Supporting Information

Mercaptothiacalixarenes Steer 24 Copper(I) Centers to form a Hollow-Sphere Structure Featuring Cu₂S₂ Motifs with Exceptionally Short Cu···Cu Distances

Nicolas Frank, André Dallmann, Beatrice Braun-Cula, Christian Herwig, and Christian Limberg*

anie_201915882_smMiscellaneous_information.pdf
Supporting Information

Table of Contents

Experimental Procedures p. 1
   General Considerations
   Synthesis of [(Ph3PCu)4L]6
   Synthesis of [LCu4]6
NMR and XRD studies p. 3
   DOSY Experiments
   Detection of Et2NH in the Cavity of [LCu4]6
   1H NMR spectroscopic monitoring of titration studies with [LCu4]6 and MeCN
   Variable temperature 1H NMR studies concerning the interaction of [LCu4]6 with MeCN
   Variable temperature 1H NMR studies concerning the interaction of [LCu4]6 with CH4
X-ray crystallographic information p. 7
Density functional calculations p. 9
References p. 24

Experimental Procedures

General Considerations

All manipulations were carried out under an argon atmosphere using schlenk techniques or in gloveboxes under argon atmosphere maintained below 1 ppm of O2 and H2O. Solvents were purified in an MBraun solvent purification system and stored under argon atmosphere over activated molecular sieves. [Ph3PCuH]6 and CH4 were used as received from Sigma Aldrich. LH4 was synthesized after literature procedures. Instead of column chromatography, recrystallization from dichloromethane was employed to purify the compounds between steps.[1] [CuNEt2]4 was prepared according to a known procedure.[2] ATR-IR spectra were recorded on a Bruker Alpha spectrometer with an ATR sampling unit under argon atmosphere. Elemental analyses were performed with a HEKA Euro 3000 elemental analyser. NMR Spectra were recorded on Bruker NMR spectrometers (Avance DPX 300 MHz, Avance II 300 MHz, Avance 600 MHz). Chemical shifts are referenced to the signal of C5D5H (δ = 7.16 ppm). In mixtures of C6D6 and toluene-d8 the shifts are referenced to the signal of the C6D5CD2H signal of toluene-d8, which has the same shift (δ = 2.11 ppm) in both solvents. Electrochemical studies were carried out using a PalmSens EmStat Blue potentiostat under computer control in a glovebox under argon atmosphere using a three-electrode configuration with a glassy carbon disc (7.0 mm²) as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudo-reference electrode. The mid-peak potentials are referenced internally to the FeCp2/FeCp2+ redox couple, which was measured in a reference scan after adding ferrocene.

The DOSY NMR spectra were recorded on a Bruker Avance 600 MHz using a BBI Bruker 5 mm z-gradient probe, which allows to use field gradients up to about 53.5 G·cm⁻¹. The temperature was not regulated as this introduced strong thermal fluctuations and thus was left to equilibrate to room temperature at approximately 293.4 K, and the NMR tube was not spun. The diffusion NMR experiments were performed with a pulsed-gradient stimulated echo sequence using bipolar gradient (ledbpgp2s). DOSY NMR spectra were generated with Topspin 3.6. The samples were prepared by dissolving the solid samples in C6D6 with an average concentration of about 4.0 mmol/L. Sequence delays were Δ = 100 ms (diffusion delay), τ = 1.2 ms (after gradient recovery delay), and Te = 3 ms (LED recovery delay). For each data set, 8192 complex points were collected for each 16 experiments in which the
Supporting Information

Gradient strength was exponentially incremented from approximately 1 to 47.5 G·cm$^{-1}$. The gradient duration $\delta/2$ was adjusted to observe a near complete signal loss (signal intensity <10%) at 47.5 G·cm$^{-1}$. The $\delta/2$ delay was chosen as 1100 ms for [LCu$_4$]$_6$ and 1350 ms for [(Ph$_3$PCu)$_4$L]. A 5 s recycle delay was used between scans for all data shown. The number of scan was adapted to the sample, but never less than eight scans. For each data set, the spectral axis was processed with sine-bell, and a Fourier transformation was applied in order to obtain 16384 real points. A spline baseline correction was finally applied. The spectrum was then processed according to the Bruker DOSY manual with standard parameters.

Synthesis of [(Ph$_3$PCu)$_4$L]

[Ph$_3$PCuH]$_6$ (126.3 mg, 0.064 mmol, 4 equiv.) was dissolved in 60 mL toluene and LH$_4$ (84.1 mg, 0.107 mmol, 6 equiv.) was dissolved in 15 mL toluene. The solution of [Ph$_3$PCuH]$_6$ was added dropwise to the calixarene solution under constant stirring at -80 °C. The solution was warmed up to room temperature and stirred for 20 h. Subsequently, the volatiles were removed under high vacuum, and the residue was dissolved in 2.5 mL of toluene. The solution was layered with $n$-hexane. Within 5 d, 120.0 mg (0.057 mmol, 59.0%) of bright yellow crystals of the product could be isolated.

Scheme S1. Assignments of the NMR signals for [(Ph$_3$PCu)$_4$L].

$^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 7.82 - 7.65$ (m, 24H, H12), 7.49 (s, 8H, H4/H5), 6.96 – 6.71 (m, 36H, H9/H11), 1.08 (s, 36H, H1) ppm.

$^{31}$P{1H} NMR (121 MHz, C$_6$D$_6$) $\delta = -0.3$ (s) ppm.

$^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta = 158.6$ (C8) 143.15 (C3), 137.75 (C6/7), 135.87 (C10), 135.49 (C11), 134.69 (C12), 134.49 (C12), 131.49 (C4/5), 128.68 (C9), 128.55 (C9), 34.07 (C2), 31.48 (C1) ppm.

ATR-IR (solid): $\nu =$ 3049 (w), 2950 (m), 2902 (w), 2864 (w), 1584 (w), 1571 (w), 1494 (m), 1476 (m), 1433 (m), 1388 (m), 1360 (m), 1327 (m), 1247 (m), 1180 (m), 1149 (m), 1123 (m), 1092 (m), 1041 (m), 1026 (w), 996 (w), 969 (s), 917 (s), 880 (m), 868 (m), 847 (s), 740 (s), 690 (m), 618 (m), 605 (m), 519 (s), 491 (s), 464 (s), 423 (s) cm$^{-1}$.

Elemental analysis calc. (%) for C$_{112}$H$_{104}$Cu$_4$P$_4$S$_8$ (2084.62 g/mol$^{-1}$): C 64.53 H 5.03 S 12.31; found: C 64.62 H 5.09 S 12.26.

Synthesis of [LCu$_4$]$_6$

[CuNEt$_2$]$_6$ (69.1 mg, 0.127 mmol, 1 equiv.) was dissolved in 1 mL of toluene. LH$_4$ (100.0 mg, 0.127 mmol, 1 equiv.) was dissolved in 3 mL toluene and then added slowly to the solution of [CuNEt$_2$]$_6$ at -80 °C under constant stirring in the course of 2 min. The solution was stirred for 2 h at room temperature and subsequently layered with 0.5 mL of toluene and 15 mL of acetonitrile. Intense orange crystals formed within 4 d (Figure S1). The solution was decanted off, the crystals were washed with acetonitrile and dried under high vacuum. Yield 117.0 mg (0.018 mmol, 88.7%).

Figure S1. Left: Crystals of [LCu$_4$]$_6$ in a Schlenk tube containing a test tube; right: View through a microscope of crystals of [LCu$_4$]$_6$ in oil.
Scheme S2. Assignments of the NMR signals for [LCu₄]₆.

1H NMR (300 MHz, C₆D₆) δ = 6.74 (d, J = 2.2 Hz, 24H, H4/H5), 7.50 (d, J = 2.2 Hz, 24H, H4/H5), 0.98 (s, 216H, H1) ppm.

13C NMR (75 MHz, C₆D₆) δ = 153.1 (C8), 145.2 (C3), 140.1 (C6/C7), 139.8 (C6/C7), 133.6 (C4/C5), 132.9 (C4/C5), 34.0 (C2), 31.2 (C1) ppm.

ATR-IR (solid): ν = 2953 (s), 2904 (m), 2868 (m), 1572 (w), 1502 (w), 1477 (m), 1462 (m), 1391 (vs), 1376 (s), 1362 (s), 1261 (vs), 1204 (s), 1182 (m), 1145 (m), 1117 (s), 1035 (s), 870 (m), 807 (m), 782 (m), 722 (m), 709 (m), 632 (m), 623 (m), 597 (m), 555 (m), 534 (m), 496 (m), 476 (m), 420 (m) cm⁻¹.

Even after drying the powder under high vacuum over 60 h, residual toluene (~3 equiv.) was still found in the sample, as revealed by the 1H NMR spectrum and the elemental analysis.

Elemental analysis calc. (%) for C₂₄₀H₂₆₄Cu₂₄S₄₈ x 3(C₇H₈) x (C₄H₁₁N) (6561.43 g/mol⁻¹): C 48.51; H 4.58; S 23.46; found: C 48.24; H 4.56; S 23.41.

NMR and XRD studies

DOSY Experiments

The DOSY NMR experiments were performed to determine whether [LCu₄]₆ is stable in solution. The diffusion coefficients of [(Ph₃PCu)₄L] and [LCu₄]₆ were compared. Using the Stokes-Einstein equation the hydrodynamic radius Rᵥ was calculated from the diffusion coefficients. The kinematic viscosities of THF [3] (5.379·10⁻⁴ pa s) and benzene [4] (6.4965·10⁻⁴ pa s) at 20 °C were used as reported in the literature.

Table S1. Results of the DOSY NMR experiments of [LCu₄]₆ and [(Ph₃PCu)₄L].

| DOSY Experiment    | Diffusion Coefficient [m² s⁻¹] | Hydrodynamic radius [Å] | Hydrodynamic diameter [Å] | Largest extent of molecule in X-ray structure [Å] |
|-------------------|-------------------------------|--------------------------|----------------------------|-----------------------------------------------|
| [(Ph₃PCu)₄L] in C₆D₆ | 7.638·10⁻¹⁰                   | 4.32                     | 8.64                       | 15                                            |
| [LCu₄]₆ in C₆D₆   | 2.88·10⁻¹⁰                    | 11.48                    | 22.96                      | 25                                            |
| [LCu₄]₆ in THF-d₈ | 3.63·10⁻⁸                     | 11.18                    | 22.36                      | 25                                            |

Considering that the molecules do not represent perfect spheres, but are shaped like a cylinder ([(Ph₃PCu)₄L]) or an octahedron ([LCu₄]₆), these results are in line with the expectations based on the solid state structures, indicating that the structures remain intact upon dissolution. The largest distance between two tert-butyl groups in the crystal structure of [LCu₄]₆ is roughly 25 Å, whereas the largest distance between a tert-butyl and a phenyl-group in [(Ph₃PCu)₄L] is 15 Å.

Detection of Et₂NH in the Cavity of [LCu₄]₆

In addition to the signals of [LCu₄]₆ and acetonitrile the 1H NMR spectrum of [LCu₄]₆ showed three signals at 5.01 ppm 4.01 ppm and 3.20 ppm with integrals equal to 4, 1 and 6 protons. These resonances did not disappear after drying of the powdered solid under vacuum for 6 d. The COSY NMR spectrum exhibits crosspeaks between the signal at 5.01 ppm and each of the two other signals, while for the signal at 3.20 ppm, there is only one crosspeak to the signal at 5.01 ppm. The HSQC NMR spectrum reveals crosspeaks between the signals at 5.01 ppm and 3.20 ppm and the 13C NMR signals at 47.3 ppm and 17.9 ppm, while the signal at 4.01 ppm does not show any crosspeak. In the HMBC NMR spectrum, the signal at 4.01 ppm shows crosspeaks to the 13C NMR signals at 47.3 ppm and 17.9 ppm. Taken together these observations suggest an assignment of these signals to diethylamine, which is a side product of the synthesis of [LCu₄]₆. The ratio of the integrals of these signal in comparison to those of [LCu₄]₆ amounts to 1.
(i.e. one Et₂NH molecule per [LCu₄]₆ entity) and the fact that they exhibit a considerable downfield shift in comparison to the resonances of free Et₂NH in C₆D₆ (2.49 ppm 0.99 ppm and 0.25 ppm) indicates that the diethylamine molecule is located within the hollow inner cage of [LCu₄]₆. When Et₂NH was added to a solution of [LCu₄]₆ no exchange between free Et₂NH and guest Et₂NH was observed. The DOSY NMR spectrum clearly shows that the Et₂NH guest molecule has the same diffusion coefficient as [LCu₄]₆. Finally, a ROESY NMR spectrum evidences the absence of coupling between the signals of Et₂NH and the aromatic signals of [LCu₄]₆, i.e. the absence of contacts between the respective protons through space, rendering a location of amine molecule in the calixarene cavities unlikely.

**Figure S2.** Section of the COSY NMR spectrum of [LCu₄]₆ dissolved in C₆D₆.

Based on the information from the NMR spectra, a VOID (or Squeeze) analysis of the crystal structure was conducted, which revealed a total electron density of 51 electrons located in the central cavity. This would indeed fit to a molecule of Et₂NH, as suggested by the NMR data. However, due to the high symmetry of the crystal structure, such a Et₂NH molecule should be expected to experience severe disordering and as a matter of fact all modelling attempts failed. Therefore, the single crystal X-ray data does not fully confirm the presence of Et₂NH but it is in line with the assessment based on the NMR data. Further information on the squeeze analysis is provided in the SI chapter: X-ray crystallographic information.

**1H NMR spectroscopic monitoring of titration studies with [LCu₄]₆ and MeCN**

[LCu₄]₆ was dried under high vacuum for 60 h. 6.2 mg (1.0 μmol) [LCu₄]₆ were dissolved in 0.7 mL of C₆D₆ in a young NMR tube to give a yellow solution. A 1H NMR spectrum was measured to make sure there was no MeCN left in solution. A stock solution of MeCN in C₆D₆ was prepared in the glovebox. Small amounts of this solution were added to the young tube and a 1H NMR spectrum was measured after each addition (Figure S3). The exact amount of the added acetonitrile was determined later by integration of the exchange peak. It becomes obvious that the peak at -0.81 ppm, which represents an averaged resonance of signals caused by free acetonitrile and intercalated acetonitrile, shifts to lower fields, as the concentration of non-intercalated acetonitrile, which has a larger chemical shift value, increases. After the addition of a total of 560 equivalents of MeCN the averaged peak is found at a chemical shift higher than the one of free acetonitrile in pure C₆D₆ at (>0.58 ppm). This shift occurs because C₆D₆ cannot be considered as the only solvent anymore and acetonitrile influences the chemical shift as a solvent as well.
Figure S3. $^1$H NMR spectroscopic monitoring of the titration experiment. To [LCu$_4$]$_6$ in C$_6$D$_6$ the given amounts of acetonitrile dissolved in C$_6$D$_6$ were added. Labels over each spectrum display the total amount of acetonitrile, which was present.

Variable temperature $^1$H NMR studies concerning the interaction of [LCu$_4$]$_6$ with MeCN

6.0 mg (0.97 μmol) of [LCu$_4$]$_6$ were dissolved in 0.2 mL of C$_6$D$_6$ and 0.5 mL of toluene-d$_8$ were added. The mixture was transferred to a young NMR tube and 12 equiv. of MeCN were added. NMR spectra were measured at temperatures between +25 and -70 °C (Figure S4). The signal at 0.00 ppm disappears below -10 °C and after cooling below -30 °C two new signals evolved at 0.29 ppm and -2.18 ppm. The signal at -2.18 ppm was assigned to acetonitrile molecules in the guest position within the calixarene ligands, as observed in the crystal structure. The signal at 0.29 ppm can be assigned to free acetonitrile at -70°C. This measurement thus confirms that the signal displayed at +25 °C at 0.00 ppm represents the averaged resonances of guest MeCN molecules and free MeCN molecules.
Variable temperature $^1$H NMR spectra of $[LCu_4]_6$ dissolved in C$_6$D$_6$, with 12 equiv. of MeCN added. (~) silicone grease, (#) averaged signal of free MeCN and MeCN in guest position, (+) free MeCN, (*) MeCN in guest position.

Variable temperature $^1$H NMR studies concerning the interaction of $[LCu_4]_6$ with CH$_4$

7.0 mg (1.13 μmol) of $[LCu_4]_6$ were dissolved in 0.2 mL of C$_6$D$_6$ and 0.6 mL of toluene-d$_8$ were added. The mixture was transferred to a young NMR tube and CH$_4$ was bubbled through the solution with a cannula for 30s. $^1$H NMR spectra were measured at temperatures between +22 and -70 °C (Figure S5). The new CH$_4$ signal at 0.11 ppm shifts significantly upon lowering of the temperature and disappears below -60 °C. No new signals evolve at lower temperatures. Free methane in C$_6$D$_6$/toluene-d$_8$ at 25 °C would give rise to a signal at 0.16 ppm. The results therefore suggest that at low temperatures methane is increasingly included as a guest in the calixarene moieties, so that the averaged resonance shifts to higher field. As in case of MeCN a decoalescence should be expected at low temperatures, but this point is not reached at -70°C. The significant broadening, however, suggests that the point is close.
Figure S5. Variable temperature $^1$H NMR spectra of $[\text{LCu}_4]_6$ dissolved in $\text{C}_6\text{D}_6$, after CH$_4$-bubbling for 30 s. (*) $[\text{LCu}_4]_6$, (#) silicone grease, (~) methane in guest position.

X-ray crystallographic information

General

The data collections were performed with a BRUKER D8 VENTURE area detector with Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Multi-scan absorption corrections implemented in SADABS$^{[5]}$ were applied to the data. The structures were solved by intrinsic phasing method (SHELXT-2013)$^{[6]}$ and refined by full matrix least square procedures based on $F^2$ with all measured reflections (SHELXL-2014)$^{[7]}$ in the graphical user interface (SHELXle)$^{[8]}$ with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. The calculation of the voids in the structure was achieved with the Platon Program.$^{[9]}$ For more information: http://www.cryst.chem.uu.nl/spek/platon/pl000302.html$^{[10]}$

CCDC 1970788 ($[\text{LCu}_4]_6 \cdot 6(\text{C}_2\text{H}_3\text{N})$), 1970789 ($[(\text{Ph}_3\text{PCu})_4\text{L}] \cdot 2(\text{C}_7\text{H}_8)$) 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.

Analysis and comparison of the Cu···Cu distance in the Cu$_2$S$_2$ motif

A search concerning the Cu$_2$S$_2$ diamond-core motif without any further requirements about the quality of the Data in the CSD (25.11.19, CSD Version 5.40 + 3 Updates) yielded 681 hits (Figure S6). The shortest Cu···Cu distance found in this search was 2.516 Å. This makes the Cu···Cu distance in $[\text{LCu}_4]_6$ (2.4725(16) Å) the shortest one hitherto reported for a Cu$_2$S$_2$ motif.
Further refinement of the search criteria towards high quality structures yielded only 130 hits (Figure S7). An analysis of the 33 structures containing Cu···Cu distances below (2.6 Å) identified those as either mixed valence complexes as well as all-copper(I) complexes.

Squeeze/Void Analysis

In addition to the void inside the Cu2S24 cage, three additional voids can be located in the crystal structure. A larger void of about 111 electrons outside the cluster corresponds most probably to disordered Et2NH molecules on a special position. The largest void of 2684 electrons, which interconnects all channels around the cluster, may be attributed to more than a hundred disordered solvent molecules. Therefore, we considered squeeze refinement appropriate. The presence of these molecules is conceivable, as crystals were subjected to the X-ray analysis directly after they had been taken out of the layered solution. In contrast the NMR spectra were measured for solutions of crystals that had been dried over 3 d under vacuum. Due to this only the one equiv. of Et2NH inside the [LCu4] cavity as well as a small amount of residual toluene are visible in the NMR spectra.

Crystallographic Data for [(Ph3PCu)L]2(C2H4): C123H64Cu2P4S8, 2(C2H4), Mr = 2268.90, triclinic, P-1, yellow block, 0.630 x 0.350 x 0.230 mm, a = 14.7564(8) Å, b = 16.3238(8) Å, c = 27.7136(14) Å, α = 78.038(2) °, β = 78.471(2) °, γ = 65.463(2) °, V = 5892.2(5) Å³, Z = 4, ρ = 1.279 g·cm⁻³, µ = 0.955 mm⁻¹, Mo-Kα radiation (λ = 0.71073 Å), T = 100(2) K, Θ = 2.29 - 26.45 °, F000 = 2360, reflections collected 101690, reflections unique 20920 [Rint = 0.0357], GooF = 1.077, R1 = 0.0356, wR2 = 0.0946, largest diff. peak and hole 0.902 and -0.661 eÅ³.

Crystallographic Data for [LCu4]6·6(C2H3N): C240H264Cu24S48, 6(C2H3N), Mr = 6458.66, cubic, F432, yellow prism, 0.360 x 0.350 x 0.220 mm, a = 34.0103(11) Å, b = 34.0103(11) Å, c = 34.0103(11) Å, α = 90 °, β = 90 °, γ = 90 °, V = 39340(4) Å³, Z = 4, ρ = 1.090 g·cm⁻³, µ = 1.556 mm⁻¹, Mo-Kα radiation (λ = 0.71073 Å), T = 100(2) K, Θ = 2.395 - 25.033 °, F000 = 13200, reflections collected 29329, reflections unique 20920 [Rint = 0.0482], GooF = 1.092, R1 = 0.0418, wR2 = 0.1240, largest diff. peak and hole 0.441 and -0.584 eÅ³.
Density functional calculations

Geometry optimizations were performed in redundant internal coordinates using the Gaussian09 program package. The molecular structure of the compound \([\text{LCu}_4]\) as determined by X-ray diffraction analysis was used as starting point. The symmetry was restricted to octahedral as in the crystal structure. The B3LYP functional has been employed amended by the D3 version of Grimme’s dispersion, together with the Def2-TZVP basis set as implemented in Gaussian. Very tight convergence criteria have been chosen for the SCF procedure and a pruned (99,590) “ultrafine” integration grid was used for numerical integrations. Visualization of molecular structures was accomplished with the program Gauss View (Gaussian, Inc.).

The structure of \([\text{LCu}_4]\) in its singlet ground state is very similar to that determined by X-ray diffraction analysis (Figure S8). A comparison of selected bond lengths and angles is shown in Table S2.

Table S2. Selected bond lengths and angles.

| bond length [Å] or angle [°]                      | \([\text{LCu}_4]\) by X-ray diffraction analysis | \([\text{LCu}_4]\) by DFT (singlet ground state) |
|------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Cu1'···Cu1#                                      | 2.4725(16)                                    | 2.556                                         |
| Cu1'–S1'                                        | 2.2524(17)                                    | 2.304                                         |
| Cu1'–S2'                                        | 2.2396(18)                                    | 2.319                                         |
| Cu1'–S1*                                        | 2.4718(17)                                    | 2.537                                         |
| Cu1'–S1+                                        | 2.2408(18)                                    | 2.276                                         |
| S2'–Cu1'–S1'                                    | 94.84(6)                                      | 92.1                                          |
| S1'–Cu1'–S1*                                    | 98.66(8)                                      | 96.8                                          |
| S2'–Cu1'–S1*                                    | 89.86(11)                                     | 88.1                                          |
| S1'–Cu1'–S1'                                    | 114.16(5)                                     | 113.8                                         |
| Cu1'–S1*–Cu1#                                   | 63.04(8)                                      | 63.9                                          |

Figure S8. Optimized molecular structure of \([\text{LCu}_4]\) (B3LYP-D3/Def2-TZVP, singlet state). Hydrogen atoms are omitted for clarity.

The Cu···Cu distance is overestimated by DFT by 0.083 Å. By choosing functionals which work especially well for Cu thiolate complexes, as investigated by Schmidt and Henkel, this deviation can be reduced to 0.031 Å (Table S3).
Table S3. Cu···Cu in [LCu4]₆ depending on the functional.

|           | B3LYP-D3/Def2-TZVP | PBE0-D3/Def2-TZVP | TPSSh/Def2-TZVP |
|-----------|--------------------|-------------------|-----------------|
| Cu₁···Cu₂ distance [Å] | 2.556              | 2.528             | 2.504           |
| Deviation from experiment | 0.083              | 0.055             | 0.031           |

For comparison, the Cu₂S₂ diamond core motif (cf. Scheme 2 in the main text) including the surrounding two calixarene fragments [SRSRS]²⁻ (R = t-butyl-phenylene) was extracted from the crystal structure of [LCu4]. To obtain a neutral molecule with two Cu ions as in the [LCu4] original, the two remote thiolate functions were protonated, and the structure of the resulting molecule [Cu₂(SRSRS)₂]²⁻ was optimised for different spin states. The structure of the singlet ground state is shown in Figure S9 (left).

![Figure S9](image)

Figure S9. Optimised molecular structures of neutral molecules containing the Cu₂S₂ diamond core motif (B3LYP-D3/Def2-TZVP): left: with 2 protonated thiolate functions ([Cu₂(SRSRS)₂]²⁻, singlet ground state), middle: with 1 protonated thiolate function ([SRSRS]CuICuII[SRSRS]), doublet ground state), right: without protonation ([CuII₂(SRSRS)₂], triplet ground state).

Table S4. Cu···Cu distance in optimised molecular structures containing the Cu₂S₂ diamond core motif.

|                | [Cu₂(SRSRS)₂] | [[SRSRS]CuICuII[SRSRS]] | [CuII₂(SRSRS)₂] |
|----------------|---------------|--------------------------|-----------------|
| Cu₁···Cu₂ distance [Å] | 2.559         | 2.828                     | 2.827           |

Compared to the calculated Cu···Cu distance in [LCu4] (2.556 Å, Table S2), the corresponding distance in [Cu₂(SRSRS)₂] is almost the same (2.559 Å, Table S4).

To investigate the influence of the copper oxidation state, also the structures of the neutral molecules containing the Cu₂S₂ diamond core with one and with no protonated thiolate function have been optimised (Figure S9), corresponding to molecules with one or two Cu ions replaced by Cu⁺ ions, respectively. In these molecules, the Cu···Cu distances are much longer (Table S4). Furthermore, in order to test whether the choice of protons for charge compensation is appropriate, also a more sophisticated model was investigated, where the surrounding of the Cu₂S₂ diamond core motif is more similar to that in the [LCu4] complex. In [Cu₂(SRSRSL⁺)]²⁻ the two remote thiolate functions are not protonated, but neutralised each by a Cu⁺ ion, coordinated by a 1,4,7-trithiaclononane ligand L⁺ (Figure S10). The Cu···Cu distance was predicted to be 2.534 Å (Table S5), which is comparable to the distances of both, [LCu4] and [Cu₂(SRSRS)₂].

In contrast, if the two remote thiolate residues are just left to be anionic, resulting in a dianion [Cu₂(SRSRS)₂]²⁻, the Cu···Cu distance becomes much longer (3.884 Å, see Figure S10 and Table S5), due to electrostatic interaction.

![Figure S10](image)

Figure S10. Optimised molecular structures of neutral [Cu₂(SRSRSL⁺)]²⁻ (left) and dianionic [Cu₂(SRSRS)₂]²⁻ (right) (B3LYP-D3/Def2-TZVP, singlet ground state).
Table S5. Cu···Cu distance in optimised molecular structures containing the Cu$_2$S$_2$ diamond core motif.

|                  | [Cu$_i$(SRSRL$^i$)$_2$]$_n^-$ | [Cu$_i$(SRSRS)$_2$]$^{2-}$ |
|------------------|-------------------------------|-----------------------------|
| Cu1···Cu2 distance [Å] | 2.534                         | 3.884                       |

Cartesian coordinates (Å) for the theoretical structure of the singlet state (ground state) of [LCu$_4$]$_6$:
B3LYP-D3/Def2-TZVP, E = -67799.6153866 hartree

|      | x         | y         | z         |
|------|-----------|-----------|-----------|
| Cu   | -3.163644 | -1.104432 | 4.072391  |
| Cu   | 3.163644  | 1.104432  | 4.072391  |
| Cu   | 1.104432  | -3.163644 | 4.072391  |
| Cu   | -1.104432 | 3.163644  | 4.072391  |
| Cu   | -1.104432 | 4.072391  | -3.163644 |
| Cu   | 3.163644  | 4.072391  | -1.104432 |
| Cu   | 1.104432  | 4.072391  | 3.163644  |
| Cu   | -1.104432 | 4.072391  | 1.104432  |
| Cu   | 3.163644  | 4.072391  | 1.104432  |
| Cu   | -3.163644 | 4.072391  | -1.104432 |
| Cu   | -3.163644 | -4.072391 | -1.104432 |
| Cu   | 3.163644  | -4.072391 | 1.104432  |
| Cu   | -3.163644 | -4.072391 | 3.163644  |
| Cu   | 3.163644  | -4.072391 | 3.163644  |
| Cu   | -3.163644 | 3.163644  | -4.072391 |
| Cu   | 3.163644  | 3.163644  | -4.072391 |
| Cu   | -3.163644 | 4.072391  | 3.163644  |
| Cu   | 3.163644  | 4.072391  | 3.163644  |
| Cu   | -3.163644 | 4.072391  | 1.104432  |
| Cu   | 3.163644  | 4.072391  | 1.104432  |
| Cu   | -3.163644 | -4.072391 | -1.104432 |
| Cu   | 1.104432  | 4.072391  | -1.104432 |
| Cu   | 3.163644  | 4.072391  | -1.104432 |
| Cu   | 1.104432  | 4.072391  | -1.104432 |
| Cu   | 1.104432  | -3.163644 | 3.163644  |
| Cu   | 1.104432  | -3.163644 | -4.072391 |
| Cu   | 1.104432  | -3.163644 | 4.072391  |
| Cu   | 1.104432  | 3.163644  | -1.104432 |
| Cu   | 1.104432  | 3.163644  | 1.104432  |
| Cu   | 1.104432  | 3.163644  | 4.072391  |
| Cu   | 1.104432  | 3.163644  | 4.072391  |
| S     | -1.219594 | -2.253569 | 4.526702  |
| S     | -3.831679 | -1.190730 | 6.291356  |
| S     | 2.253569  | -1.219594 | 4.526702  |
| S     | 1.190730  | -3.831679 | 6.291356  |
| S     | -2.253569 | 1.219594  | 4.526702  |
| S     | -1.190730 | 3.831679  | 6.291356  |
| S     | 1.219594  | 2.253569  | 4.526702  |
| S     | 3.831679  | 1.190730  | 6.291356  |
| S     | -2.253569 | 4.526702  | -1.219594 |
| S     | -1.190730 | 6.291356  | -3.831679 |
| S     | -1.219594 | 4.526702  | 2.253569  |
| S     | -3.831679 | 6.291356  | 1.190730  |
| S     | 1.190730  | 6.291356  | 3.831679  |
| S     | 2.253569  | 4.526702  | 1.219594  |
| S     | 1.190730  | 6.291356  | 3.831679  |
| S     | -2.253569 | 4.526702  | 1.219594  |
| S     | -1.190730 | 6.291356  | 3.831679  |
| S     | -1.219594 | 4.526702  | 2.253569  |
| S     | -3.831679 | 6.291356  | 1.190730  |
| S     | 1.190730  | 6.291356  | 3.831679  |
| S     | -2.253569 | 4.526702  | 1.219594  |
| S     | -1.190730 | 6.291356  | 3.831679  |
| S     | -1.219594 | 4.526702  | 2.253569  |
| S     | -3.831679 | 6.291356  | 1.190730  |
| S     | 1.190730  | 6.291356  | 3.831679  |
| S     | -2.253569 | 4.526702  | 1.219594  |
| S     | -1.190730 | 6.291356  | 3.831679  |
| S     | -1.219594 | 4.526702  | 2.253569  |
| S     | -3.831679 | 6.291356  | 1.190730  |
| S     | 1.190730  | 6.291356  | 3.831679  |
| S          | -4.526702 | 1.219594 | -2.253569 |
| S          | -6.291356 | 3.831679 | -1.190730 |
| S          | -4.526702 | 2.253569 | 1.219594  |
| S          | -6.291356 | -1.190730| 3.831679  |
| S          | -4.526702 | -1.219594| -2.253569 |
| S          | -6.291356 | -3.831679| -1.190730 |
| S          | -4.526702 | 2.253569 | -1.190730 |
| S          | -6.291356 | 3.831679 | 1.190730  |
| S          | -4.526702 | 2.253569 | -1.190730 |
| S          | -6.291356 | 3.831679 | 1.190730  |
| S          | -4.526702 | 2.253569 | -1.190730 |
| S          | -6.291356 | 3.831679 | 1.190730  |
| C          | -1.400999 | 2.653548 | 6.238444  |
| C          | -2.533043 | 2.245783 | 6.981023  |
| C          | -2.717983 | 2.631144 | 8.306809  |
| C          | -1.781502 | 3.387843 | 8.998507  |
| C          | -0.630425 | 3.733712 | 8.293752  |
| C          | -0.419925 | 3.365831 | 6.971194  |
| C          | -1.941713 | 3.786219 | 10.469071 |
| C          | -3.347896 | 3.477927 | 11.003217 |
| C          | -1.687100 | 5.296290 | 10.641776 |
| C          | -0.915609 | 2.993742 | 11.305330 |
| C          | 2.653548  | -1.400999| 6.238444  |
| C          | 2.245783  | -2.533043| 6.981023  |
| C          | 2.631144  | -2.717983| 8.306809  |
| C          | 3.387843  | -1.781502| 8.998507  |
| C          | 3.733712  | -0.630425| 8.293752  |
| C          | 3.365831  | -0.419925| 6.971194  |
| C          | 3.786219  | -1.941713| 10.469071 |
| C          | 3.477927  | -3.347896| 11.003217 |
| C          | 5.296290  | -1.687100| 10.641776 |
| C          | 2.993742  | -0.915609| 11.305330 |
| C          | -2.653548 | 1.400999 | 6.238444  |
| C          | -2.245783 | 2.533043 | 6.981023  |
| C          | -2.631144 | 2.717983 | 8.306809  |
| C          | -3.387843 | 1.781502 | 8.998507  |
| C          | -3.733712 | 0.630425 | 8.293752  |
| C          | -3.365831 | 0.419925 | 6.971194  |
| C          | -3.786219 | 1.941713 | 10.469071 |
| C          | -3.477927 | 3.347896 | 11.003217 |
| C          | -5.296290 | 1.687100 | 10.641776 |
| C          | -2.993742 | 0.915609 | 11.305330 |
| C          | 1.400999  | 2.653548 | 6.238444  |
| C          | 2.533043  | 2.245783 | 6.981023  |
| C          | 2.717983  | 2.631144 | 8.306809  |
| C          | 1.781502  | 3.387843 | 8.998507  |
| C          | 0.630425  | 3.733712 | 8.293752  |
| C          | 0.419925  | 3.365831 | 6.971194  |
| C          | 1.941713  | 3.786219 | 10.469071 |
| C          | 3.347896  | 3.477927 | 11.003217 |
| C          | 1.687100  | 5.296290 | 10.641776 |
| C          | 0.915609  | 2.993742 | 11.305330 |
| C          | -2.653548 | 6.238444 | -1.400999 |
|    | X         | Y         | Z         |
|----|-----------|-----------|-----------|
| C  | 2.717983  | -8.306809 | 2.631144  |
| C  | 1.781502  | -8.998507 | 3.387843  |
| C  | 0.630425  | -8.293752 | 3.733712  |
| C  | 0.419925  | -6.971194 | 3.365831  |
| C  | 1.941713  | -10.469071| 3.786219  |
| C  | 3.347896  | -11.003217| 3.477927  |
| C  | 1.687100  | -10.641776| 5.296290  |
| C  | 0.915609  | -11.305330| 2.993742  |
| C  | 2.653548  | -6.238444 | -1.400999 |
| C  | 2.245783  | -6.981023 | -2.530434 |
| C  | 2.631144  | -8.306809 | -2.717983 |
| C  | 3.387843  | -8.998507 | -1.781502 |
| C  | 3.733712  | -8.293752 | -0.630425 |
| C  | 3.365831  | -6.971194 | -0.419925 |
| C  | 3.786219  | -10.469071| -1.941713 |
| C  | 3.477927  | -11.003217| -3.347896 |
| C  | 5.296290  | -10.641776| -1.687100 |
| C  | 2.993742  | -11.305330| -0.915609 |
| C  | -6.238444 | -2.635348 | 1.400999  |
| C  | -6.981023 | -2.245783 | 2.530434  |
| C  | -8.306809 | -2.631144 | 2.717983  |
| C  | -8.998507 | -1.781502 | 3.387843  |
| C  | -8.293752 | -0.630425 | 3.733712  |
| C  | -6.971194 | -0.419925 | 3.365831  |
| C  | -10.469071| -1.941713 | 3.786219  |
| C  | -11.003217| -3.347896 | 3.477927  |
| C  | -10.641776| -1.687100 | 5.296290  |
| C  | -11.305330| -0.915609 | 2.993742  |
| C  | -6.238444 | 1.400999  | -2.635348 |
| C  | -6.981023 | 2.530434  | -2.245783 |
| C  | -8.306809 | 2.717983  | -2.631144 |
| C  | -8.998507 | 3.387843  | 1.781502  |
| C  | -8.293752 | 0.630425  | -3.733712 |
| C  | -6.971194 | 0.419925  | -3.365831 |
| C  | -10.469071| 1.941713  | -3.786219 |
| C  | -11.003217| 3.347896  | -3.477927 |
| C  | -10.641776| 1.687100  | -5.296290 |
| C  | -11.305330| 0.915609  | -2.993742 |
| C  | -6.238444 | 2.635348  | 1.400999  |
| C  | -6.981023 | 2.245783  | 2.530434  |
| C  | -8.306809 | 2.631144  | 2.717983  |
| C  | -8.998507 | 3.387843  | 1.781502  |
| C  | -8.293752 | 3.733712  | 0.630425  |
| C  | -6.971194 | 3.365831  | 0.419925  |
| C  | -10.469071| 3.786219  | 1.941713  |
| C  | -11.003217| 3.477927  | 3.347896  |
| C  | -10.641776| 5.296290  | 1.687100  |
| C  | -11.305330| 2.993742  | 0.915609  |
| C  | 6.238444  | -2.635348 | 1.400999  |
| C  | 6.981023  | -2.245783 | 2.530434  |
| C  | 8.306809  | -2.631144 | 2.717983  |
### SUPPORTING INFORMATION

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 8.998507  | -3.387843 | 1.781502  |
| C  | 8.293752  | -3.733712 | 0.630425  |
| C  | 6.971194  | -3.365831 | 0.419925  |
| C  | 10.469071 | -3.786219 | 1.941713  |
| C  | 11.003217 | -3.477927 | -3.347896 |
| C  | 10.641776 | -5.296290 | 1.687100  |
| C  | 11.305330 | -2.993742 | 0.915609  |
| C  | 6.238444  | -1.400999 | -2.653548 |
| C  | 6.981023  | -2.533043 | -2.245783 |
| C  | 8.306809  | -2.717983 | -2.631144 |
| C  | 8.998507  | -1.781502 | -3.387843 |
| C  | 8.293752  | -0.630425 | -3.733712 |
| C  | 6.971194  | -0.419925 | -3.365831 |
| C  | 10.469071 | -1.941713 | -3.786219 |
| C  | 11.003217 | -3.477927 | -3.477927 |
| C  | 10.641776 | -1.687100 | -5.296290 |
| C  | 11.305330 | -0.915609 | -2.993742 |
| C  | 6.238444  | 1.400999  | 2.653548  |
| C  | 6.981023  | 2.533043  | 2.245783  |
| C  | 8.306809  | 2.717983  | 2.631144  |
| C  | 8.998507  | 1.781502  | 3.387843  |
| C  | 8.293752  | 0.630425  | 3.733712  |
| C  | 6.971194  | 0.419925  | 3.365831  |
| C  | 10.469071 | 1.941713  | 3.786219  |
| C  | 11.003217 | 3.477927  | 3.477927  |
| C  | 10.641776 | 1.687100  | 5.296290  |
| C  | 11.305330 | 0.915609  | 2.993742  |
| C  | 6.238444  | 2.653548  | -1.400999 |
| C  | 6.981023  | 2.533043  | -2.245783 |
| C  | 8.306809  | 2.717983  | -2.631144 |
| C  | 8.998507  | 1.781502  | -3.387843 |
| C  | 8.293752  | 0.630425  | -3.733712 |
| C  | 6.971194  | 0.419925  | -3.365831 |
| C  | 10.469071 | 1.941713  | -3.786219 |
| C  | 11.003217 | 3.477927  | -3.477927 |
| C  | 10.641776 | 1.687100  | -5.296290 |
| C  | 11.305330 | 0.915609  | -2.993742 |
| C  | 6.238444  | -2.653548 | -1.400999 |
| C  | 6.981023  | -2.533043 | -2.245783 |
| C  | 8.306809  | -2.717983 | -2.631144 |
| C  | 8.998507  | -1.781502 | -3.387843 |
| C  | 8.293752  | -0.630425 | -3.733712 |
| C  | 6.971194  | -0.419925 | -3.365831 |
| C  | 10.469071 | -1.941713 | -3.786219 |
| C  | 11.003217 | -3.477927 | -3.477927 |
| C  | 10.641776 | 5.296290  | 1.687100  |
| C  | 11.305330 | 0.915609  | 2.993742  |
| C  | 6.238444  | 2.653548  | 1.400999  |
| C  | 6.981023  | 2.533043  | 2.245783  |
| C  | 8.306809  | 2.717983  | 2.631144  |
| C  | 8.998507  | 1.781502  | 3.387843  |
| C  | 8.293752  | 0.630425  | 3.733712  |
| C  | 6.971194  | 0.419925  | 3.365831  |
| C  | 10.469071 | 1.941713  | 3.786219  |
| C  | 11.003217 | 3.477927  | -1.941713 |
| C  | 10.641776 | 5.296290  | -1.687100 |
| C  | 11.305330 | -2.993742 | -11.305330 |
| C  | 2.653548  | -1.400999 | -6.238444 |
| C  | 2.245783  | -2.533043 | -6.981023 |
| C  | 2.631144  | -2.717983 | -8.306809 |
| C  | -3.387843 | -1.781502 | -8.998507 |
| C  | -3.733712 | -0.630425 | -8.293752 |
| C  | -3.365831 | -0.419925 | -6.971194 |
| C  | -3.786219 | -1.941713 | -10.469071|
| C  | -3.477927 | -3.47896  | -11.003217|
| C  | -5.296290 | -1.687100 | -10.641776|
| C  | -2.993742 | -0.915609 | -11.305330|
| C  | 2.653548  | 1.400999  | -6.238444 |
| C  | 2.245783  | 2.533043  | -6.981023 |
| C  | 2.631144  | 2.717983  | -8.306809 |
| C  | 3.387843  | 1.781502  | -8.998507 |
### SUPPORTING INFORMATION

|  |  |  |  |
|---|---|---|---|
| C | 3.733712 | 0.630425 | -8.293752 |
| C | 3.365831 | 0.419925 | -6.971194 |
| C | 3.786219 | 1.941713 | -10.469071 |
| C | 3.477927 | 3.347896 | -11.003217 |
| C | 5.296290 | 1.687100 | -10.641776 |
| C | 2.993742 | 0.915609 | -11.305330 |
| C | -1.400999 | 2.653548 | -6.238444 |
| C | -2.533043 | 2.245783 | -6.981023 |
| C | -1.781502 | 3.387843 | -8.998507 |
| C | -0.630425 | 3.733712 | -8.293752 |
| C | -0.419925 | 3.365831 | -6.971194 |
| C | -1.941713 | 3.786219 | -10.469071 |
| C | -3.347896 | 3.477927 | -11.003217 |
| C | -1.687100 | 5.296290 | -10.641776 |
| C | -0.915609 | 2.993742 | -11.305330 |
| H | -3.630706 | -2.324563 | 8.792446 |
| H | 0.141904 | -4.308021 | 8.784108 |
| H | -3.426301 | -3.804749 | 12.041714 |
| H | -4.117750 | -3.997213 | 10.429026 |
| H | -3.567076 | -2.409468 | 10.982071 |
| H | -1.808225 | -5.581788 | 11.689295 |
| H | -0.678387 | -5.578583 | 10.339158 |
| H | -2.391078 | -5.878770 | 10.044532 |
| H | -0.991496 | -3.260572 | 12.362442 |
| H | -1.084942 | -1.919635 | 11.208762 |
| H | 0.103803 | -3.199799 | 10.977412 |
| H | 2.324563 | -3.630706 | 8.792446 |
| H | 4.308021 | 0.141904 | 8.784108 |
| H | 3.804749 | -3.426301 | 12.041714 |
| H | 3.997213 | -4.117750 | 10.429026 |
| H | 2.409468 | -3.567076 | 10.982071 |
| H | 5.581788 | -1.808225 | 11.689295 |
| H | 5.578583 | -0.678387 | 10.339158 |
| H | 5.878770 | -2.391078 | 10.044532 |
| H | 3.260572 | -0.991496 | 12.362442 |
| H | 1.919635 | -1.084942 | 11.208762 |
| H | 3.199799 | 0.103803 | 10.977412 |
| H | -2.324563 | 3.630706 | 8.792446 |
| H | -4.308021 | -0.141904 | 8.784108 |
| H | -3.804749 | 3.426301 | 12.041714 |
| H | -3.997213 | 4.117750 | 10.429026 |
| H | -2.409468 | 3.567076 | 10.982071 |
| H | -5.581788 | 1.808225 | 11.689295 |
| H | -5.578583 | 0.678387 | 10.339158 |
| H | -5.878770 | 2.391078 | 10.044532 |
| H | -3.260572 | 0.991496 | 12.362442 |
| H | -1.919635 | 1.084942 | 11.208762 |
| H | -3.199799 | -0.103803 | 10.977412 |
| H | 3.630706 | 2.324563 | 8.792446 |
| H | -0.141904 | 4.308021 | 8.784108 |
| H | 3.426301 | 3.804749 | 12.041714 |
| H | 4.117750 | 3.997213 | 10.429026 |
| H | 3.567076 | 2.409468 | 10.982071 |
| H | 1.808225 | 5.581788 | 11.689295 |
| H | 0.678387 | 5.578583 | 10.339158 |
| H | 2.391078 | 5.878770 | 10.044532 |
| H | 0.991496 | 3.260572 | 12.362442 |
| H | 1.084942 | 1.919635 | 11.208762 |
| H | -0.103803 | 3.199799 | 10.977412 |
| H | -2.324563 | 8.792446 | -3.630706 |
|   | X             | Y             | Z             |
|---|---------------|---------------|---------------|
| H | -4.308021     | 8.784108      | 0.141904      |
| H | -3.804749     | 12.041714     | -3.426301     |
| H | -3.997213     | 10.429026     | -4.117750     |
| H | -2.409468     | 10.982071     | -3.567076     |
| H | -5.581788     | 11.689295     | -1.808225     |
| H | -5.578583     | 10.339158     | -0.678387     |
| H | -5.878770     | 10.044532     | -2.391078     |
| H | -3.260572     | 12.362442     | -0.991496     |
| H | -1.919635     | 11.208762     | -1.084942     |
| H | -3.199799     | 10.977412     | 0.103803      |
| H | -3.630706     | 8.792446      | 2.324563      |
| H | 0.141904      | 8.784108      | 4.308021      |
| H | -3.426301     | 12.041714     | 3.804749      |
| H | -4.117750     | 10.429026     | 3.997213      |
| H | -3.567076     | 10.982071     | 2.409468      |
| H | -1.808225     | 11.689295     | 5.581788      |
| H | -0.678387     | 10.339158     | 5.578583      |
| H | -2.391078     | 10.044532     | 5.878770      |
| H | -0.991496     | 12.362442     | 3.260572      |
| H | -1.084942     | 11.208762     | 1.919635      |
| H | 0.103803      | 10.977412     | 3.199799      |
| H | 3.630706      | 8.792446      | -2.324563     |
| H | -0.141904     | 8.784108      | -4.308021     |
| H | 3.426301      | 12.041714     | -3.804749     |
| H | 4.117750      | 10.429026     | -3.997213     |
| H | 3.567076      | 10.982071     | -2.409468     |
| H | 1.808225      | 11.689295     | -5.581788     |
| H | 0.678387      | 10.339158     | -5.578583     |
| H | 2.391078      | 10.044532     | -5.878770     |
| H | 0.991496      | 12.362442     | -3.260572     |
| H | 1.084942      | 11.208762     | -1.919635     |
| H | -0.103803     | 10.977412     | -3.199799     |
| H | 2.324563      | 8.792446      | 3.630706      |
| H | 4.308021      | 8.784108      | -0.141904     |
| H | 3.804749      | 12.041714     | 3.426301      |
| H | 3.997213      | 10.429026     | 4.117750      |
| H | 2.409468      | 10.982071     | 3.567076      |
| H | 5.581788      | 11.689295     | 1.808225      |
| H | 5.578583      | 10.339158     | 0.678387      |
| H | 5.878770      | 10.044532     | 2.391078      |
| H | 3.260572      | 12.362442     | 0.991496      |
| H | 1.919635      | 11.208762     | 1.084942      |
| H | 3.199799      | 10.977412     | -0.103803     |
| H | -2.324563     | -8.792446     | 3.630706      |
| H | -4.308021     | -8.784108     | -0.141904     |
| H | -3.804749     | -12.041714    | 3.426301      |
| H | -3.997213     | -10.429026    | 4.117750      |
| H | -2.409468     | -10.982071    | 3.567076      |
| H | -5.581788     | -11.689295    | 1.808225      |
| H | -5.578583     | -10.339158    | 0.678387      |
| H | -5.878770     | -10.044532    | 2.391078      |
| H | -3.260572     | -12.362442    | 0.991496      |
| H | -1.919635     | -11.208762    | 1.084942      |
| H | -3.199799     | -10.977412    | -0.103803     |
| H | -3.630706     | -8.792446     | -2.324563     |
| H | 0.141904      | -8.784108     | -4.308021     |
| H | -3.426301     | -12.041714    | -3.804749     |
| H | -4.117750     | -10.429026    | -3.997213     |
| H | -3.567076     | -10.982071    | -2.409468     |
| H | -1.808225     | -11.689295    | -5.581788     |
| H | -0.678387     | -10.339158    | -5.578583     |
| H   | -2.391078  -10.044532  -5.878770 |
| H   | -0.991496  -12.362442  -3.260572 |
| H   | -1.084942  -11.208762  -1.919635 |
| H   | 0.103803  -10.977412  -3.199799 |
| H   | 3.630706  -8.792446   2.324563 |
| H   | -0.141904  -8.74108   4.308021 |
| H   | 3.426301  -12.041714  3.804749 |
| H   | 4.117750  -10.429026  3.997213 |
| H   | 3.567076  -10.982071  2.409468 |
| H   | 1.808225  -11.689295  5.581788 |
| H   | 0.678387  -10.339158  5.578583 |
| H   | 2.391078  -10.044532  5.878770 |
| H   | 0.991496  -12.362442  3.260572 |
| H   | 1.084942  -11.208762  1.919635 |
| H   | -0.103803  -10.977412  3.199799 |
| H   | 2.324563  -8.792446  -3.630706 |
| H   | 4.308021  -8.74108   0.141904 |
| H   | 3.804749  -12.041714  -3.426301 |
| H   | 3.997213  -10.429026  -4.117750 |
| H   | 2.409468  -10.982071  -3.567076 |
| H   | 5.581788  -11.689295  -1.808225 |
| H   | 5.578583  -10.339158  -0.678387 |
| H   | 5.878770  -10.044532  -2.391078 |
| H   | 3.260572  -12.362442  -0.991496 |
| H   | 1.919635  -11.208762  -1.084942 |
| H   | 3.199799  -10.977412  0.103803 |
| H   | -8.792446  -2.324563  -3.630706 |
| H   | -8.784108  -4.308021  0.141904 |
| H   | -12.041714  -3.804749  -3.426301 |
| H   | -10.429026  -3.997213  -4.117750 |
| H   | -10.982071  -2.409468  -3.567076 |
| H   | -11.689295  -5.581788  -1.808225 |
| H   | -10.339158  -5.578583  -0.678387 |
| H   | -10.044532  -5.878770  -2.391078 |
| H   | -12.362442  -3.260572  -0.991496 |
| H   | -11.208762  -1.919635  -1.084942 |
| H   | -10.977412  -3.199799  0.103803 |
| H   | -8.792446  -3.630706  2.324563 |
| H   | -8.784108  0.141904  4.308021 |
| H   | -12.041714  -3.426301  3.804749 |
| H   | -10.429026  -4.117750  3.997213 |
| H   | -10.982071  -3.567076  2.409468 |
| H   | -11.689295  -1.808225  5.581788 |
| H   | -10.339158  -0.678387  5.578583 |
| H   | -10.044532  -2.391078  5.878770 |
| H   | -12.362442  -0.991496  3.260572 |
| H   | -11.208762  -1.084942  1.919635 |
| H   | -10.977412  0.103803  3.199799 |
| H   | -8.792446  3.630706  -2.324563 |
| H   | -8.784108  -0.141904  -3.426301 |
| H   | -12.041714  3.804749  -3.426301 |
| H   | -10.429026  4.117750  -3.997213 |
| H   | -10.982071  3.567076  -2.409468 |
| H   | -11.689295  1.808225  -5.581788 |
| H   | -10.339158  0.678387  -5.578583 |
| H   | -10.044532  2.391078  -5.878770 |
| H   | -12.362442  0.991496  -3.260572 |
| H   | -11.208762  1.084942  -1.919635 |
| H   | -10.977412 -10.3803  -3.199799 |
| H   | -8.792446  2.324563  3.630706 |
| H   | -8.784108  4.308021  -0.141904 |
|   |   |   |   |
|---|---|---|---|
| H | -12.041714 | 3.804749 | 3.426301 |
| H | -10.429026 | 3.997213 | 4.117750 |
| H | -10.982071 | 2.409468 | 3.567076 |
| H | -11.689295 | 5.581788 | 1.808225 |
| H | -10.339158 | 5.575853 | 0.678387 |
| H | -10.044532 | 5.878770 | 2.391078 |
| H | -12.362442 | 3.260572 | 0.991496 |
| H | -11.208762 | 1.919635 | 1.084942 |
| H | -10.977412 | 3.199799 | -0.103803 |
| H | 8.792446 | -2.324563 | 3.630706 |
| H | 8.784108 | -4.308021 | -0.141904 |
| H | 12.041714 | -3.804749 | 3.426301 |
| H | 10.429026 | -3.997213 | 4.117750 |
| H | 10.982071 | -2.409468 | 3.567076 |
| H | 11.689295 | -5.581788 | 1.808225 |
| H | 10.339158 | -5.575853 | 0.678387 |
| H | 10.044532 | -5.878770 | 2.391078 |
| H | 12.362442 | -3.260572 | 0.991496 |
| H | 11.208762 | -1.919635 | 1.084942 |
| H | 10.977412 | -3.199799 | -0.103803 |
| H | 8.792446 | -3.630706 | -2.324563 |
| H | 8.784108 | 0.141904 | -4.308021 |
| H | 12.041714 | -3.426301 | -3.804749 |
| H | 10.429026 | -4.117750 | -3.997213 |
| H | 10.982071 | -3.567076 | -2.409468 |
| H | 11.689295 | -1.808225 | 5.581788 |
| H | 10.339158 | -0.678387 | -5.575853 |
| H | 10.044532 | -2.391078 | -5.878770 |
| H | 12.362442 | -0.991496 | -3.260572 |
| H | 11.208762 | 1.084942 | 1.919635 |
| H | 10.977412 | -0.103803 | 3.199799 |
| H | 8.792446 | 2.324563 | -3.630706 |
| H | 8.784108 | 4.308021 | 0.141904 |
| H | 12.041714 | 3.804749 | -3.426301 |
| H | 10.429026 | 3.997213 | -4.117750 |
| H | 10.982071 | 2.409468 | -3.567076 |
| H | 11.689295 | 5.581788 | -1.808225 |
| H | 10.339158 | 5.575853 | -0.678387 |
| H | 10.044532 | 5.878770 | -2.391078 |
| H | 12.362442 | 3.260572 | -0.991496 |
| H | 11.208762 | 1.919635 | -1.084942 |
| H | 10.977412 | 3.199799 | 0.103803 |
| H | 3.630706 | -2.324563 | -8.792446 |
| H | -0.141904 | -4.308021 | -8.784108 |
| H | 3.426301 | -3.804749 | -12.041714 |
| H | 4.117750 | -3.997213 | -10.429026 |
| H | 3.567076 | -2.409468 | -10.982071 |
| H | 1.808225 | -5.581788 | -11.689295 |
| H | 0.678387 | -5.575853 | -10.339158 |
| H | 2.391078 | -5.878770 | -10.044532 |
Cartesian coordinates (Å) for the theoretical structure of the singlet state (ground state) of [CuI₂(SRSRSH)₂]:
B3LYP-D3/Def2-TZVP, E = -6753.76233747 hartree

| x          | y          | z          |
|------------|------------|------------|
| Cu         | 1.033387   | 0.842243   | -1.481013  |
| Cu         | -1.033387  | -0.842243  | -1.481013  |
| S          | -1.419050  | 1.402394   | -1.220284  |
| S          | 1.945916   | 2.721063   | -2.595084  |
| S          | 1.276072   | 2.224626   | 0.564403   |
| S          | -1.945916  | -2.721063  | -2.595084  |
| S          | -1.276072  | -2.224626  | 0.564403   |
| S          | 1.419050   | -1.402394  | -1.220284  |
| C          | -1.400370  | 1.425987   | 0.556481   |
| C          | -2.549168  | 1.051803   | 1.267051   |
| C          | -2.572667  | 1.012674   | 2.651158   |
| C          | -1.451536  | 1.357520   | 3.408819   |
| C          | -0.314854  | 1.762919   | 2.720230   |
| C          | -0.280846  | 1.793767   | 1.326036   |
| C          | -1.464176  | 1.254533   | 4.910153   |
| C          | 1.213003   | 4.008283   | -1.579379  |
| C          | 0.902029   | 3.784103   | -0.234911  |
| C          | 0.314854   | 4.808412   | 0.509027   |
| C          | 0.012549   | 6.041345   | -0.053240  |
| C          | 0.348882   | 6.254096   | -1.393426  |
| C          | 0.954682   | 5.259428   | -2.140030  |
### Cartesian coordinates (Å) for the theoretical structure of the doublet (ground state) of [(SRSRSH)CuІCuІІ(SRSRS)]:

|       | x        | y        | z        |
|-------|----------|----------|----------|
| Cu    | -1.303886| -1.823045| 0.049396 |
| Cu    | 0.665800 | -0.765743| 1.782163 |
| S     | -1.573694| -0.150712| 1.831302 |
| S     | -3.431725| -2.756397| -0.549822|
| S     | -2.055845| 0.088731 | -1.432345|
| S     | 2.551674 | 0.153768 | 2.473132 |
| S     | 1.497232 | -0.038221| -0.745591|
| S     | 0.580736 | -2.894451| 0.776965 |
| C     | -1.230613| 1.331732 | 0.918175 |
| C     | -0.650331| 2.424378 | 1.575452 |
| C     | -0.267882| 3.562664 | 0.887524 |
| C     | -0.452852| 3.675668 | -0.491652|
| C     | -1.060249| 2.611408 | -1.150407|
| C     | -1.446165| 1.458677 | -0.467160|
| C     | 0.040077 | 4.882876 | -1.241487|

B3LYP-D3/Def2-TZVP, $E = -6753.15328789$ hartree
Supporting Information

Cartesian coordinates (Å) for the theoretical structure of the triplet state (ground state) of [CuII₂(SRSRS)₂]:

\[ E = -6752.54072236 \text{ hartree} \]

| Element | x          | y          | z          |
|---------|------------|------------|------------|
| Cu      | 1.197229   | -0.751540  | -1.480930  |
| Cu      | -1.197239  | 0.751558   | -1.480916  |
| S       | 0.984080   | 1.461202   | -2.156549  |
| S       | 2.651975   | -2.442976  | -1.339019  |
| S       | 1.857170   | -0.033884  | 0.667426   |
| S       | -2.651990  | 2.442992   | -1.338995  |
| S       | -1.857174  | 0.033898   | 0.667429   |
| S       | -0.984095  | -1.461182  | -2.156546  |
| C       | 1.497375   | 2.350914   | -0.705592  |
| C       | 1.480697   | 3.750221   | -0.748671  |
### Supporting Information

|   |   |   |   |
|---|---|---|---|
| C | 1.838095 | 4.507395 | 0.352058 |
| C | 2.207421 | 3.908040 | 1.559447 |
| C | 2.214437 | 2.519597 | 1.612954 |
| C | 1.897823 | 1.745344 | 0.495559 |
| C | 2.580031 | 4.741356 | 2.755726 |
| C | 3.803390 | -1.753091 | -0.200416 |
| C | 3.547928 | -0.620032 | 0.594520 |
| C | 4.541954 | -0.057746 | 1.392487 |
| C | 5.820452 | -0.596846 | 1.435165 |
| C | 6.066184 | -1.753318 | 0.684452 |
| C | 5.083817 | -2.324700 | -0.099488 |
| C | 6.908258 | 0.028260 | 2.266103 |
| C | -3.803411 | 1.753083 | -0.200412 |
| C | -3.547939 | 0.620021 | 0.594516 |
| C | -4.541965 | 0.057712 | 1.392468 |
| C | -5.820472 | 0.596792 | 1.435138 |
| C | -6.066213 | 1.753268 | 0.684434 |
| C | -5.083847 | 2.350900 | -0.099491 |
| C | -1.838057 | -4.507381 | 0.352073 |
| C | -2.207370 | -3.908026 | 1.559467 |
| C | -2.214399 | -2.519584 | 1.612971 |
| C | -1.897807 | -1.745331 | 0.495569 |
| C | -2.579951 | -4.741344 | 2.755754 |
| H | 1.808136 | 5.888568 | 0.280885 |
| H | 2.452436 | 2.024751 | 2.546032 |
| H | 4.316747 | 0.816580 | 1.987851 |
| H | 7.049050 | -2.09571 | 0.716575 |
| H | -4.316751 | -0.816618 | 1.987823 |
| H | -7.049087 | 2.09506 | 0.716551 |
| H | -1.808090 | -5.886554 | 0.280902 |
| H | -2.452392 | -2.024736 | 2.546050 |
| H | 3.547764 | 5.228099 | 2.606723 |
| H | -3.547663 | -5.228129 | 2.606753 |
| H | 2.648484 | 4.135632 | 3.659734 |
| H | -2.648431 | -4.135613 | 3.659755 |
| H | 1.845305 | 5.529693 | 2.931661 |
| H | -1.845193 | -5.529650 | 2.931700 |
| H | 7.700308 | 0.435085 | 1.631590 |
| H | -7.700318 | -0.435161 | 1.631534 |
| H | 6.524469 | 0.842465 | 2.881404 |
| H | -6.524484 | -0.842549 | 2.881350 |
| H | 7.371447 | -0.706396 | 2.928890 |
| H | -7.371478 | 0.706303 | 2.928854 |
| H | 5.301454 | -3.212547 | -0.679130 |
| H | 1.165113 | 4.238496 | -1.661183 |
| H | -1.165107 | -4.238482 | -1.661178 |
| H | -5.301492 | 3.212521 | -0.679128 |

### References

[1] a) H. Akdas, E. Graf, M. W. Hosseini, P. Rao, A. de Cian, J. Supramolecular Chemistry 2002, 2, 21-28; b) M. H. Patel, V. B. Patel, P. S. Shrivastav, Tetrahedron 2008, 64, 2057-2062.
[2] H. Hope, P. P. Power, Inorg. Chem. 1984, 23, 936-937.
[3] M. Singh, Phys. Chem. Liq. 2006, 44, 579-584.
[4] H. Bauer, G. Meerlender, Rheol. Acta 1984, 23, 514-521.
[5] G. M. Sheldrick, SADABS 1996, University of Göttingen, Germany.
[6] G. M. Sheldrick, Acta Crystallogr. A 2015, 71, 3-8.
[7] G. M. Sheldrick, Acta Crystallogr. C 2015, 71, 3-8.
[8] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, J. appl. crystallogr. 2011, 44, 1281-1284.

[9] A. L. Spek, Acta Crystallogr. D, Biological crystallography 2009, 65, 148-155.

[10] P. van der Sluis, A. L. Spek, Acta Crystallogr. A 1990, 46, 194-201.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuaseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

[12] a) A. D. Becke Phys. Rev. A 1988, 38, 3098-3100; b) C. Lee, W. Yang, R. G. Parr Phys. Rev. B 1988, 37, 785-789; c) A. D. Becke J. Chem. Phys. 1993, 98, 5648-5652.

[13] S. Grimme, S. Ehrlich, L. Goerigk J. Comp. Chem. 2011, 32, 1466-1466.

[14] a) F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305; b) F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.

[15] M. Witte, U. Gerstmann, A. Neuba, G. Henkel, W. G. Schmidt, J. Comp. Chem. 2016, 37, 1005-1018.