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# An $S_4$-Symmetric Mixed-Valent Decacopper Cage Comprised of $[Cu^{II}(L\text{-}S_2N_2)]$ Complexes Bridged by $Cu^{I}(MeCN)_n$ ($n$ = 1 or 2) Cations

Skylar J. Ferrara, Bo Wang and James P. Donahue *,†

**Abstract**. Oxidative addition of 1,2,11,12-tetrathia-5,8,15,19-tetra(*N*-methylamino)cycloicosane, the bis(disulfide) form of *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)ethylenediamine ($L$-$N_2S_2$) to $[Cu(MeCN)_4][BF_4]$ (2.5 eq) in MeCN produces good yields of the decacopper cage compound $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4][BF_4]_6\cdot 2.25MeCN$, $[\mathbf{1}][BF_4]_6\cdot 2.25MeCN$. This mixed-valent hexacation shows idealized $S_4$ point group symmetry and is composed of four $[Cu^{II}(L\text{-}N_2S_2]$ centers held in distorted four-coordinate environments and joined by $\mu_2$-$Cu^{I}(MeCN)_2$/$\mu_3$-$Cu^{I}(MeCN)$ ions that bridge their thiolate sulfur atoms. Each four-coordinate $[Cu^{II}(L\text{-}N_2S_2)]$ center is related to the other three by successive executions of the $S_4$ operation. A dark violet color is observed for $[\mathbf{1}]^{6+}$ and attributed to a combination of metal-to-ligand (S), ligand (S)-to-metal, and, at lower energy, intermetal charge transfer transitions, as found for $Cu_5$ cage compounds with a compositional relationship to $[\mathbf{1}]^{6+}$.

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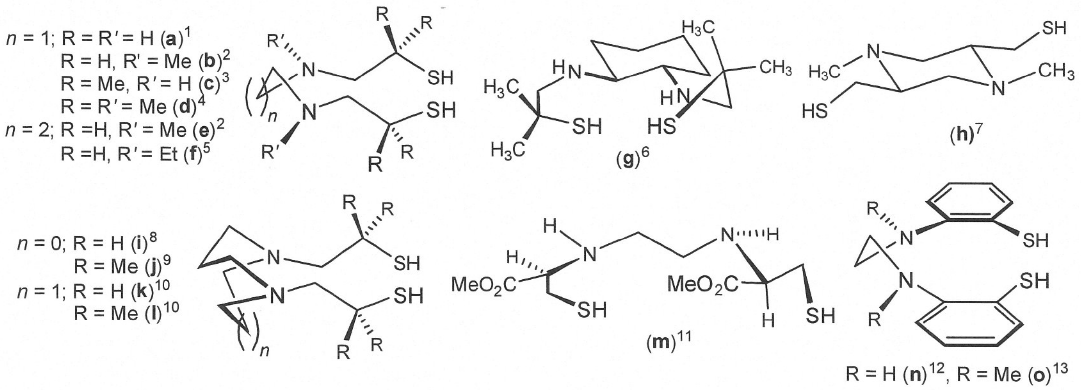
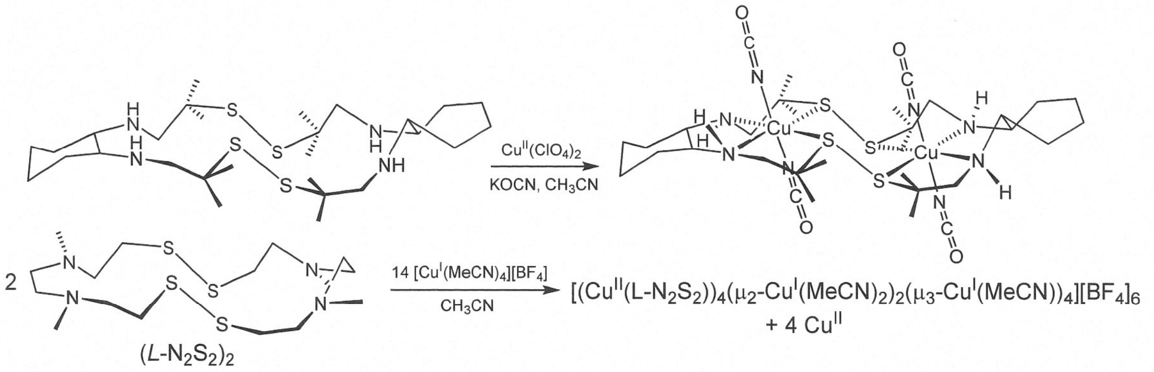


**Figure 1**. A summary of selected bis(amine) bis(thiol) ligands, L-$N_2S_2$.[1-13]

## Introduction

Tetradentate bis(amino) bis(thiolate) ligands, represented generically hereafter as *L*-$N_2S_2$, have been employed extensively as supporting ligands in the synthesis of coordination complexes intended as analogues of metal sites in biology, where the *N*-donor and *S*-donor atoms approximate histidine/amide nitrogen and cysteinate binding, respectively. Among the advantages of this general ligand type are facile modification of the ligand architecture, including the alkyl chain spacing between nitrogen atoms, alkylation of the amine nitrogen atom, placement of substituents on the linkers joining amine nitrogen and thiolate sulfur atoms, and incorporation of either alkyl-type or aryl-type thiolate. **Figure 1** illustrates selected variants of this ligand type.[1-13] Over the preceding several decades, numerous *L*-$N_2S_2$ complexes with the transition metals have been reported as spectroscopic, redox, structural and reactivity benchmarks against which metal sites in biology have been usefully compared and assessed.[14]

In studies aimed at the synthesis of analogues of the $Cu_Z$ and $Cu_A$ sites of nitrous oxide reductase, an important enzyme occurring in various proteobacteria and archaea which accomplishes the last step in nitrate dissimilation,[15] we have been motivated to examine the coordination chemistry of copper with various tetradentate bis(amino) bis(thiolate) ligands. Currently, the principal structure types found for



**Scheme 1** Use of the disulfide form of ligand (**g**) in **Figure 1** with a Cu(II) source results in copper incorporation with intact disulfide (top). A Cu(I) source with disulfide form of (**b**), **Figure 1**, produces a decanuclear cage compound (bottom).

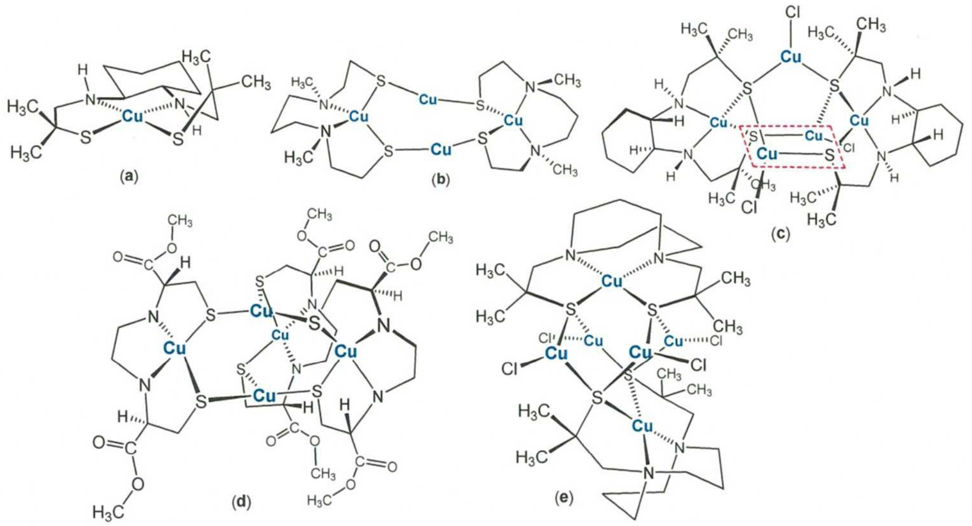


**Figure 2**. The distinctive structure types formed by bis(amine) bis(thiolate) ligands with copper.

copper with this ligand type are mononuclear $[Cu^{II}(L\text{-}N_2S_2)]$,[6,16,17] tetranuclear $[(Cu^{I}(L\text{-}N_2S_2))_2(\mu\text{-}Cu^{I})_2]$,[5] pentanuclear $[(Cu^{II}(L\text{-}N_2S_2))_2(\mu_2\text{-}Cu^{I}Cl)_3]$[16,18] and $[(Cu^{II}(L\text{-}N_2S_2))_3(\mu_3\text{-}Cu^{I})_2]^{2+}$ [11] and hexanuclear $[(Cu^{II}(L\text{-}N_2S_2))_3(\mu_2\text{-}Cu^{I}Cl)_4]$[19] (**Figure 2**). The preparation of these complexes usually involves either the displacement of halide from Cu(I)[5] or exchange of acetylacetonate from $Cu^{II}(acac)_2$ by protonolysis with the bis(amino) bis(thiol) form of the ligand.[6,16,17] Synthesis of mixed-valent multinuclear species generally follows from addition of a Cu(I) source to isolated $[Cu^{II}(L\text{-}N_2S_2)]$.[16,19] Addition of a bis $L\text{-}N_2S_2$ disulfide, the oxidized form of the bis(thiol) ligand, to $Cu^{II}$ results in incorporation of metal with preservation of the disulfide linkages and with exogenous ligand occupying the axial positions in an octahedral configuration (**Scheme 1**, top).[6] Upon introducing the bis(disulfide) version of ligand (**b**) (**Figure 1**) to a $Cu^{I}$ source, rather than $Cu^{II}$, we have identified a type of multi-copper cage compound with the $L\text{-}N_2S_2$ ligand that has not previously been reported, the preparation and structure of which are reported herein.

## Synthesis and Structure

Addition of 1,2,11,12-tetrathia-5,8,15,19-tetra(*N*-methylamino)cycloicosane, the bis(disulfide) form of *N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)ethylenediamine ((**b**), **Figure 1**) to $[Cu^{I}(MeCN)_4][BF_4]$ in dry MeCN is attended by the rapid onset of a deep violet color that is indicative of $Cu^{I}/Cu^{II}$ mixed valency. Readily crystallized by diffusion of $^{t}$BuOMe vapor into a MeCN solution, this violet species was identified by X-ray crystallography as $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4][BF_4]_6$, $[\mathbf{1}][BF_4]_6$ (**Scheme 1**, **Figure 3**). The eight reducing equivalents necessary to produce eight thiolate sulfur ions, in conjunction with the incorporation of only four cupric cations, requires the consumption of an additional four Cu(I) ions as reducing agent. The assembly of $[\mathbf{1}]^{6+}$ thus demands the use of 14 eq of

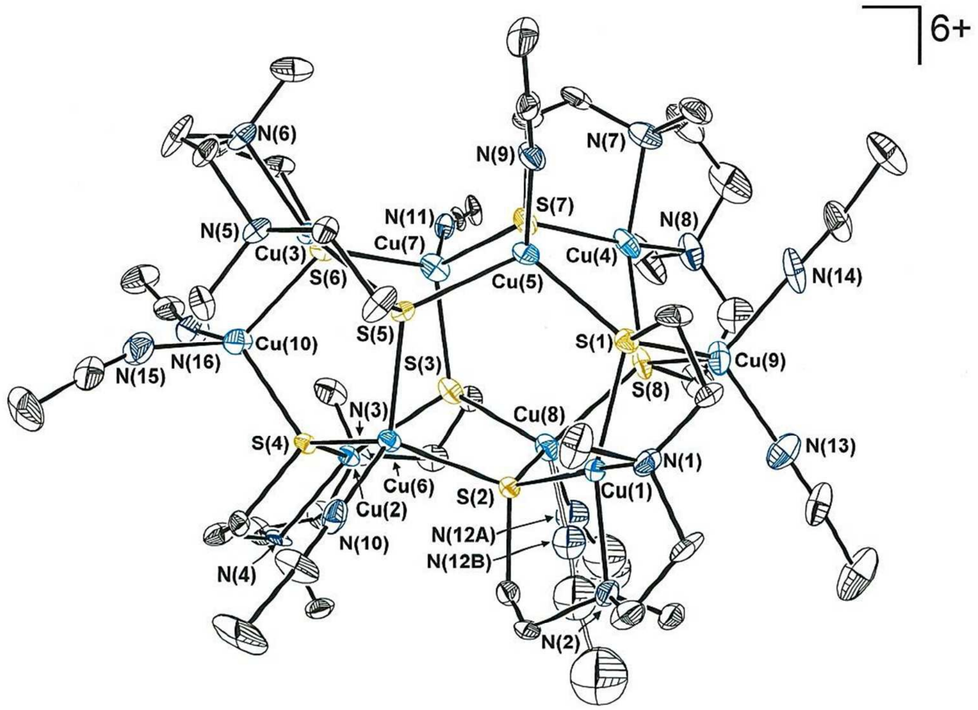


**Figure 3**. Thermal ellipsoid plot of $[\mathbf{1}]^{6+}$ at the 40% probability level. One of two independent cations in the asymmetric unit of the cell is shown. Hydrogen atoms are omitted for clarity.

$[Cu^I(MeCN)_4][BF_4]$. The UV-vis absorption spectrum of $[\mathbf{1}]^{6+}$ reveals a shoulder at ~320 nm and broad absorption bands at ~ 370 and ~570 nm that are undoubtedly comprised of multiple overlapping bands (**Figure S1**). The absorption spectrum of the pentacopper compound shown as (**c**) in **Figure 2** has been deconvoluted and modeled as six distinct bands arising from a combination of metal-to-ligand (S), ligand (S)-to-metal, and, at lower energy, intermetal charge transfer transitions. Given that (**c**) in **Figure 2** has the same ratio of $Cu^{II}/Cu^I$ as $[\mathbf{1}]^{6+}$, with the same type of bridging thiolate ligands between them, it is undoubtedly the case that a qualitatively similar mixture of transitions produces the violet color of $[\mathbf{1}]^{6+}$.

A thermal ellipsoid plot of one of two independent cations of $[\mathbf{1}]^{6+}$ is presented in **Figure 3**; unit cell and refinement data are collected in **Table 1**, while **Table 2** summarizes selected averaged interatomic distances and angles. A drawing of the three-dimensional structure of $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^I(MeCN)_2)_2(\mu_3\text{-}Cu^I(MeCN))_4]^{6+}$, drawn with fidelity to the crystallographically determined structure (**Figure 4**), is shown in **Figure 4** (**a**) but in an orientation rotated by 90° from the arrangement in **Figure 3**. Bond distances and angles in $[\mathbf{1}]^{6+}$ are similar to corresponding parameters found for (**a**) and (**c**), **Figure 2**. The nonbonding Cu(9)···Cu(10) distance is 8.679(3) Å.

Although the roughly oblong shape to $[\mathbf{1}]^{6+}$ does not effectively convey attention to any particular symmetry, close inspection shows that its idealized structure belongs to the $S_4$ point group. This fact is more easily appreciated in the colored presentation of the same drawing in **Figure 4**, (**b**). The $S_4$ axis is

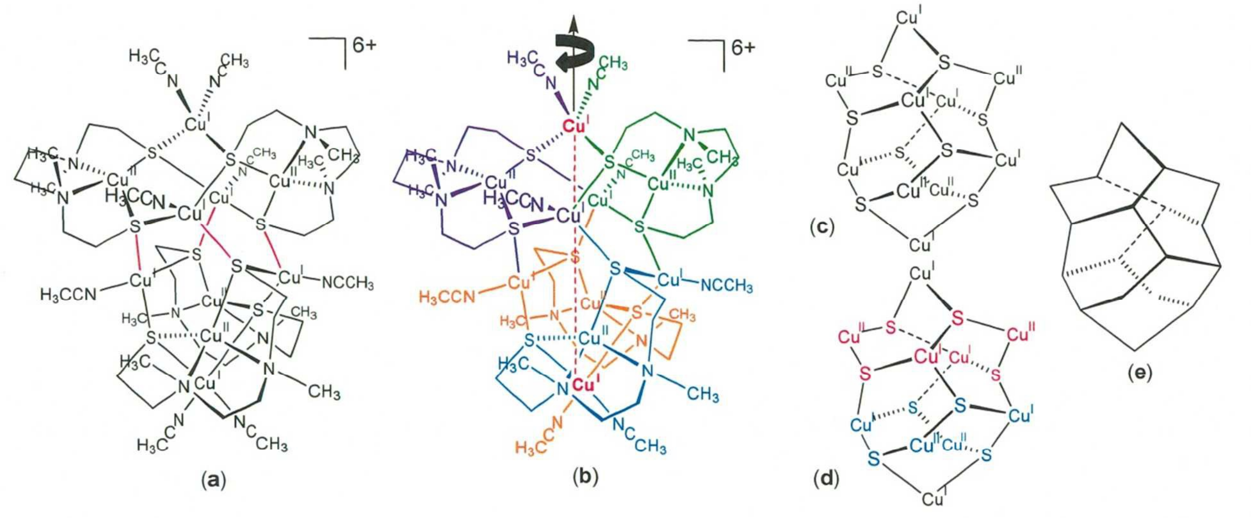


**Figure 4**. Drawings of cation $[\mathbf{1}]^{6+}$ showing (**a**) its relationship to pentacopper compound (**c**), **Figure 2** by "dimerization' via the formation of $Cu^I\cdots S$ interactions (in red); (**b**) the four distinct "quadrants" of $[\mathbf{1}]^{6+}$, which are symmetry-related by an $S_4$ axis; (**c**) the core topology of $[\mathbf{1}]^{6+}$, as defined by the copper and thiolate sulfur ions; (**d**) the core structure as formed by the fusion of two eight-membered rings of alternating Cu and S ions; (**e**) the core architecture of $[\mathbf{1}]^{6+}$ represented as a line drawing.

defined by the vertically disposed $Cu^I$ ions shown in red (Cu(9) and Cu(10), **Figure 4**), while the four quadrants that are interchanged by the $S_4$ operation are identified with different colors. Beginning with the section colored in green, clockwise execution of the $S_4$ operation moves that green section successively to the blue, the violet, and the orange portions before return to the initial position. This cation bears a structural relationship to the $C_2$-symmetric pentacopper compound shown as (**c**) in **Figure 2**. The fusion of two such pentacopper molecules by the joining their $Cu_2S_2$ faces outlined in red (**Figure 2**, (**c**)) with four new Cu·····S contacts results in a condensation product possessing the same structure as $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^I(MeCN)_2)_2(\mu_3\text{-}Cu^I(MeCN))_4]^{6+}$ in **Figure 4** (**a**). Correspondingly, severing of the structure in (**a**) of **Figure 4** across the dative S → Cu(I) interactions shown in red illustrates how $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^I(MeCN)_2)_2(\mu_3\text{-}Cu^I(MeCN))_4]^{6+}$ could be separated into $C_2$-symmetric halves that are analogous to (**c**) in **Figure 2**. The fusion of these two $C_2$-symmetric fragments with an anti-parallel disposition of their $C_2$ axes gives rise to the $S_4$ axis, the existence of which requires that the separate $Cu_5$ fragments constituting the top and bottom halves of the $Cu_{10}$ cage be mirror images. The chirality at the pyramidal nitrogen atoms of the $L$-$N_2S_2$ ligands in the top half of the cation (green and violet) is all (*S*), while the opposite (*R*) handedness is present at the four pyramidal nitrogens at bottom (blue and orange). The core topology of this cage species, illustrated in **Figure 4** (**c**) with all peripheral ligands excised, can be described as a set of eight fused cyclohexyl rings. Two pairs of cyclohexyl rings occur at top and bottom, defined by the colored cyclooctyl rings, with a Cu(I) ion bridging the 1,5 positions. The joining of these eight-membered rings by new Cu···S contacts at alternating vertices (in red, (**c**) in **Figure 4**)

**Table 1**. Summary of Crystal Data

| | [**1**][$BF_4$]$_6$·2.25MeCN |
|---|---|
| Empirical formula | $C_{52.5}H_{102.75}B_6Cu_{10}F_{24}N_{18.25}S_8$ |
| Formula weight | 2402.51 |
| Temperature, K | 150 |
| Wavelength, Å | 0.71073 |
| Crystal system | monoclinic |
| Space group | *Pn* |
| *a*, Å | 14.014(3) |
| *b*, Å | 31.074(6) |
| *c*, Å | 21.818(4) |
| $\alpha$, deg. | 90 |
| $\beta$, deg. | 90.39(3) |
| $\gamma$, deg. | 90 |
| $V$, Å$^3$ | 9501(3) |
| $Z$ | 4 |
| $\rho_{\text{calcd}}$, g·cm$^{-3}$ | 1.680 |
| $\mu$, mm$^{-1}$ | 2.457 |
| F(000) | 4838 |
| Crystal size, mm | 0.42 x 0.37 x 0.34 |
| Color, habit | purple block |
| θ range, data collection | 1.842 – 26.373 |
| Reflections collected | 142,127 |
| Independent reflections | 38,673 |
| Trans. factors (min/max) | 0.362, 0.487 |
| Data/restraints/param. | 38673/44/2066 |
| R1,[a] wR2[b] (I > 2σ(I)) | 0.0750, 0.1671 |
| R1,[a] wR2[b] (all data) | 0.0798, 0.1691 |
| Goodness-of-fit | 1.136 |
| Largest difference peak | 1.341 |
| Largest difference hole | -1.434 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

creates an additional set of four fused six-member rings. The $C_{18}H_{24}$ hydrocarbon that is topologically analogous to the core structure of [**1**]$^{6+}$ (**Figure 4**, (**e**)), with $CH_2$ and CH groups substituting for $\mu_2$-Cu and for $\mu_3$-S or $\mu_3$-Cu, respectively, has been assessed computationally but appears to have never been synthesized.

**Table 2**. Selected averaged[a] interatomic distances (Å) and angles (deg.) for [**1**]$^{6+}$.

| | | | |
|---|---|---|---|
| $Cu^{II}—S$ | 2.247[1] | $S—Cu^{II}—S$ | 100.71[5] |
| $Cu^{II}—N$ | 1.904[3] | $N—Cu^{II}—N$ | 86.9[2] |
| $(MeCN)Cu^{I}—S$ | 2.308[1] | $N—Cu^{II}—S_{cis}$ | 88.7[1] |
| $(MeCN)_2Cu^{I}—S$ | 2.296[1] | $N—Cu^{II}—S_{trans}$ | 161.7[1] |
| $(MeCN)_2Cu^{I}\cdots Cu^{I}(MeCN)_2$ | 8.652[2] | $S—Cu^{I}(MeCN)—S$ | 109.18[3] |
| $\theta^{b}$ | 23.4 | $S—Cu^{I}(MeCN)_2—S$ | 101.40[7] |

[a]Uncertainties in averaged quantities are propagated according to the general formula for uncertainty in a function of several variables as detailed by Taylor, J. R. *An Introduction to Error Analysis*; University Science Books: Sausalito, California, 1997, pp. 73-77. [b]θ = average angle between $S–Cu^{II}–S$ and $N–Cu^{II}–N$ planes.

## Concluding remarks

A defining characteristic of mononuclear $[M(L\text{-}N_2S_2)]^n$ complexes is their capacity to act as chelating bis(thioether) ligands, particularly toward soft metal ions such as $Cu^I$ and $Ag^I$. It is undoubtedly this tendency that, once some quantity of $[Cu^{II}(L\text{-}N_2S_2)]$ has formed by oxidative addition to Cu(I) of bis(disulfide) form of ligand **b**, drives the formation of $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4]^{6+}$ and depletes the remaining free Cu(I). Comprised of ten copper ions, $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4]^{6+}$ is, to the best of our knowledge, the highest nuclearity species to have been isolated with a bis(amino) bis(thiolate) tetradentate ligand. It is probable that the variants of this ligand type with methyl groups germinal to the thiolate sulfur donor ((**c**), (**d**), (**g**), (**j**), (**l**) in **Figure 1**) are unable to form this structure type because of the interior congestion that would be occasioned by dimerizing two $Cu_5$ fragments, as illustrated in **Figure 4** (**a**). At the same time, no obvious factor seems to preclude the formation of structures even larger than $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4]^{6+}$. For example, the two $Cu^{I}(MeCN)_2$ ions that reside on the $S_4$ axis (**Figure 4**, (**b**)) could undergo displacement of the MeCN ligands by additional $[Cu^{II}(L\text{-}S_2N_2)]$, thereby forming a dodecanuclear species while preserving the $S_4$ symmetry and overall charge. We venture the supposition that multiple factors - ligand sterics, charge accumulation, initial ratio of $L\text{-}N_2S_2$ ligands to $M^I$, initial concentration – exert collective effect on the product outcome and that deeper, more systematic study of these variables may disclose new structure types.

## Experimental

**General considerations.** The following reaction and associated manipulations were performed under a $N_2$ atmosphere using modified Schlenk techniques and a glove box. Acetonitrile was distilled according to standard protocol,[20] $Et_2O$ was dried using a system of drying columns from the Glass Contour Company, and $^t$BuOMe was dried over calcium sulfate and stored over activated molecular sieves. The *N*,*N′*-dimethyl-*N*,*N′*-bis(2-mercaptoethyl)ethylenediamine ligand was prepared according to literature procedure,[2] while the UV-vis spectrum was recorded with a Hewlett-Packard 8452A diode array spectrophotometer.

**Synthesis.** To a light yellow semi-suspension of 1,2,11,12-tetrathia-5,8,15,19-tetra(*N*-methylamino)cycloicosane (0.1089 g, 0.2638 mmol) in 35 mL of dry MeCN was added $[Cu^{I}(MeCN)_4][BF_4]$ (0.2075 g, 0.6595 mmol) in one portion, which induced the formation of a uniform, dark purple solution. This solution was stirred at ambient temperature for 2 hr and then evaporated to dryness. The resulting deep violet residue was washed with $Et_2O$ (2 x 10 mL). Dissolution in MeCN (15 mL) followed by filtration through a packed Celite pad under $N_2$ and evaporation of the filtrate to dryness afforded a deep purple solid. Yield: 0.139 g, 97% based upon $Cu^{I}$ as limiting reagent). Large, deep violet slab-shaped crystals were grown by diffusion of $^{t}$BuOMe vapor into a concentrated MeCN solution. UV-vis (MeCN), $\lambda_{max}$ ($\varepsilon_M$): 321 (shoulder, 4310), 365 (shoulder, 3830), 569 (1690).

**Physical methods.** Purple block-shaped crystals of $[Cu^{II}(L\text{-}N_2S_2)]_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4][BF_4]_6\cdot 2.25MeCN$ were obtained by slow diffusion of $^{t}$BuOMe vapor into a MeCN solution. A crystal was coated with paratone oil and mounted on the end of a nylon loop attached to the end of the goniometer. Data were collected with a Bruker APEX CCD diffractometer equipped with a Kryoflex attachment supplying a nitrogen stream at 150 K. Using frame times of 60 seconds/frame, a full sphere of data was obtained by collecting three sets of 400 frames in $\omega$ (0.5°/scan), collected at $\varphi$ = 0.00, 90.00 and 180.00° followed by two sets of 800 frames in $\varphi$ (0.45°/scan) collected with $\omega$ constant at -30.00 and 210.00°. Data were collected under control of the *APEX2*[21] software packages. Raw data were reduced to $F^2$ values using the *SAINT*[22] software, and a global refinement of unit cell parameters was performed using 9191 selected reflections from the full data set. Data were corrected for absorption on the basis of multiple measurements of symmetry equivalent reflections with the use of *SADABS*.[23]

The space group was identified as noncentric *Pn* on the basis of intensity statistics ($|E^*E - 1|$ = 0.724; 0.736 for noncentrosymmetry). The structure was solved by direct methods using *SHELXT*,[24] while refinement was accomplished by full-matrix least-squares procedures using *SHELXL*.[25] In the late stages of refinement, the structure was flagged as a two-component inversion twin; the distribution between these components was determined with use of TWIN and BASF options in SHELXL (Flack parameter = 0.164(18)). Disordered acetonitrile ligands were found on both of the two independent of $[(Cu^{II}(L\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4]^{6+}$ cations in the asymmetric unit and were refined as a best-fit distributions between two positional variants as determined by the refinement software. One of the interstitial acetonitrile molecules showed density indicative of partial site occupancy and was therefore refined with half-site occupancy. Of the $[BF_4]^{1-}$ anions, only one was disordered in a way that could be modeled over two positions with appropriate distance constraints. Several of the others were refined isotropically owing to large thermal parameters, but most of the $[BF_4]^{1-}$ anions were refined with anisotropic thermal parameters. One carbon atom (C9) of one of the organic ligands showed non-positive definite behavior when refined anisotropically, likely due to a poor absorption correction. It was therefore allowed to refine isotropically. All hydrogen atoms were added in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the carbon atoms to which they were attached.

The thermal ellipsoid images were created with the use of *XP*, which is part of the *SHELXTL* package.[26] The structure was checked for overlooked symmetry and other errors by the checkCIF service provided by the International Union of Crystallography.[27] Final unit cell data and refinement statistics are collected in **Table 1**. Selected interatomic distances and angles are presented as averages in **Table 2**.

## Acknowledgments

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## Supporting information

The crystallographic information file (CIF) for $[[Cu^{II}(L\text{-}N_2S_2)]_4(\mu_2\text{-}Cu^I(MeCN)_2)_2(\mu_3\text{-}Cu^I(MeCN))_4]][BF_4]_6\cdot 2.25MeCN$ is available from the Cambridge Crystallographic Data Center (Deposition code: CCDC 1432783). Thermal ellipsoid plots with complete atom labeling; UV-vis absorption spectrum of [**1**]$[BF_4]_6\cdot 2.25MeCN$ in MeCN.

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(**22**) *SAINT*, Bruker AXS, Inc., Madison, Wisconsin, 2013.

(**23**) *SADABS*, Bruker AXS, Inc., Madison, Wisconsin, 2013.

(**24**) *SHELXT*, Bruker AXS, Inc., Madison, Wisconsin, 2013.

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(**26**) (**a**) *SHELXTL*, Version 6.10, Bruker-AXS, Madison, WI, 2000. (**b**) *SHELXTL*, Version 2008/4, Bruker-AXS, Madison, WI, 2008.

(**27**) See http://checkcif.iucr.org/

# An $S_4$-Symmetric Mixed-Valent Decacopper Cage Comprised of $[Cu^{II}(L\text{-}S_2N_2)]$ Complexes Bridged by $Cu^{I}(MeCN)_n$ ($n$ = 1 or 2) Cations

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Oxidative addition of 1,2,11,12-tetrathia-5,8,15,19-tetra(*N*-methylamino)cycloicosane to $[Cu(MeCN)_4][BF_4]$ yields an $S_4$-symmetric decacopper cage compound with four cupric ions in distorted square planar bis(amino) bis(thiolato) ligand environments bridged by six cuprous ions with MeCN ligands.