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Endogenous Arene Hydroxylation Promoted by Copper(I) Cluster Helicates

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Abstract: A novel neutral triple-stranded hexanuclear copper(I) cluster helicate $[Cu^I_6\mathbf{L}_3]\cdot 2\,CH_3CN$ derived from a thiosemicarbazone ligand could be synthesized and crystallographically characterized. The MALDI mass spectrum of this complex suggests that the tetranuclear copper(I) cluster helicate $[Cu^I_4\mathbf{L}_2]$ is also present in solution. These copper(I) cluster helicates are capable, in the presence of O_2, of hydroxylating the arene linker of their supporting ligand strands. The resulting dinuclear complex $[Cu^{II}_2\mathbf{L}'(OH)]$ is formed by two copper(II) centers, a new ligand arising from the hydroxylation reaction, and one hydroxide group. The magnetic investigation of this compound shows a strong antiferromagnetic coupling between the two Cu^{II} centers. The kinetic studies for the hydroxylation process show values of $\Delta H^{\neq} = -70\ kJ\,mol^{-1}$, similar to those mediated by the tyrosinase enzymes.

Keywords: aromatic hydroxylation · cluster compounds · copper · self-assembly · tyrosinase mimic

Introduction

Supramolecular helicates are a special class of metal complexes in which two or more ligands wrap around the axis defined by two or more metallic centers.[1] Hundreds of examples and several reviews on these compounds and their properties have been published since their introduction into the literature by Lehn et al. in 1987.[2] Besides the intrinsic importance that helicates have in the study of self-assembly processes directed by metal ions,[3] there is great interest in finding functional applications for this class of compounds and this is motivated by the unique chemical and physical properties arising from their special structural features. However, literature reports on functional helicates are still scarce.[4–9]

We recently reported a route for the synthesis of a new family of helical complexes, the cluster helicates,[10] which we defined as polynuclear helicates in which the metal centers are arranged to form a polyhedron around the helical axis. These metallo-supramolecular compounds combine the special structural features of helicates with the synergistic properties and applications of cluster compounds. Despite the increasing number of studies on cluster helicates that have appeared in the literature, practical applications for these compounds have not been reported to date.[11]

Here we report the synthesis, characterization and reactivity studies of novel polynuclear copper(I) cluster helicates derived from a thiosemicarbazone ligand that are capable of promoting, in the presence of O_2, the arene hydroxylation of their supporting ligand strands. The cluster helicates reported here represent new models of tyrosinase, an enzyme that catalyzes the hydroxylation of aromatic compounds.[12] The search for synthetic models of this copper enzyme is an area of high scientific relevance due to their biological significance[13] and also because of the potential industrial applicability of the catalytic transformation of organic substrates by metal complexes.[14] In contrast to the arene hydroxylation by dinuclear complexes studied in the pioneering works by Karlin[15] and others,[16] our systems are polynuclear metallo-supramolecular cluster compounds. To our knowledge, this is the first example of a functional cluster helicate and,

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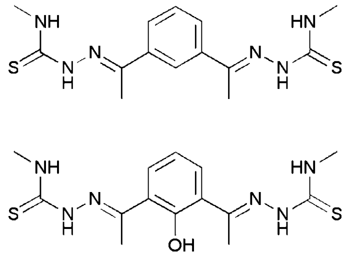
moreover, of an arene hydroxylation process promoted by cluster compounds. Low temperature UV-visible kinetic studies provided information about the mechanism.

Results and Discussion

The ligand bis(4-methyl-3-thiosemicarbazone)-(1,3)-diacetylbenzene (**H_2L**, Scheme 1) was designed to promote the formation of a polynuclear Cu^I cluster helical complex.[10b] Single brown plate crystals were obtained after two days of slow evaporation of the mother liquors of the electrochemical reaction[8] and the crystal structure of the copper complex **1** ($[Cu^{II}_2$**L′**$(OH)]$) was determined by X-ray crystallography (Figure 1).[17]



Scheme 1. Ligand H_2L[10b] (top) and its hydroxylated derivative H_3L' (bottom).

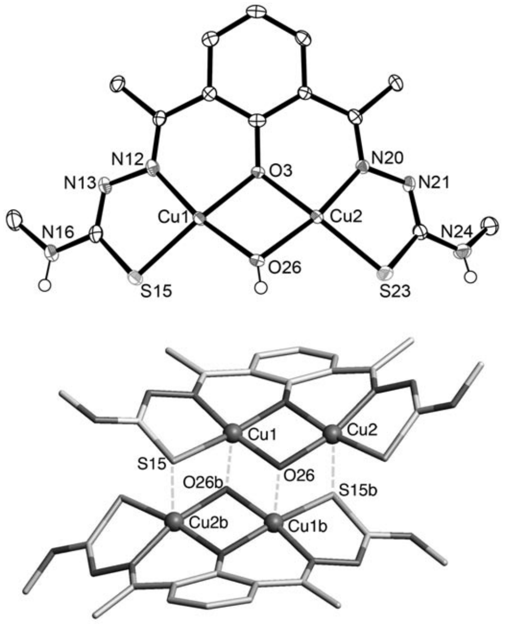


Figure 1. Top: ORTEP representation of complex $[Cu^{II}_2L'(OH)]$ (1). The hydrogen atoms belonging to carbon atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% of probability. Bottom: Ball-and-stick representation of part of the crystal cell of 1, showing the intermolecular weak contacts between neighbouring complex units.

To our surprise, compound **1** proved to be a neutral dinuclear Cu^{II} complex in which the original ligand **H_2L** underwent a hydroxylation process at the central carbon atom of the benzene spacer, giving rise to the new hydroxylated ligand **H_3L'** (see Scheme 1). The structure of **H_3L'** is also supported by the MALDI mass spectrum of the brown crystals, suggesting that the hydroxylated dinuclear copper(II) complex is the only species present in solution. Each of the two copper ions of the complex is coordinated to an imine nitrogen atom and to a sulfur atom of the trianionic ligand **H_3L'**. Moreover, the phenolate oxygen atom, arising from the hydroxylation process, and one hydroxide group act as μ_2-bridges between the metal centers. Thus, the coordination geometry of each copper(II) ion can be described as distorted square planar. The distortion from an ideal planar geometry is shown by the angles around Cu1, which range from 78.9 to 100.7°, and around Cu2, which range from 78.5 to 103.3°. The Cu···Cu distance in **1** (3.0008 Å) is in the same order as those previously reported for complexes with Cu_2^{II}-μ-η^2:η^2-phenoxo-hydroxo cores.[18] Additionally, two weak intermolecular contacts in **1** are worthy of note: one of the copper centers is bound to a μ_2-hydroxide oxygen atom [Cu1−O26b: 2.487(4) Å] and the other metal ion interacts with a thioamide sulfur atom [Cu2−S15b: 2.9731(9) Å], both of which belong to a neighbouring complex molecule.

As expected on the basis of magnetostructural considerations[19] and literature reports on complexes with structurally similar magnetically coupled cores,[20] the magnetic investigation of **1** shows a strong antiferromagnetic coupling between the two Cu^{II} centers (see Figure S6 in Supporting Information). The complex is in a fully populated singlet state up to 50 K; only above this temperature does the χ value start to increase due to population of the excited triplet, passing through a broad maximum at around 290 K. Accordingly, fitting of the data with the Bleaney–Bowers equation for $S = 1/2$ dimers gives a best fit value of $J = 300 \pm 2\ cm^{-1}$ ($R^2 = 0.99987$).

In order to avoid oxidation of the Cu^I ions and the hydroxylation of the ligand **H_2L**, we repeated the electrochemical synthesis of the copper complex and the subsequent crystallization process in the absence of oxygen. Following the same procedure under an Ar atmosphere, this resulted in the formation of abundant yellow crystals, from which the crystal structure of complex **2** ($[Cu^I_6$**L_3**$]\cdot 2\,CH_3CN$) was determined by X-ray crystallography (Figure 2).[21]

The structure of **2** comprises six Cu^I ions, three doubly anionic **L^{2-}** ligands and two solvating molecules of acetonitrile, and can be described as a neutral triple-stranded hexanuclear copper(I) cluster helicate. A racemic mixture of both enantiomers was observed in the unit cell. Two of the **L^{2-}** units are bound to the Cu^I_6 central core in a non-helical box-type fashion, with the third strand intertwining them, thus giving rise to the helical structure. To the best of our knowledge, this is the first example of a hexanuclear cluster helicate.

Four Cu^I centers of the metallic core (Cu1, Cu2, Cu3 and Cu6) occupy a three-coordinate, distorted trigonal environment in which they are bound by two μ_2-thiolate sulfur atoms from different ligand strands and one imine nitrogen

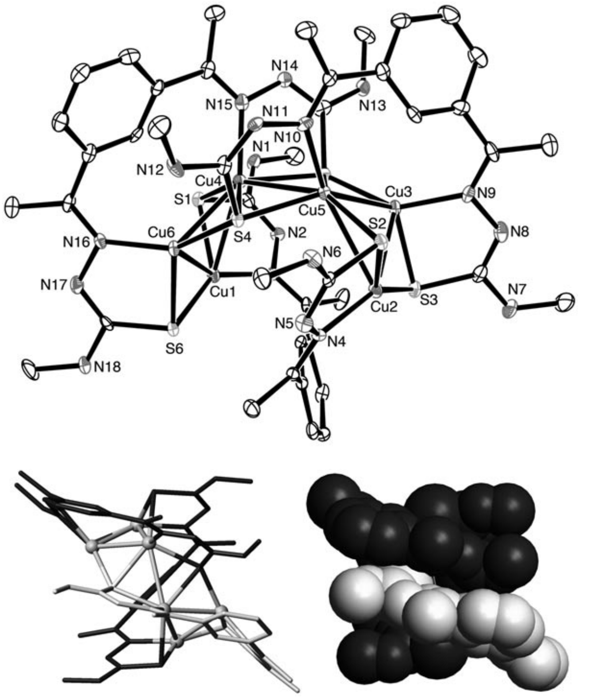


Figure 2. Top: ORTEP representation of complex $[\mathrm{Cu^I_6}\mathbf{L}_3]\cdot 2\mathrm{CH_3CN}$ (**2**). All hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% level of probability. Bottom-left: ball-and-stick representation of complex **2**. Bottom-right: space-filling representation of complex **2**, showing the helicity of the complex. The three ligand strands are individually colored in red, blue and white.

atom. The other two $\mathrm{Cu^I}$ ions (Cu4 and Cu5) are four-coordinated by two μ_2-thiolate sulfur atoms and one μ_3-thiolate sulfur atom from different ligands and one imine nitrogen atom. Thus, the three ligands act as $\mathrm{N_2S_2}$ bis-bidentate donors. The distortion from an ideal trigonal geometry is shown by the angles involving the nitrogen, copper and sulfur atoms, which range from 86.57 to 144.57°. Moreover, the distortion from an ideal tetrahedral coordination is shown by the angles involving the same atoms, which in this case range from 84.98 to 110.82°. The double deprotonation of the ligand units upon coordination is evident from the observed bond lengths in the cluster.

The $\mathrm{Cu^I_6}$ central core (Figure 3) can be described as two triangles (Cu1-Cu4-Cu6 and Cu2-Cu3-Cu5) connected by their closest vertices (Cu4 and Cu5). The distances between the metal centers (2.59–2.94 Å) are close to the sum of the van der Waals radii for two copper atoms (2.80 Å),[22] which is in agreement with the proposed existence of metal–metal interactions.[23] These contacts would mean that the coordination number of the $\mathrm{Cu^I}$ ions in **2** should increase from 3 to 5 (Cu1, Cu2, Cu3, Cu6) and from 4 to 7 (Cu4, Cu5).

Interestingly, the MALDI mass spectrum of crystals of **2** registered in acetone (Figure S1) shows that the hexanuclear copper(I) cluster helicate is not the only species present in solution. As previously was observed for related systems,[10] peaks were found that correspond to the tetranuclear copper(I) cluster helicate $[\mathrm{Cu^I_4}\mathbf{L}_2]$ derivative. This fact was confirmed by registering the ^{1}H NMR spectra of complex **2** at different temperatures in [D$_6$]acetone (Figure S2). The results obtained clearly indicate the existence of two species in solution at room temperature. These two species show similar chemical shifts in the NMR spectrum, as it is expected for two $\mathrm{Cu^I}$ cluster-type complexes derived from the same ligand (Figure S2). The assignment of the two sets of signals was performed on the basis of the data previously obtained by our research group for a $\mathrm{Cu^I}$ cluster helicate.[10b] When the temperature is lowered the intensity of the signals attributed to the tetranuclear compound experiences a slight decrease. Therefore, the two $\mathrm{Cu^I}$ clusters co-exist in acetone solution at low temperature.

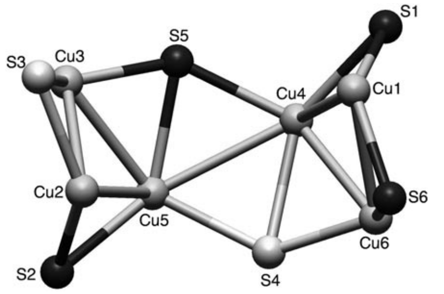


Figure 3. Ball-and-stick representation of the $\mathrm{Cu^I_6S_6}$ central core of complex **2**. Copper(I) ions are colored in green and sulfur atoms are colored in red, blue and white. The sulfur atoms with the same colour belong to the same ligand strand.

The hydroxylation of the arene residue of the copper(I) complex **2** in the presence of molecular oxygen, as observed in the electrochemical cell, indicates the formation of oxygen-derived active species. Two main types of $\mathrm{Cu_2O_2}$ species are known to be capable of hydroxylating aromatic ligand residues in dinuclear complexes, namely μ-η^2:η^2-peroxidodicopper(II) and bis(μ-oxido)dicopper(III) species.[13] These systems show different spectroscopic features but have similar stability since in some complexes the isomerisation between the two forms can be performed by changing the polarity of the solvent.[13ab] Usually, the dioxygen binding mode is determined by characterizing the $\mathrm{Cu_2O_2}$ species at low temperature.

When an anaerobic solution of copper(I) complex **2** ($2\cdot10^{-4}$ M) in dry acetone at −80 °C was exposed to $\mathrm{O_2}$ (1 atm), a band partly covered by the strong absorption of the solvent, but with an observable shoulder extending down to 400 nm, slowly developed. This band can be assigned to O(phenolate)-to-copper(II) charge transfer, as the final spectrum has the same features as those of the copper(II) complex **1**. The reaction occurs more rapidly on raising the temperature. In fact, at −70 °C almost an hour is required to reach completion but at −60 °C it takes about five minutes and only two minutes if the temperature is increased to −55 °C. At all temperatures the reaction occurs without accumulation of observable intermediates. On monitoring the absorbance changes at 390 nm, where the absorbance variation with time allows reliable data to be obtained, the reaction profiles follow a clear first-order behavior at any temperature, thus confirming the lack of accumulation of intermediates and allowing the determination of the first-order rate constant k_{obs} (see Table S1). The value of this constant increases with the temperature, as expected. The family of UV-visible spectra recorded during the endogenous hydroxylation reaction is shown in Figure S5 along with the fit of the curves at 390 nm for the reaction carried out at −60 °C/213 K.

The lack of accumulation of Cu_2O_2 intermediates is consistent with the following mechanism, assuming that the dilute solution employed in the kinetic experiments is composed by a mixture of the tetranuclear and hexanuclear copper(I) clusters, containing dinuclear "functional units" of the type $[Cu^I_2\mathbf{L}]$:

$$[Cu^I_2\mathbf{L}] + O_2 \rightleftharpoons [Cu_2\mathbf{L}O_2] \quad \text{(fast)} \tag{1}$$

$$[Cu_2\mathbf{L}O_2] \rightarrow [Cu^{II}_2\mathbf{L}'(OH)] \quad \text{(slow)} \tag{2}$$

According to this mechanism, the $[Cu_2\mathbf{L}O_2]$ species is formed in a fast pre-equilibrium, but this is shifted towards the reagents for the low affinity binding of molecular oxygen to the copper(I) complex. The second step is the irreversible ligand hydroxylation, which represents the rate determining step of the process. The $[Cu_2\mathbf{L}O_2]$ species does not accumulate because Reaction (1) is shifted to the left.

The reaction rate depends on the binding constant for Reaction (1) K_B, the oxygen concentration, and the rate constant for the ligand hydroxylation k_{ox}. Since K_B has a small value, the reaction rate is given by:

$$\text{rate} = k_{ox} \times K_B \times [O_2] \times [Cu^I_2\mathbf{L}]$$

According to this hypothesis, the observed first-order rate constant is given by:

$$k_{obs} = k_{ox} \times K_B \times [O_2]$$

that is, it contains both the binding constant of molecular oxygen to the copper(I) complex and the first-order rate constant for the hydroxylation of the ligand. This implies that:

$$k_{obs}/[O_2] = k_{ox} \times K_B$$

Application of the Eyring equation to $k_{obs}/[O_2]$ would give the apparent activation parameters, as a combination of kinetic and thermodynamic parameters, given by the following equations:

$$\Delta H^{\ddagger}_{app} = \Delta H^{\circ} + \Delta H^{\ddagger} \tag{3}$$

$$\Delta S^{\ddagger}_{app} = \Delta S^{\circ} + \Delta S^{\ddagger} \tag{4}$$

where ΔH° and ΔS° are the enthalpy and entropy changes, respectively, associated with the dioxygen binding to the Cu^I complex [Reaction (1)], while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation parameters for the hydroxylation step [Reaction (2)]. ΔS° is expected to be large and negative.[13]

To obtain the activation parameters for the hydroxylation reaction of $[Cu^I_2\mathbf{L}]$, the Eyring treatment was applied to the rate constants divided by the solubility of dioxygen in acetone at low temperature.[24] Fitting of the $k_{obs}/[O_2]$ data (Table S1) with the Eyring equation gives the graph shown in Figure 4, which yields $\Delta H^{\ddagger}_{obs} = (69 \pm 7)\ \text{kJ mol}^{-1}$ and $\Delta S^{\ddagger}_{obs} = (80 \pm 30)\ \text{J K}^{-1}\text{mol}^{-1}$.

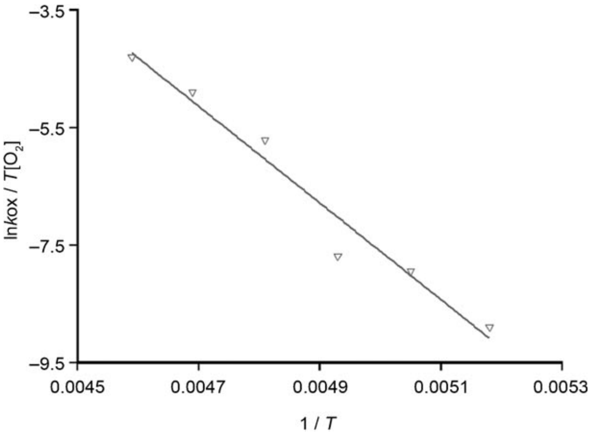


Figure 4. Fitting of the $k_{obs}/[O_2]$ data to the Eyring equation.

Considering the entropic term $\Delta S^{\ddagger}_{obs}$ given by Equation (4), the fact that the binding of O_2 to Cu^I complexes occurs with large and negative ΔS° values (in the range between −100 and $-250\ \text{J K}^{-1}\text{mol}^{-1}$) implies that the activation entropy for the hydroxylation process must be large and positive in order to overcome ΔS°. This leads to the conclusion that the $[Cu_2\mathbf{L}O_2]$ intermediate has a rigid structure and undergoes significant strain release on passing to the transition state.

Enthalpy parameters for the binding of O_2 to Cu^I complexes are usually negative,[13,15,25] but the lack of accumulation of the dioxygen adduct of $[Cu^I_2\mathbf{L}]$ suggests that here ΔH° must be small. The value of $\Delta H^{\ddagger}_{obs}$ and Equation (3) indicate that the enthalpic activation barrier for the intramolecular aromatic hydroxylation is large and positive, larger with respect to the values reported for a similar reaction with related dinuclear copper systems (which show values around $50\ \text{kJ mol}^{-1}$).[13,15,26] The larger value found here could be associated with a lower reactivity of the Cu_2O_2 species, which may need to overcome a larger barrier to reach the transition state, or to a different intrinsic mechanism.

In order to verify if the active species generated by reacting $[Cu^I_2\mathbf{L}]$ with O_2 are able to hydroxylate an exogenous substrate, 3,5-di-*tert*-butylphenol was added to a solution of complex **2** in acetone at low temperature (from −80 to −55 °C) before exposure to O_2 and allowed to react for several hours. This process was performed both in the presence and absence of a basic reagent. The workup of the reaction mixture did not show the formation of detectable amounts of 3,5-di-*tert*-butylcatechol or 3,5-di-*tert*-butylquinone in either case. This could mean that the endogenous reaction is strongly favored stereochemically with respect to the hydroxylation of the electron-rich phenol or that the coordination of the phenolic substrate to copper is sterically hindered.

Conclusion

We report the first example of a hexanuclear Cu^I cluster helicate. In solution, the complex has the practical application of promoting an endogenous arene hydroxylation process. As a result of this reaction the corresponding hydroxylated dinuclear copper(II) complex was obtained (Figure 5). The kinetic studies for the hydroxylation reaction showed a ΔH^{+} value of around 70 $kJ\,mol^{-1}$, which is similar to those found for the hydroxylations mediated by tyrosinase.[27] We believe that this approach could open new perspectives for the design of functional helicates with catalytic activity.

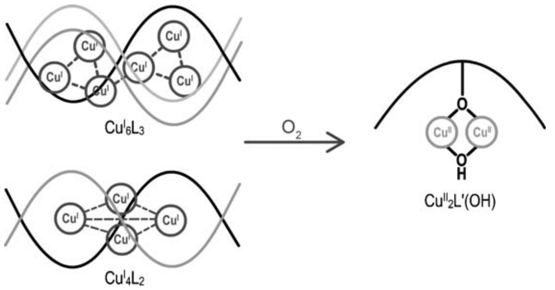


Figure 5. The Cu^I cluster helicates derived from the thiosemicarbazone-1,3-diacetylbenzene ligand $\mathbf{H_2L}$ promote, in the presence of O_2, an endogenous arene hydroxylation process that results in the formation of the corresponding hydroxylated dinuclear Cu^{II} complex.

Experimental Section

General methods: See Supporting Information.

Synthesis of $[Cu^{II}_2L'(OH)]$ (1) and $[Cu^I_6L_3]\cdot 2CH_3CN$ (2): The Cu^{II} and Cu^I complexes were obtained by an electrochemical procedure. An acetonitrile solution of the ligand bis(4-ethyl-3-thiosemicarbazone)-1,3-diacetylbenzene ($\mathbf{H_2L}$), containing tetramethylammonium perchlorate (ca. 10 mg) as supporting electrolyte, was electrolyzed using a platinum wire as the cathode and a copper plate as the anode. The cell system can be summarized as Pt(−)/MeCN + H_2L/Cu(+). The synthesis of the complexes was carried out as follows:

Synthesis of $[Cu^{II}_2L'(OH)]$ (1): A suspension of the ligand $\mathbf{H_2L}$ (0.1 g, 0.273 mmol) in acetonitrile (80 cm^3) was electrolyzed for 1.5 h using a current of 10 mA. The resulting brown solution was filtered and slowly evaporated in air for two days, giving rise to brown plate crystals of **1**, which were studied by X-ray diffraction.

Selected data for **1**: ^1H NMR ([D_6]DMSO): δ = 9.81 (d, 2H, J=7.45 Hz, H^3), 6.68 (t, 1H, J=7.45 Hz, H^4), 6.44 (m, 1H, H^2), 3.51 (m, 6H), 1.22 ppm (s, 6H) [see Figure S3]. ^1H NMR ([D_6]acetone): δ = 9.91 (d, 2H, J=7.45 Hz, H^3), 9.14 (s, 1H, H^5), 6.82 (m, 2H, H^2), 6.74 (t, 1H, J=7.45 Hz, H^4), 3.33 (m, 6H), 1.23 ppm (s, 6H) [see Figure S4]; IR (KBr): $\tilde{\nu}$ = 3437 (w, ν(OH)), 3371 (m, ν(NH)), 1554, 1553 (s, ν(C=N)+(C−N)), 1105, 795 (w, ν(C=S)), 1059 cm^{-1} (m, ν(N−N)); elemental analysis calcd (%) for $Cu_2C_{14}H_{18}N_6S_2O_2$: C 34.0, H 3.7, N 17.0, S 13.0; found: C 34.3, H 4.0, N 17.5, S 13.3; MS (MALDI): m/z: 492.8 for $[Cu_2\mathbf{L'}+H]^+$.

Synthesis of $[Cu^I_6L_3]\cdot 2CH_3CN$ (2): A suspension of the ligand $\mathbf{H_2L}$ (0.1 g, 0.273 mmol) in acetonitrile (40 cm^3) was electrolysed under Ar atmosphere for 1.5 h using a current of 10 mA. The resulting yellow solution was placed in a freezer under an Ar atmosphere for one week, giving rise to pale yellow prismatic crystals of **2**, which were studied by X-ray diffraction.

Selected data for **2**: ^1H NMR ([D_6]acetone): 10.59 (s, 1H, H^{5t}), 9.58 (brs, 1H, H^{5h}), 8.20 (s, 2H, H^{2t}), 7.89 (d, 2H, H^{3t}), 7.61 (m, 2H, H^{2h}), 7.55 (m, 2H, H^{3h}), 7.50 (t, 1H, H^{4t}), 5.9 (m, 1H, H^{4h}), 2.79 (s, br, 6H), 2.58 (s, br, 6H), 2.50 (s, 6H), 2.46 ppm (s, 6H) [see Figure S2]; IR (KBr): $\tilde{\nu}$ = 3299 (m, ν(NH)), 1627, 1588, 1515 (s, s, m, ν(C=N)+(C−N)), 1084, 806 (s, ν-(C=S)), 1053 cm^{-1} (m, ν(N−N)); elemental analysis calcd (%) for $Cu_6C_{46}H_{54}N_{18}S_6.(CH_3CN)_2$: C 37.7, H 4.1, N 19.1, S 13.1; found: C 37.6, H 4.3, N 19.1, S 13.5; MS (MALDI): m/z: 921.9 for $[Cu_4\mathbf{L}_2+H]^+$, 1385.0 for $[Cu_6\mathbf{L}_3+H]^+$.

Acknowledgements

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[17] Crystal structure analysis of **1**: X-ray diffraction data were collected from a brown prismatic crystal ($0.10\times0.07\times0.04$ mm^3) by means of a Smart CCD-1000 BRUKER diffractometer by using graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda=0.71073$ Å) from a fine-focus sealed-tube source. Crystal data for $Cu_2C_{14}H_{18}N_6S_2O_2$: $M_r=493.54$, $T=100(2)$ K, monoclinic $P21/c$, $a=13.7440(5)$, $b=6.4570(3)$, $c=20.7280(7)$ Å, $\beta=108.449(2)°$, $V=1744.97(13)$ Å^3, $Z=4$, $\rho_{calcd}=1.879$ g cm^{-3}, $\mu=1.827$ mm^{-1}, 18515 measured reflections, 4010 independent reflections ($R_{int}=0.0559$), 2983 independent reflections with $I>2\sigma(I)$, 251 parameters refined, GOF$=0.999$, $R_1=0.0350$ ($I>2\sigma(I)$) and 0.0568 (for all data), $R_{2w}=0.0723$ ($I>2\sigma(I)$)and 0.0775 (for all data), max./min. residual electron density 0.597/-0.465 e Å^{-3}.[21b,c]

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[21] a) Crystal structure analysis of **2**: X-ray diffraction data were collected from a pale yellow prismatic crystal ($0.15\times0.08\times0.03$ mm^3) by means of a Smart CCD-1000 BRUKER diffractometer using graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda=0.71073$ Å) from a fine-focus sealed-tube source. Crystal data for $Cu_{1.5}C_{11.5}H_{15}N_5S_{1.5}$: $M_r=366.68$, $T=100$ (2) K, triclinic $P\bar{1}$, $a=11.2032(12)$, $b=12.6954(13)$, $c=21.885(2)$ Å, $\alpha=92.663(6)$, $\beta=97.945(6)$, $\gamma=110.058$ (6)°, $V=2881.0$ (5) Å^3, $Z=8$, $\rho_{calcd}=1.691$ g cm^{-3}, $\mu=2.446$ mm^{-1}, 42252 measured reflections, 11748 independent reflections ($R_{int}=0.0957$), 7219 independent reflections with $I>2\sigma(I)$, 717 parameters refined, GOF$=0.992$, $R_1=0.0516$ ($I>2\sigma(I)$) and 0.1076 (for all data), $R_{2w}=0.0959$ ($I>2\sigma(I)$)and 0.1085 (for all data), max./min. residual electron density 0.916/-0.564 e Å^{-3}; b) All the crystal structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 using SHELX-97 software.[28] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at calculated positions; c) CCDC-768740 (**1**) and 768741 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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