-} ligand {For example Cu_4 is bound to $S1$, plus thiolate S_4 and N_3 }, thus the angle subtended is close to 90° (and not 120°). Note, that these thiolates, $S_2, S_3, S_4, S_2A, S_3A, S_4A$, are μ_3 -coordinated to additional external outer shell copper(I) ions, two of them, e.g., S_4 is bound to Cu_5 and Cu_6A (Fig. 1).

The outermost copper ions, (Cu_5, Cu_6, Cu_7 , and Cu_5A, Cu_6A , and Cu_7A), are also three-coordinate, nearly planar and with all angles within 10° of 120° ; the ligand donors are two μ_3 -thiolates and a pyridine nitrogen donor, one thiolate and the pyridine originating from the same L^{S-} ligand (Fig. 1).

Each sulfide anion ($S1$ and $S1A$) with four cuprous ions in the core of the cluster compound forms a distorted pyramidal geometry, which quite reasonably structurally models the corresponding Cu_4S cluster in N_2OR . (Table 1) The average Cu–sulfide distance (2.247 Å, excluding the axial distance 2.182 Å to the

fourth copper, $Cu1$) is fairly similar to that of N_2OR , which has a Cu_4S seesaw geometry. For additional comparison, a tetranuclear Cu_4S cluster compound possessing *dppm* (bis(di-phenylphosphino)methane) outer co-ligands, $[Cu_4(\mu-dppm)_4(\mu_4-S)]^{2+}$, has a distorted square pyramidal arrangement of the cuprous and sulfide ions (Table 1).^{9,10}

As mentioned, reductive cleavage of the C–S bond has occurred during the synthesis of $[(L^{S-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (**1**). We have not presently examined the mechanism of this reaction in this case, but the process has precedent. A disulfide moiety in a dicopper(II) complex $[(Tp)Cu]_2(\mu_2S_2^{2-})$ ($Tp =$ hydrotris(3,5-diiso-propyl-1-pyrazolyl)borate) derives from C–S cleavage chemistry of the thiolate in a precursor complex $(Tp)Cu^{II}-SCPh_3$.¹¹ There are many other examples of metal (e.g., Nb, Zr, Re) mediated thiol C–S bond activation.¹²

In summary, a novel pinwheel shaped cuprous ion complex, $[(L^{S-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ (**1**), has been generated, transformed from a (L^{SH})-copper(I) precursor complex. The cluster possesses μ_3 -thiolato coordination, which in fact is relatively rare.⁸ The environment about the central μ_4 -sulfido atom provides the first example of a distorted pyramidal construction of a Cu_4S core, which like N_2OR also has nitrogen ligands bound to copper, thus comparing favourably to a large number of other Cu–S clusters with respect to its similarity to the Cu_Z center of N_2OR . $[(L^{S-})_6Cu^{I}_{13}(S^{2-})_2]^{3+}$ possesses cuprous and sulfido ions, as well as thiolates, thus many fully reduced sites. Thus, future studies will be directed toward small molecule substrate reduction reactions, including transformation of the kinetically inert biologically important N_2O molecule.

K. D. K. gratefully acknowledges support from the National Institutes of Health (USA) for research support.

Notes and references

† In the active site of galactose oxidase (a copper enzyme oxidizing alcohols to aldehydes), an unusual cross-linked tyrosine–cysteine moiety is found. Histidine–cysteine cross-linkages are found in catechol oxidase, molluscan hemocyanins and tyrosinase (*Neurospora crassa*). The formation of these moieties occurs during post-translational protein processing, via copper mediated oxidative (with O_2) chemistry.

‡ L^{SH} ligand synthesis: 2-(2-methylaminoethyl) pyridine (1.14 g, 8.12 mmol) and propylene sulfide (0.75 g, 9.91 mmol) were refluxed in acetonitrile (50 ml) for 4 h under Ar. After cooling, the solvent was removed by rotary evaporation. The resulting organic mixture was purified by column chromatography (Al_2O_3 , Eluent: 3/2 hexane/ethyl acetate, $R_f = 0.7$) to give yellow oil (1.24 g, 72.7%). δ_H (400 MHz; $CDCl_3$; Me_4Si): 8.52(1H, dq, py),

7.59 (1H, td, py), 7.19 (1H, d, py), 7.11 (1H, dd, py), ~2.9 (5H, m, CH₂), 2.40 (2H, m, CH₂), 2.30 (3H, s, NMe), 1.21 (3H, d, Me).

§ [L^{SH}Cu^I](ClO₄)(Et₂O)_{1/6} synthesis: L^{SH} (0.79 g, 3.7 mmol) and [Cu^I(MeCN)₄](ClO₄) (1.2 g, 3.7 mmol) were stirred in acetonitrile (50 ml) under Ar at room temperature. The complex was precipitated as a yellow solid upon addition of diethyl ether. The solvent was decanted, washed two times with diethyl ether and dried under vacuum giving 1.38 g (96%). δ_{H} (400 MHz; Acetonitrile-*d*₃): 10.3 (1H, br, SH), 8.58 (1H, br, py), 7.82 (1H, tt, py), ~7.35 (2H, m, py), ~3.20 (7 H, m, CH₂), 3.41 (q, diethylether-CH₂), 2.91 (3H, br, NMe), ~1.4 (3H, br, Me), 1.12 (t, diethylether-CH₃); δ_{C} (Acetonitrile-*d*₃): 158.9, 149.3, 139.2, 124.9, 123.7, 66.1 (diethylether), 65.0, 57.1, 40.1, 29.2, 28.6, 24.2, 15.6 (diethylether). The thiol proton peak (10.3 ppm) disappeared upon addition of D₂O; Elemental analysis: %C = 36.06 (Calc. 36.33), %H = 5.16 (Calc. 5.14), %N = 7.07 (Calc. 7.26). Alternative formulations for [L^{SH}Cu^I](ClO₄)(Et₂O)_{1/6}, i.e., as a disulfide-Cu^I₂ complex or as a neutral thiolate-Cu^I species, are ruled out, the former on the basis of ¹H-NMR spectroscopy (the thiol SH proton is present, see above) and the latter because the presence of perchlorate (by IR spectroscopy and elemental analysis) has been confirmed.

¶ A suitable single crystal of [(L^{S-})₆Cu^I₁₃(S²⁻)₂](ClO₄)₃ (**1**) was mounted in Paratone-N oil on the end of a glass fiber and transferred to the N₂ cold stream of an Oxford Diffraction Xcalibur3 system equipped with Enhance optics and a CCD detector. The frames were integrated with the Oxford Diffraction *CrysAlisRED* software package. (*CrysAlis* CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta) A face indexed absorption correction and an inter-frame scaling correction were also applied. The structure was solved using direct methods and refined using the Bruker *SHELXTL* (v6.1) software package. (Sheldrick, G.M. (2000) The program SQUEEZE (Platon) was used to eliminate the electronic contribution of ill-defined solvent. (*Acta Crystallogr.*, 1990, **A36**, C34). **Crystal structure determination of [(L^{S-})₆Cu^I₁₃(S²⁻)₂](ClO₄)₃, compound **1**:** Crystal data. C₆₆H₁₀₂N₁₂S₈Cu₁₃, 3 (ClO₄) 0.8 (C₂H₃N), 0.4 (H₂O), *M* = 2484.50, triclinic, *a* = 14.4548(6) Å, *b* = 15.4470(9) Å, *c* = 23.9059(8) Å, α = 90.538(5)°, β = 104.774(3)°, γ = 117.284(4)°, *T* = 110 K, space group *P*-1, *Z* = 2, μ (Mo-K α) = 3.31138 mm⁻¹, 64 153 reflections measured, 20 897 unique (*R*_{int} = 0.0340). The final *R*₁ (*I* > 2 σ (*I*)) was 0.0463. CCDC 285664. The crystal contains two distinct clusters in each unit cell. The connectivity of each is identical; there are slight variations in the torsion angles of the thiolate ligands. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513768c

|| The generation of the cluster (**1**) proceeds according to the procedure outlined above in modest yields (<30%), but it is reproducible, as confirmed by X-ray (unit cell determination). ESI mass spectrometry does not yield the parent ion, but gave peaks (centered at *m/z* 609) corresponding to two thiolate ligands and three cuprous ions, not whole cluster mass peaks.

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