Copper-Sulfur Complexes Supported by N-Donor Ligands: Towards Models of the Cu$_Z$ Site in Nitrous Oxide Reductase

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Abstract

The distinctive structure of the $[(his)_7Cu_4(\mu\text{-}S)]^{n+}$ cluster in the "Cu$_Z$" active site of nitrous oxide reductase and the intriguing mechanistic hypotheses for its catalytic reactivity provide inspiration for synthetic model studies aimed at characterizing relevant copper-sulfur compounds and obtaining fundamental insights into structure and bonding. In this brief review, we summarize such studies that have focused on the synthesis and characterization of a range of copper-sulfur complexes supported by N-donor ligands. Compounds with variable nuclearities and sulfur redox levels have been isolated, with the nature of the species obtained being dependent on the supporting ligand, sulfur source, and the reaction conditions. Spectroscopic data and theoretical calculations, often performed with a view toward drawing comparisons to oxygen analogs, have provided insight into the nature of the copper-sulfur bonding interactions in the complexes.

Keywords

copper; sulfur; nitrous oxide; disulfide

1. Introduction

Nitrous oxide (N$_2$O) is of particular interest as an energy-storing small molecule because of its potential as an environmentally clean oxidant and its role as a harmful greenhouse gas [1]. Its propensity for reduction and O-atom transfer to release the inert product N$_2$ is highly favorable (E° = 1.76 V), but high kinetic barriers limit its utility as an oxidant, notwithstanding successful heterogeneous catalytic reactions that occur at temperatures much higher than ambient [2]. In general, binding and activation of N$_2$O at a transition metal center is required in order to obtain reasonably rapid rates of reaction under mild conditions [3]. However, knowledge of the fundamental underlying coordination chemistry with which to develop useful catalytic systems has lagged behind similar efforts to understand activation of other small molecules like dioxygen, for example [4]. This problem stems in large part from the weak σ-donor and π-acceptor capabilities of N$_2$O that make it a poor ligand. Indeed, only one metal-N$_2$O complex ($[Ru(NH_3)_5(N_2O)]^{2+}$) has been isolated and characterized [5].

In biology, N$_2$O reduction is performed enzymatically under mild conditions during denitrification, a microbial respiratory process that is a key component of the biogeochemical nitrogen cycle [6]. The enzyme responsible for the reaction in eq. 1, nitrous oxide reductase

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(N$_2$OR), has been shown by X-ray crystallography [7] and spectroscopy [8,9] to contain two multicopper sites. One is a bis(cysteinato)dicopper moiety that is delocalized mixed-valent (Cu$^{+1.5}$Cu$^{+1.5}$) in its oxidized state and operates as an electron transfer center ("Cu$_A$"; not shown) [10]. The other site ("Cu$_Z$"; Figure 1, top) contains a [Cu$_4$(μ-S)]$^{n+}$ cluster ligated by 7 histidine imidazoles that is unprecedented; no other examples of such a tetracopper arrangement or a copper site with inorganic sulfur have been observed in biology [11]. This site is believed to be where N$_2$O binds and is reduced. Spectroscopic studies have demonstrated that the active form of the enzyme is in a fully-reduced state (4Cu^{+1}), and calculations suggest that the N$_2$O molecule

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$$

eq. 1

binds through the terminal N-atom to Cu$_I$ [9,12]. These theoretical studies also suggest that the lowest energy pathway for N$_2$O reduction involves binding of the O-atom to Cu$_{IV}$ to yield a bent μ-1,3-bridged fragment (Figure 1, bottom). This binding mode is suggested to maximize Cu$_Z \rightarrow$ N$_2$O π backbonding and activate the molecule for protonation. The unusual bridging sulfide is postulated to facilitate electronic delocalization throughout the tetracopper cluster, not only to increase the ability of the cluster to backbond into the N$_2$O molecule, but also to lower the reorganization energy associated with the Cu^I/Cu^{II} redox change(s) during catalysis.

While theoretical calculations provide enticing hypotheses for the mechanism of N$_2$O reduction by Cu$_Z$, experimental information is lacking about the nature of the bonding interactions between copper, inorganic sulfur, and/or N$_2$O. A useful approach to obtain such knowledge involves the study of synthetic complexes designed to mimic the structural and/or spectroscopic properties of metalloenzyme active sites and proposed intermediates [13]. Such studies of copper-sulfur complexes are motivated by the inherent challenges involved in activating N$_2$O, the novel structural topology of the Cu$_Z$ site, and the provocative mechanistic ideas for N$_2$O reduction by Cu$_Z$ proposed on the basis of theory. In this brief review, we survey recent work aimed at synthesizing and characterizing copper-sulfur complexes relevant to the Cu$_Z$ site. In progressing toward the difficult, and as of yet unattained goal of preparing an accurate model of the [(his)$_7$Cu$_4$(μ-S)]$^{n+}$ core, a wide range of compounds with variable copper nuclearities and sulfur oxidation states have been prepared, opening new vistas into the inorganic chemistry of copper and sulfur.

2. Copper-Sulfur Complexes Lacking N-Donor Supporting Ligands

A survey of crystallographically characterized molecules having copper-sulfide bonds in the Cambridge Structure Database [14] reveals a large number of structures having Cu$_3$(μ_3-S) and Cu$_4$(μ_4-S) bonding motifs. Most of these contain copper ions in large clusters with other metals such as Mo [15] and W [16], however, and have little relevance to N$_2$OR. Nonetheless, the isolation of these molecules illustrates that a wide variety of sulfur sources, including S$_8$, Li$_2$S, and Na$_2$S$_2$, are synthetically useful.

Few examples of discrete molecules with Cu$_3$(μ_3-S) and Cu$_4$(μ_4-S) cores have been reported and these can be classified as members of a large class of [Cu^I_xS$^{2-}_y$] clusters supported by abiological phosphine ligands that have garnered interest due to their potential applications in material science [17]. One example is notable in the current context because it contains multicopper centers bridged by inorganic sulfide ions in a Cu$_4$(μ_4-S) geometry that is related to that observed in Cu$_Z$ (Figure 2) [18]. The cluster [L$_4$Cu$_4$(μ_4-S)]$^{2+}$ (**1**, L = the bidentate ligand 1,3-diphenylphosphinomethane) was synthesized either through the addition of CS$_2$ to LCu^{II}(NO$_3$)$_2$ in MeOH [18a] or the addition of Na$_2$S to the dicopper(I) complex [Cu$_2$(μ-dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$ [18b]. In the former route reduction of the starting Cu^{II} centers occurs, consistent with the known propensity of phosphines to stabilize the copper(I) oxidation state [19]. Indeed, this stabilization of the copper(I) state is reflected in the chemistry of these

compounds, which are resistant to oxidation and are air stable ($E_{1/2} = 0.188$ V vs. SCE). Thus, while phosphine ligands allow for the synthesis and isolation of $[Cu^I_x S^{2-}_y]$ clusters by preventing redox chemistry that can lead to decomposition, this same redox inertness inhibits biomimetic reactivity, thus decreasing the relevance of these molecules as N_2OR Cu_Z models. From another perspective, these results underscore the importance of using N-donors to model the His supporting ligands in Cu_Z and to enable access to higher copper oxidation states within the cluster that occur during the N_2O reduction process.

3. Copper-Sulfur Complexes With N-Donor Supporting Ligands

3.1 Dinuclear Complexes

The first reported synthetic example of a copper-sulfide complex with N-donor ligation is $(Tp^{iPr2}Cu)_2(S_2)$ (**2**, Figure 3), which was initially isolated from the thermal decomposition of a copper(II)-thiolate complex [20] and was later obtained from the reaction of $Tp^{iPr2}Cu^I(MeCN)$ and S_8 [21]. This reddish-brown dinuclear complex was shown by X-ray crystallography to contain a side-on bound $\mu-\eta^2:\eta^2-$disulfido (S_2^{2-}) moiety with an S-S bond length of 2.073(4) Å. An alternative end-on bound $\mu-\eta^1:\eta^1$ binding mode for a disulfido ligand in a dicopper complex was revealed in $\{[(TMPA)Cu]_2(S_2)\}(X)_2$ (**3**, Figure 3), which was isolated from the reaction of S_8 with the copper(I) complex $[(TMPA)Cu(MeCN)]X$ in acetonitrile (TMPA = tris(2-pyridylmethyl)amine, $X = ClO_4^-$ or PF_6^-) [22]. X-ray crystallographic analysis of $\{[(TMPA)Cu]_2(S_2)\}(ClO_4)_2$ revealed an S-S bond length of 2.044 (4) Å akin to that reported for **2** despite their differing disulfide binding modes.

Complexes **2** and **3** are structurally similar to previously characterized oxygen analogs [23, 24], and in order to gain an understanding of the differences in the bonding interactions for the Cu_2E_2 systems (E = O or S), as well as between side-on and end-on coordination of the bridging moieties, detailed spectroscopic and theoretical comparisons of these complexes were conducted [21]. Key spectroscopic features are summarized in Figure 4. Each complex displays a distinctive UV-vis absorption pattern dominated by intense $E_2^{2-} \rightarrow Cu^{II}$ ligand-to-metal charge transfer (LMCT) features, irradiation into which results in the enhancement of E-isotope-sensitive $\nu(E\text{-}E)$ features in resonance Raman spectra. The complexes exhibit $d \rightarrow d$ bands indicative of copper in the +2 oxidation state, but they are EPR silent, consistent with strong antiferromagnetic coupling of the Cu^{II} ions.

Bonding pictures were developed in order to understand and compare the properties of the side-on and end-on Cu_2E_2 complexes, with that for the side-on species shown in Figure 5. In both geometries, the main bonding interaction involves strong σ-donation from the E_2^{2-} π^*_σ orbital into the d_{xy} orbitals of the two copper centers. A key finding was that the Cu-S bonding is stronger and more covalent than the Cu-O bonding within each pair of analogous structures, which may be traced to better overlap of the more diffuse and higher-energy S orbitals with the copper d-orbitals. Another important observation was that the E-E bonds in the side-on ($\mu-\eta^2:\eta^2$) structures are weak, as illustrated by low $\nu(E\text{-}E)$ values that indicate a high degree of E-E bond activation. This bond weakening is ascribed to back-donation from the Cu d_{xy} orbitals into the empty E_2^{2-} σ^* orbital.

Another example of a side-on ($\mu-\eta^2:\eta^2-S_2^{2-}$)dicopper(II) complex (**4**) was prepared using a tridentate N-donor supporting ligand (Me_2NPY2 = N,N-bis{2-[2-(N'N'-4-dimethylamino) pyridyl]ethyl}methylamine) [25]. X-ray crystallography showed the copper centers to be roughly square pyramidal, with an S-S bond length of 2.117(2). Particular emphasis in this study was placed on the reactivity of the complex. It was shown to quantitatively transfer a sulfide ion to both PPh_3 and 2,6-dimethylphenylisocyanide to form $S=PPh_3$ and the isothiocyanate, yet it did not react with benzyl bromide, suggesting that the disulfide bridge is electrophilic. This disulfide bridge is labile, as shown by the reaction of the complex with CO

or O_2 that resulted in the rapid formation of the LCu^I-CO adduct or $[(LCu)_2(O_2^{2-})]^{2+}$, respectively.

A large class of side-on $(\mu-\eta^2:\eta^2-S_2^{2-})$dicopper(II) complexes (**5a-j**) supported by bidentate, monoanionic N-donors was prepared using β-diketiminate and related anilido-imine ligands with variable substituents that conferred differing steric profiles (Figure 6) [26,27]. The initial synthesis of these complexes was by addition of the sulfide reagent $S(SiMe_3)_2$ to $LCu^{II}Cl$ in acetonitrile (L = β-diketiminate and related anilido-imine ligands). Yields of the complexes $[(LCu)_2(\mu-S_2)]$ synthesized by this metathesis approach were low (17−29%), with the concomitant formation of $LCu^I(NCCH_3)$ being confirmed by NMR, consistent with a redox process between S_2^{2-} ligands and the copper(II) centers. The syntheses were also complicated by the formation of copper(I)-thiolate byproducts resulting from attack of sulfur at the β-diketiminate methine position, exemplified by **6** (Figure 7). In an alternative synthetic route, **5a-j** were synthesized in higher yields (40−91%) by addition of one equivalent of elemental sulfur to acetonitrile solutions of $LCu^I(NCCH_3)$.

X-ray structure determinations for **5a-j** revealed S-S bond distances ranging from 2.165(3) to 2.214(10) Å, which are significantly longer than those in **2** (2.073 Å) or **3** (2.044 Å). Within the series of $(\mu-\eta^2:\eta^2-S_2^{2-})$dicopper(II) complexes **2**, **4**, and **5a-j**, lengthening of the S-S bond correlates with shortening of the Cu-Cu and Cu-S distances, as plotted in Figure 8 [27]. It is notable that the compounds with β-diketiminate and anilido-imine supporting ligands are at the extreme of long S-S and short Cu-Cu and Cu-S distances, and only when sufficient steric hindrance is introduced (**5c,i**, and **j**) do these values approach those of **2** and **4**. Consistent with these structural findings, the resonance Raman spectra of **5i-j** (λ_{ex} = 457.9 nm) contain a single strong, ^{34}S-sensitive ν(S-S) at 428−454 cm^{-1} ($\Delta^{34}S = 8−13$ cm^{-1}) that is ~50 cm^{-1} lower than observed for **2** and **3** (~ 500 cm^{-1}), suggesting greater backbonding from the copper(II) centers into the σ*-orbitals of the S-S moiety with an accompanying weakening of this bond. Taken together, the structural and spectroscopic data support stronger and more covalent Cu-S bonding and greater backdonation into the S_2^{2-} σ* orbital in **5i-j** that results in a greater degree of S-S bond activation relative to **2−4**. These effects are mitigated only when the powerfully electron donating β-diketiminate and anilido-imine supporting ligands are particularly sterically encumbered. Indeed, a more quantitative correlation of the S-S distance and ν(S-S) using Badger's rule [28] shows that the degree of S-S bond activation in **5i-j** supercedes that of a large set of metal-disulfide complexes (Figure 8) [27]. Yet despite the electron donating capabilities of the supporting ligands in **5i-j**, complete scission of the S-S bond to yield bis (sulfido)dicopper(III) species via a process akin to that identified previously in $[Cu_2(\mu-\eta^2:\eta^2-O_2)]^{2+}/[Cu_2(\mu-O)_2]^{2+}$ systems [4b,c,29] has not been observed. This implicated instability of the $[Cu_2(\mu-S)_2]^{2+}$ core has been verified by theory [26].

A dicopper(II) complex with two disulfido ligands at a different redox level than S_2^{2-} was prepared upon treatment of $[(Me_4eda)Cu(CH_3CN)]O_3SCF_3$ with S_8 (**7a**, Figure 9) [30]. A structurally similar compound with Cl$^-$ instead of $CF_3SO_3^-$ groups was recently obtained from a mixture of *N,N,N',N'*-tetramethyl-*trans*-1R,2R-diaminocyclohexane (Me$_4$chd), CuCl$_2$, and Na$_2$S$_2$ (**7b**) [31]. The S-S distances of ~1.95 Å in these compounds are shorter than in typical complexes of S_2^{2-} (see above), yet are longer than that of doubly bonded S_2 (1.892 Å [32]). In addition, resonance Raman spectra for **7** contain ν(S-S) at 613 cm^{-1} ($\Delta^{34}S = 19$ cm^{-1}), which lies between those seen for S_2^{2-} compounds and that of S_2 (718 cm^{-1} [33]); note the position of the data point for **7a** in the Badger's rule plot of Figure 8 [27]. The EPR silent complexes are thus best formulated as having a $[Cu^{II}_2(\mu-S_2^{\bullet-})_2]^{2+}$ core (i.e., with disulfido(•1−) ligands). This is a novel motif in copper chemistry, albeit one that has been identified in complexes of iron and ruthenium [34].

3.2 Trinuclear Complexes

Clusters **8a-c** were isolated from reactions of [LCu(CH$_3$CN)]X (L = Me$_4$eda, X = SbF$_6$; L = Me$_4$chd, X = PF$_6$) [35] with S$_8$ or through mixing Me$_4$chd, Cu(O$_3$SCF$_3$)$_2$, and Li$_2$S or Na$_2$S$_2$ [31] (Figure 10). These clusters are structural models of Cu$_Z$ insofar as their Cu$_3$(μ-S) "half" mimics the subcluster of Cu$_Z$ defined by Cu$_{II}$, Cu$_{III}$, Cu$_{IV}$, and S (Figure 1). X-ray crystallography results for **8a-c** show them to exist as 3+ cations consistent with the formal oxidation state assignment [Cu^{III}Cu$^{II}_2$(μ-S^{2-})$_2$]$^{3+}$. A similar overall charge and formal oxidation state assignment was identified previously for the oxygen analog [(Me$_4$chd)$_3$Cu$_3$(μ-O)$_2$]$^{3+}$ (**9**) [36]. However, while the latter was shown to adopt a valence localized structure with structurally distinct Cu^{III} and Cu^{II} sites, for **8a-c** structural, spectroscopic, and theoretical data support a fully valence delocalized core. Thus, the metal-ligand distances in each of **8a-c** are essentially identical and EPR data at room temperature and at 10 K indicate an S = 1 ground state with equivalent hyperfine coupling to the three Cu ions. While deeper insights await a more complete spectroscopic comparison of **8** and **9**, DFT calculations point to an interesting reversal of the energies of the frontier e" and a$_2$" orbitals arising from 'cross-cluster' S-S interactions that destabilizes the a$_2$" orbital as the reason for the shift from a Jahn-Teller distorted localized structure in **9** to a symmetric delocalized configuration in **8** (Figure 10) [35].

3.3 High Nuclearity Complexes

An X-ray crystal structure of an N-donor ligated cluster with bridging μ$_4$-sulfido and μ$_3$-thiolato ions between 13 copper(I) ions has been reported (Figure 11) [37]. This cluster, [(L^{S-})$_6$Cu$^I_{13}$(S^{2-})$_2$]$^{3+}$ (**10**), was isolated during attempted crystallization of [(L^{SH})Cu^I]ClO$_4$, with the sulfido groups apparently being derived from decomposition of the supporting thiolate ligand. As noted by the authors, the arrangement of four copper(I) ions about each sulfido group resembles that in the Cu$_Z$ core, and is also related to the core geometry of **1** (Figure 2).

Recently, tetra- and hexacopper clusters with bindentate N-donors and bridging disulfido ligands were isolated and structurally defined (Figure 12) [31]. The complex [(Me$_4$chd)$_4$Cu$_6$(μ-S$_2$)$_4$Cl$_4$] (**11**) was obtained from a mixture of Me$_4$chd, CuCl$_2$, and Li$_2$S, along with a copper(I) coproduct, (Me$_4$chd)Cu^{I}Cl, apparently resulting from oxidation of S^{2-} to S$_2^{2-}$ by Cu^{II}. Subsequent reaction of **11** with [[(Me$_4$chd)Cu^I(MeCN)]SbF$_6$ led to [(Me$_4$chd)$_4$Cu$_4$(μ-S$_2$)$_2$Cl$_2$](SbF$_6$)$_2$ (**12**). The μ$_4$-S$_2^{2-}$ coordination in **11** and **12** has been seen previously in transition metal complexes [38], but to our knowledge it is new for copper [39]. It is notable that with one specific supporting N-donor ligand, Me$_4$chd, compounds with core stoichiometries and redox levels ranging from [Cu$_2$(μ-S$_2$)$_2$]$^{2+}$ (**7b**), [Cu$_3$(μ-S)$_2$]$^{3+}$ (**8b,c**), [Cu$_4$(μ-S$_2$)$_2$]$^{4+}$ (**12**), to [Cu$_6$(μ-S$_2$)$_4$]$^{4+}$ (**11**) have been isolated, depending on the particular reaction conditions.

4. Concluding Comments

In efforts to prepare copper-sulfide complexes with N-donor ligands, novel structures with a variety of copper nuclearities and sulfur oxidation levels have been isolated. The nature of the clusters prepared via these approaches is sensitive to the specific N-donor ligand, sulfur source, copper salt, and reaction conditions used. For instance, with one specific supporting N-donor ligand (Me$_4$chd) compounds with core stoichiometries and redox levels ranging from [Cu$_2$(μ-S$_2$)$_2$]$^{2+}$ (**7b**), [Cu$_3$(μ-S)$_2$]$^{3+}$ (**8b,c**) [Cu$_4$(μ-S$_2$)$_2$]$^{4+}$ (**12**) to [Cu$_6$(μ-S$_2$)$_4$]$^{4+}$ (**11**) were isolated. Spectroscopic and theoretical data have provided insight into the nature of the Cu-S bonding interactions in these compounds, key findings being the particularly high degrees of S-S bond activation in disulfido-dicopper complexes supported by β-diketiminate and anilido-imine ligands and a novel delocalized mixed-valent structure in [Cu$_3$(μ-S)$_2$]$^{3+}$ cores. From the comparison with structurally similar oxygen analogs, Cu-S bonding is stronger and more

covalent, with possible implications for enhanced charge and/or spin delocalization mediated by the bridging sulfur in the Cu_Z cluster. While new insights into fundamental copper-sulfur chemistry have been obtained, much remains to be accomplished in efforts to model Cu_Z, including the development of new synthetic protocols for the synthesis of high nuclearity copper(I)-sulfur clusters supported by low denticity N-donor ligands that would enable studies of biomimetic reactivity with N_2O.

5. Acknowledgements

Biography
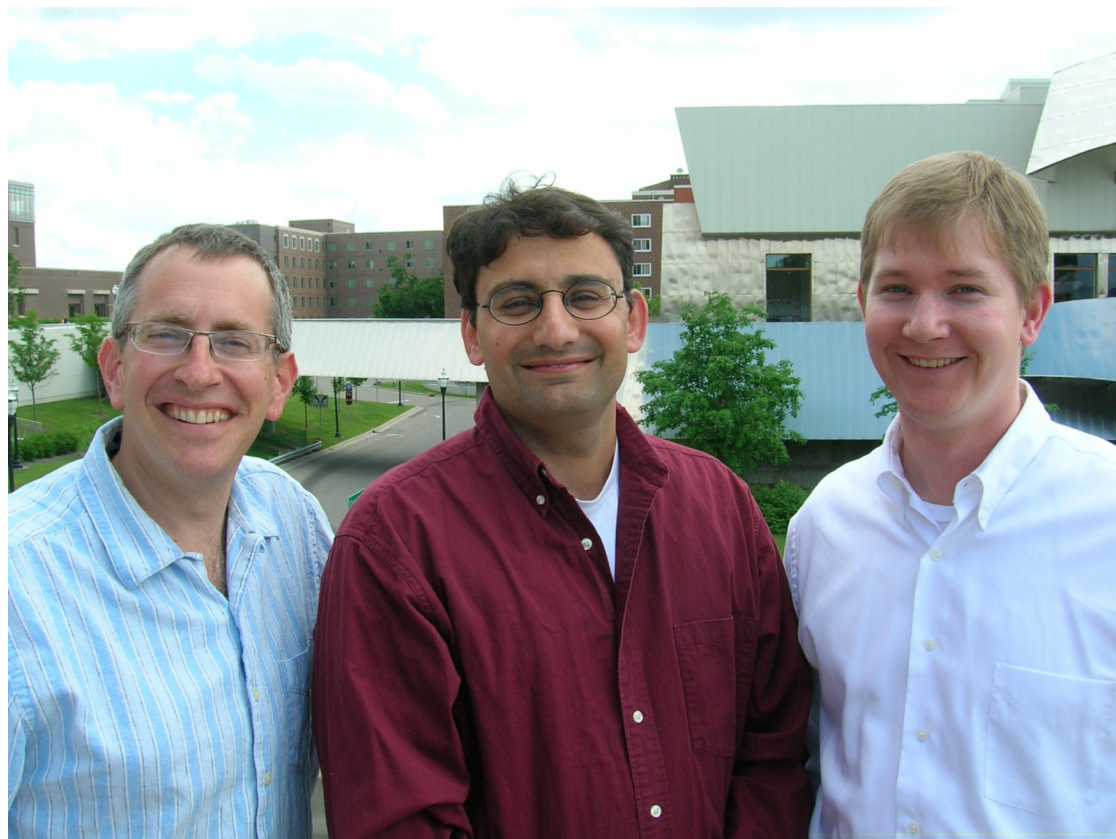
Left: William B. Tolman was an undergraduate student at Wesleyan University, Middletown, CT, and received his Ph.D. in 1987 from the University of California, Berkeley, under the tutelage of K. Peter C. Vollhardt. After a postdoctoral period at the Massachussetts Institute of Technology with Stephen J. Lippard, he began his independent career at the University of Minnesota in 1990, where he is currently a Distinguished McKnight University and Lee Irvin Smith Professor of Chemistry.

Middle: Itsik Bar-Nahum was born in Jerusalem, Israel, in 1972. He received his B.Sc. and M.Sc. in chemistry from the Hebrew University of Jerusalem, Israel, in 1999, and completed his Ph.D. on the synthesis and catalytic applications of polyoxometalate – organometallic hybrid compounds in 2005, under the supervision of Ronny Neumann at The Weizmann Institute of Science, Rehovot, Israel. Since then he has been a postdoctoral associate in the laboratory of W. Tolman at the University of Minnesota.

Right: John T. York received his B.S. in Chemical Engineering from North Carolina State University in 1995 and his B.A. in Secondary Science Education from the University of Wyoming in 2001. He recently completed his Ph.D. research on synthetic copper-sulfur and copper-dioxygen systems in the laboratory of W. Tolman at the University of Minnesota, and is beginning his independent career as Assistant Professor of chemistry at Stetson University in DeLand, Florida.

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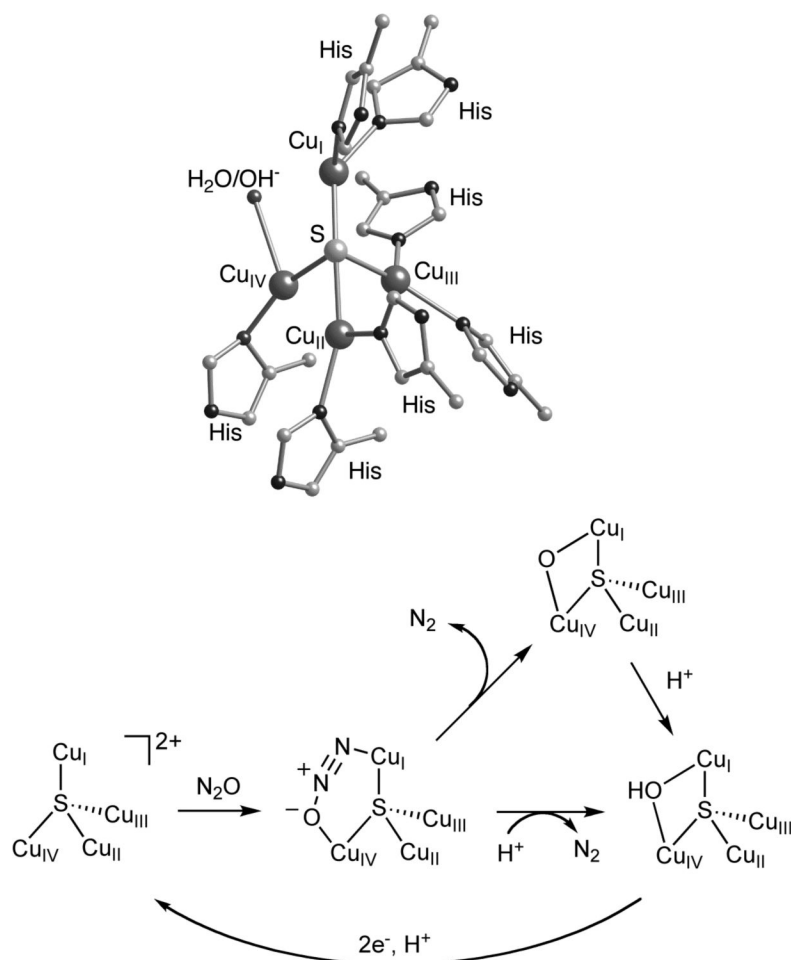**Figure 1.**
(top) Representation of the X-ray structure of the Cu_Z site of N_2OR. (bottom) Proposed mechanism for binding of activation of N_2O by Cu_Z.
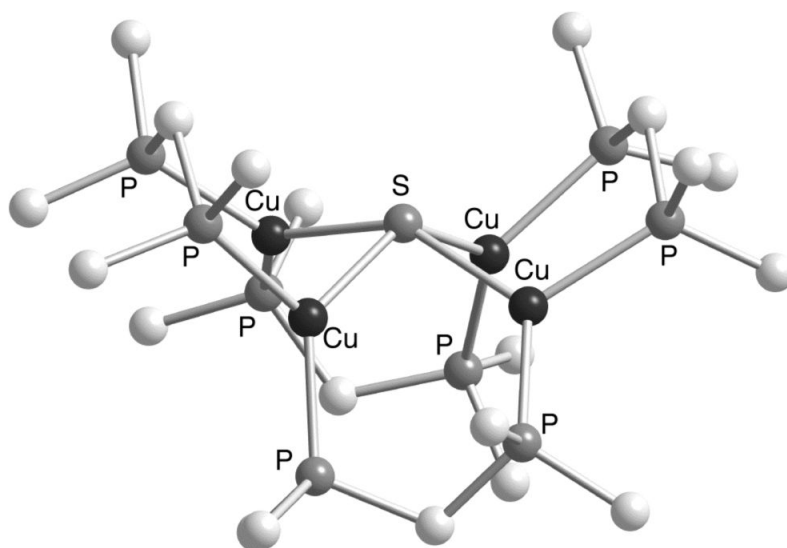
Figure 2.
Representation of the X-structure of [(dppm)$_4$Cu$_4$(μ_4-S)]$^{2+}$ (**1**), with only the ipso C atoms of the phenyl rings of the dppm ligands shown [18].
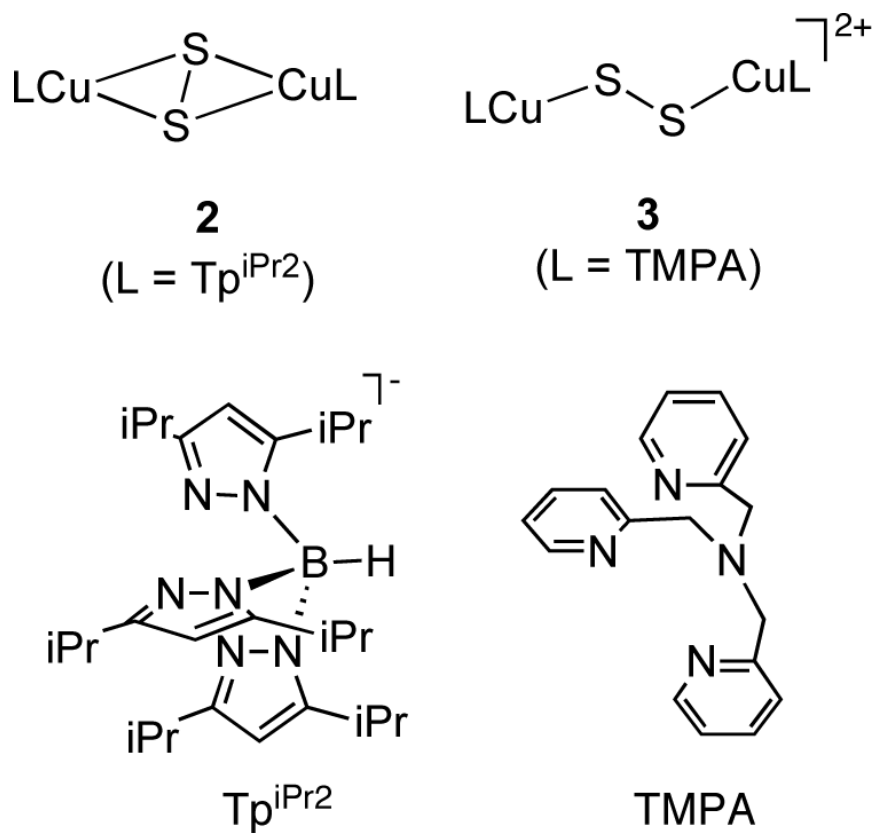
Figure 3.
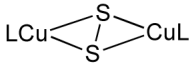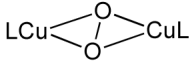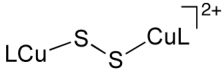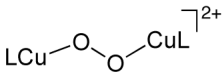Disulfido-dicopper(II) complexes supported by Tp^{iPr} and TMPA.

	LMCT Absorption Features	ν(E-E)	E-E distance
LCu$\diagdown$S$\diagdown$CuL (with S)	28,000 ($\pi^{\star}_{\sigma}$) 21,000 ($\pi^{\star}_{v}$)	500	2.073
LCu$\diagdown$O$\diagdown$CuL (with O)	28,600 ($\pi^{\star}_{\sigma}$) ~18,500 ($\pi^{\star}_{v}$)	~760	1.41
[LCu–S–S–CuL]$^{2+}$	~17,600 cm^{-1}	499	2.044
[LCu–O–O–CuL]$^{2+}$	~19,100 ($\pi^{\star}_{\sigma}$) ~16,250 ($\pi^{\star}_{v}$)	830	1.43

Figure 4.
Summary of selected spectroscopic features of the $\mu-\eta^2{:}\eta^2-$ and $\mu-\eta^1{:}\eta^1-$(disulfido/peroxo) dicopper complexes with L = Tp^{iPr2} or TMPA, respectively (E = S or O). The absorption features and ν(E-E) values are reported in cm^{-1}, and the E-E distance is reported in Å. The data were obtained from refs. 21,23, and 24.
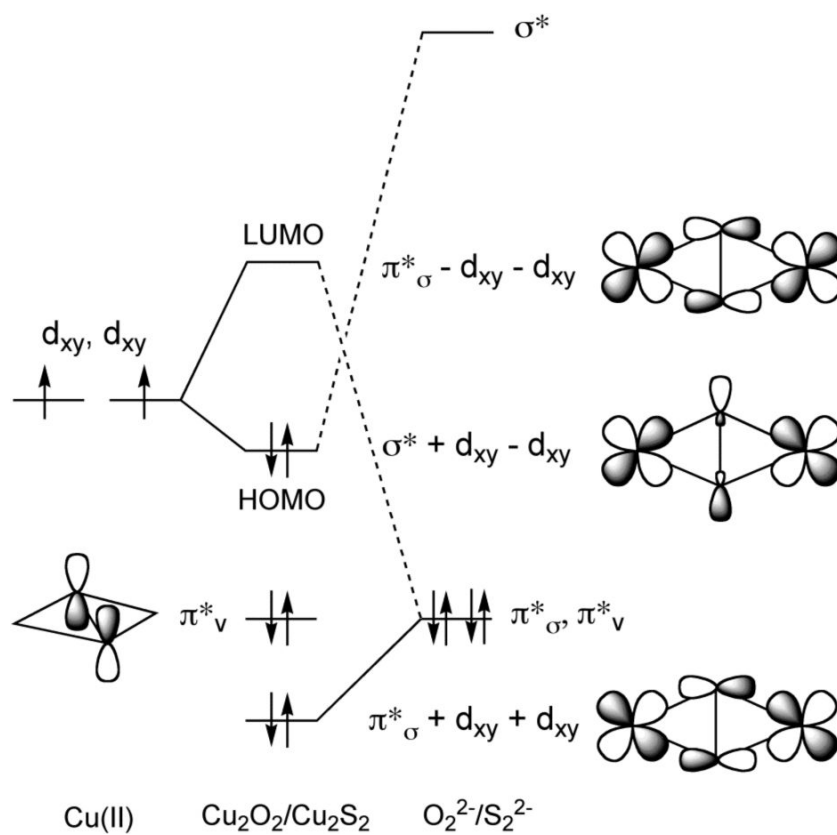
Figure 5.
Orbital energy level diagram for ($\mu-\eta^2$:η^2-peroxo/disulfido)dicopper complexes. Reproduced with permission from ref. 27.

Figure 6.
Complexes **5a-j**.

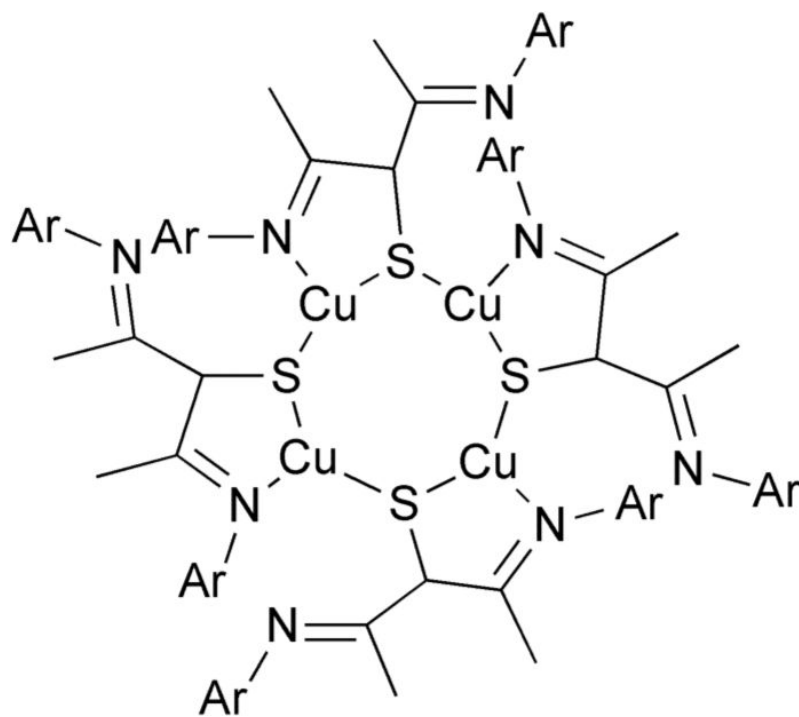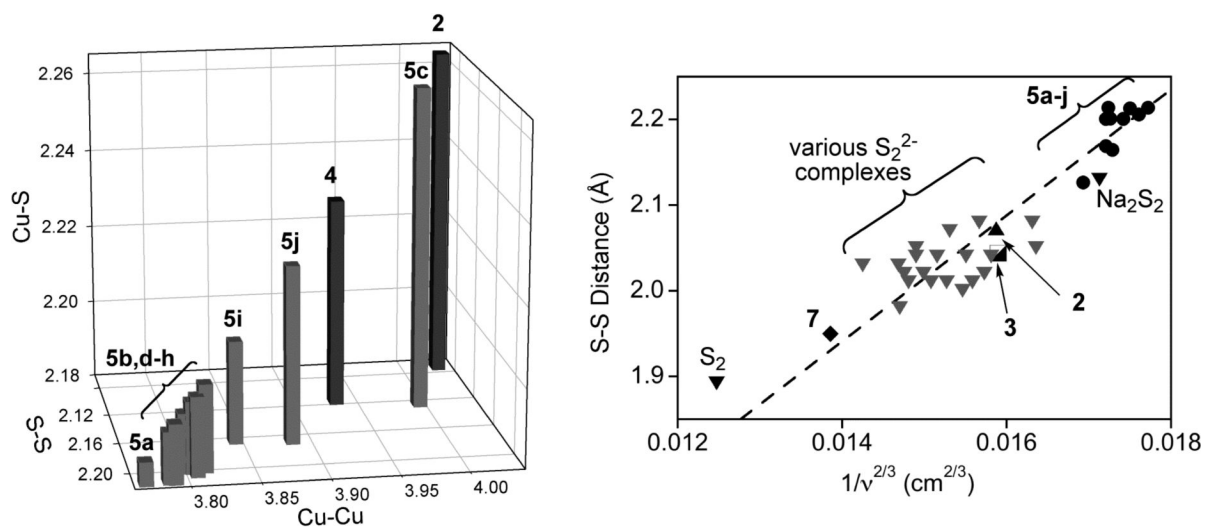**Figure 7.**
Complex **6** (Ar = aryl).

Figure 8.
(Left) Correlation of Cu-S, S-S, and Cu-Cu distances in ($\mu-\eta^2:\eta^2-S_2^{2-}$)dicopper(II) complexes **2**, **4**, and **5a-j**. (Right) Plot of S-S distances and $1/\nu^{2/3}$ ($\nu = \nu(S-S)$) for species with S-S bonds, with a fit to Badger's rule shown as a dashed line. Adapted from ref. 27.
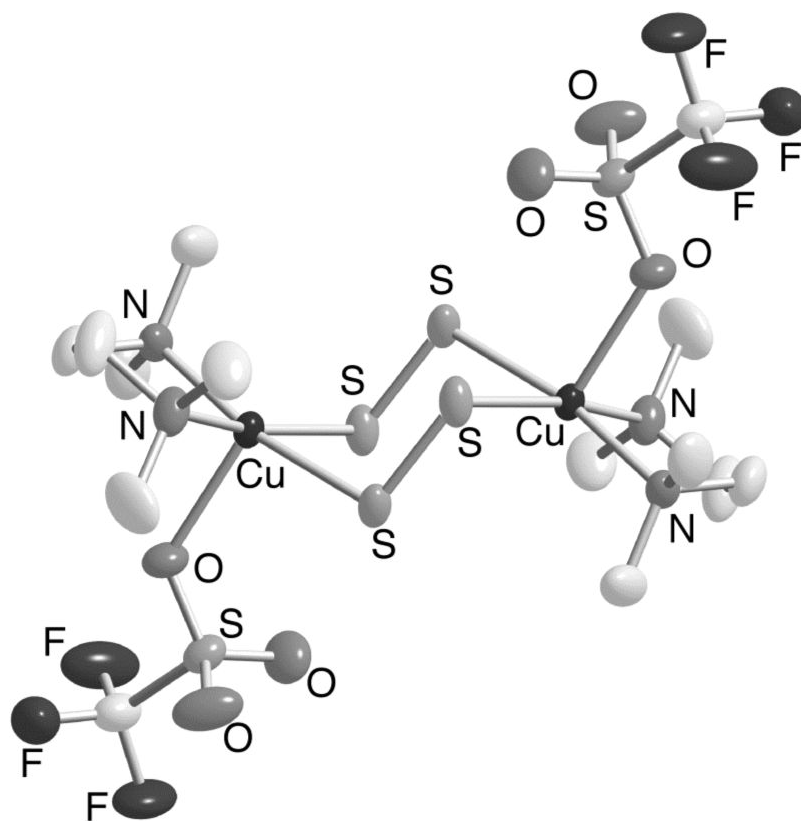
Figure 9.
X-ray structure of 7.

8a: L = Me₄eda, X = SbF₆⁻
8b: L = Me₄chd, X = PF₆⁻
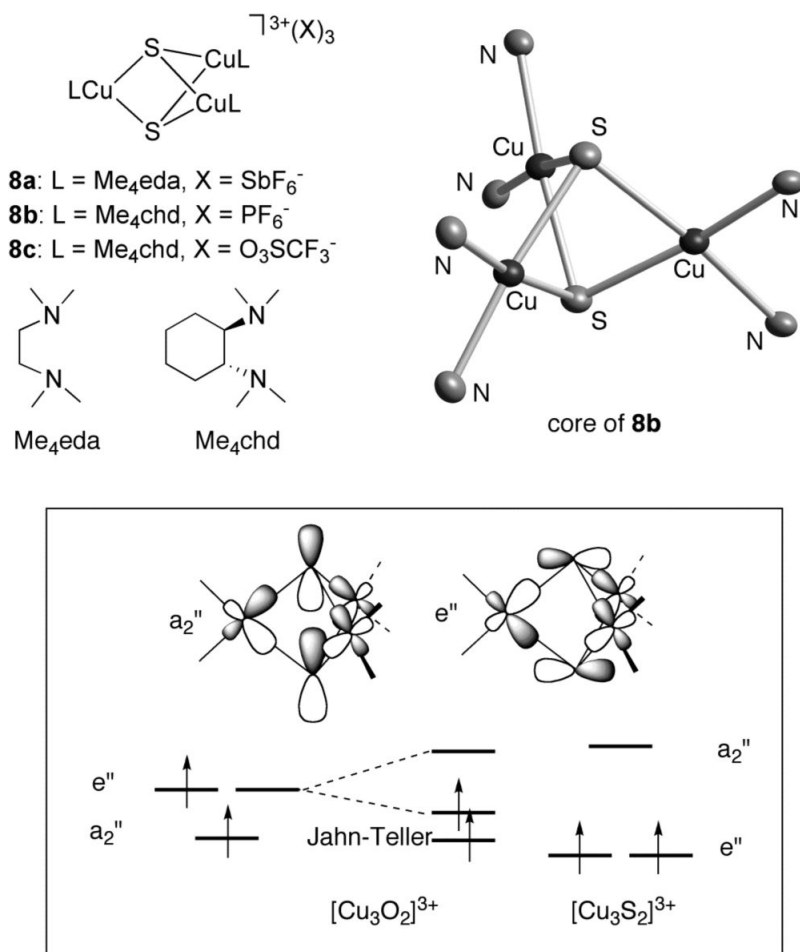**8c**: L = Me₄chd, X = O₃SCF₃⁻

core of **8b**

Figure 10.
Drawing of clusters **8a-c**, the X-ray structure of the tricationic core portion of **8b** (C and H atoms omitted), and (in the box) a partial orbital energy level diagram comparing the ordering of the frontier molecular orbitals for **8** and its oxygen analog **9**.
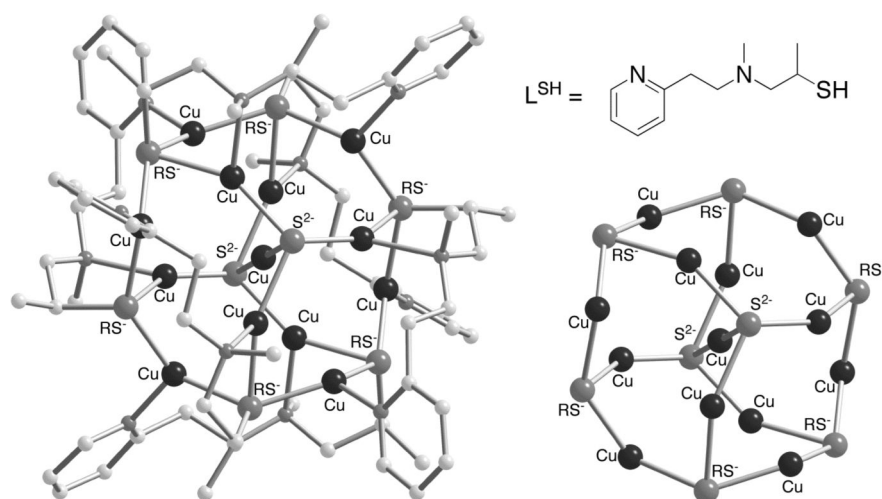
Figure 11.
X-ray structure of $[(L^{S-})_6Cu^I_{13}(S^{2-})_2]^{3+}$ (**10**) with (left) and without (right) the supporting N-donor ligand (L^{S-}) shown.
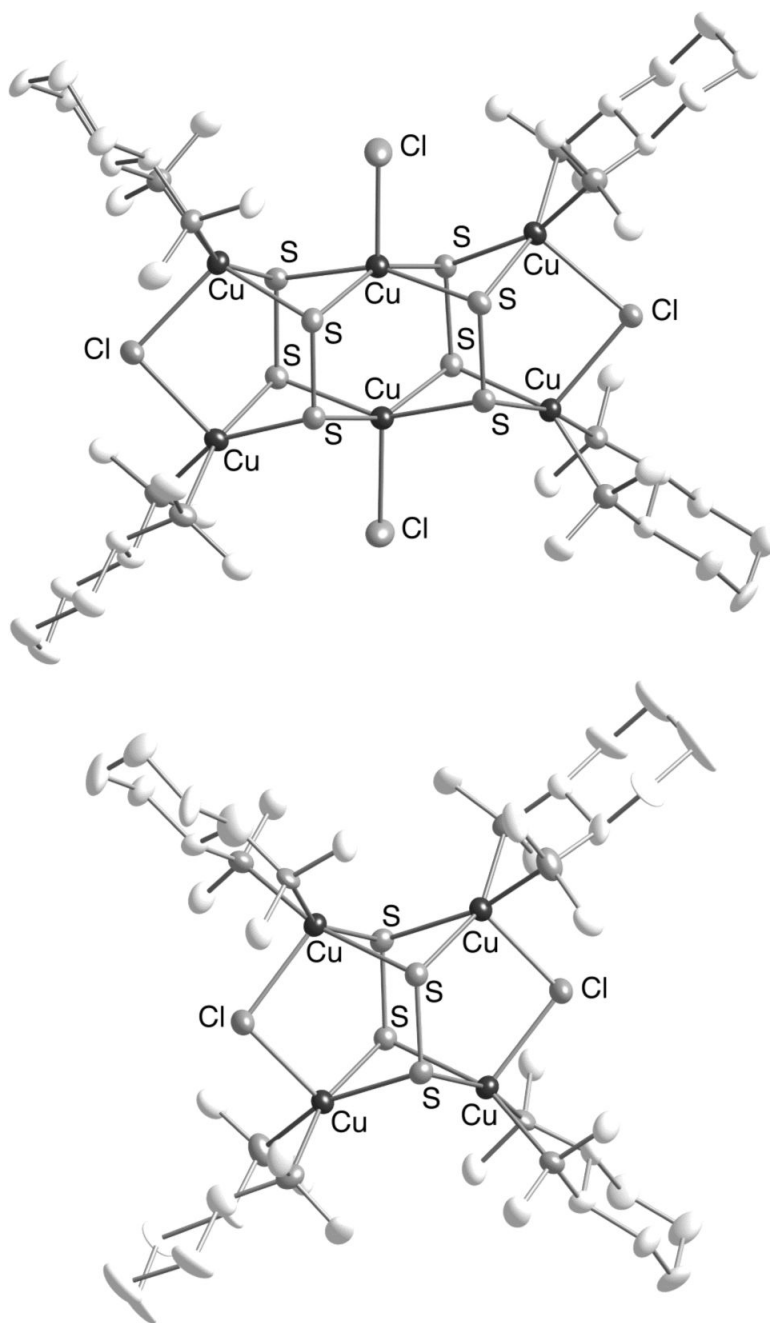
Figure 12.
X-ray structures of [(Me$_4$chd)$_4$Cu$_6$(μ-S$_2$)$_4$Cl$_4$] (**11**, top) and the cationic portion of [(Me$_4$chd)$_4$Cu$_4$(μ-S$_2$)$_2$Cl$_2$](SbF$_6$)$_2$ (**12**, bottom).