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Supporting Information

For

Unprecedented Binding and Activation of CS_2 in a Dinuclear Copper(I) Complex

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Experimental Section - General Procedures. All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer (^{1}H 300.1 MHz, ^{13}C 75.5 MHz) with CH_2Cl_2 as solvent at 20°C. The ^{1}H NMR spectra were calibrated against the residual proton, the ^{13}C NMR spectra against natural abundance ^{13}C resonances of the deuterated solvents (CD_2Cl_2 δ_H 5.32 ppm and δ_C 53.5 ppm). Microanalyses were performed on a Leco CHNS-932 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S-spectrometer. $^{13}CS_2$ was obtained from Sigma Aldrich and stored over molecular sieves in a glove box under dry argon.

Crystal Structure Determinations. Crystals of **2** x 4(C_6H_6) suitable for single crystal analysis were obtained from slow evaporation of a solution of **2** in a 1:2 mixture of CD_2Cl_2 and benzene. Data collections were performed at 100 K on a Stoe IPDS 2T diffractometer using Mo-K_α radiation (λ = 0.71073 Å); radiation source was a sealed tube generator with graphite monochromator. Numerical absorption correction based on a Gaussian algorithm was applied, which is implemented in the X-RED program (Stoe, 2002). The structure was solved by direct methods (*SHELXS-97*; G. M. Sheldrick, Program for Crystal Structure Solution, University of Göttingen, 1997) and refined by full matrix least-squares procedures based on F^2 with all measured reflections (*SHELXL-97*; G. M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, 1997). All non-hydrogen atoms were refined anisotropically except for five C atoms belonging to tert-butyl groups (C57, C58, C60, C61, C62) involved in disorder modelling. H atoms were introduced in their idealized positions and refined as riding. The crystal structure is a racemic twin; instead of performing a Flack parameter refinement, the twin refinement was done.

Table S1. Crystal data and experimental parameters for the crystal structure analysis of **2**.

	2 x 4(C_6H_6)
CCDC	817300
Formula	$C_{86}H_{92}Cu2N_4OS_2$
weight, g · mol^{-1}	1388.90
crystal system	orthorhombic
space group	*P*ca21
a, Å	18.4348(10)
b, Å	13.7677(6)
c, Å	28.5655(17)
V, Å^3	7250.1(7)
Z	4
Density, g · cm^{-3}	1.272
μ(Mo$_{K\alpha}$), mm^{-1}	0.694
F(000)	2936
GoF	0.886
R_{ind}[I>2σ(I)]	*R*1=0.0528
	*wR*2=0.1206
R_{ind} (all data)	*R*1=0.0729
	*wR*2=0.1295
$\Delta\rho_{min}$ / $\Delta\rho_{max}$, eÅ^{-3}	-0.589 / 0.551

Details on Density Functional Calculations. The molecular structure of **2** as determined by X-ray diffraction analysis was used as starting geometry for the geometry optimisation (any alkyl substituents at the ligand backbone were neglected). The B3LYP functional was employed together with the *6-311G** basis set. The calculations of the Natural Bond Orbitals as well as the IR spectra were performed on the same level employing NBO version 5.0. The graphical evaluation was carried out using the programs *Gaussview 3.09, Diamond 3.0* and *POV–Ray 3.5*.

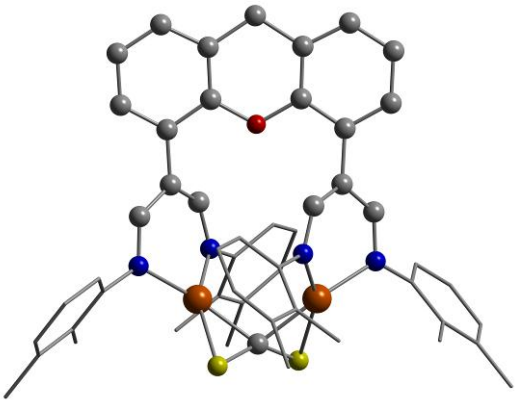

Figure S2. Geometry optimized molecular structure of **2** (B3LYP/6-311G*). Any alkyl substituents at the ligand backbone are omitted.

Table S3. Comparison of significant binding parameters of **2** determined by X-ray structure analysis and geometry optimization, respectively.

	exp.	**theo.**
Cu-N/Å	1.918(5), 1.941(5), 1.955(5), 1.926(5)	1.95 / 1.98
Cu-S/Å	2.1826(17), 2.1915(17)	2.21
Cu-C/Å	2.001(7), 2.029(6)	1.99
C-S/Å	1.646(8), 1.668(8)	1.67 / 1.67
S-C-S/°	147.2(3)	143.9

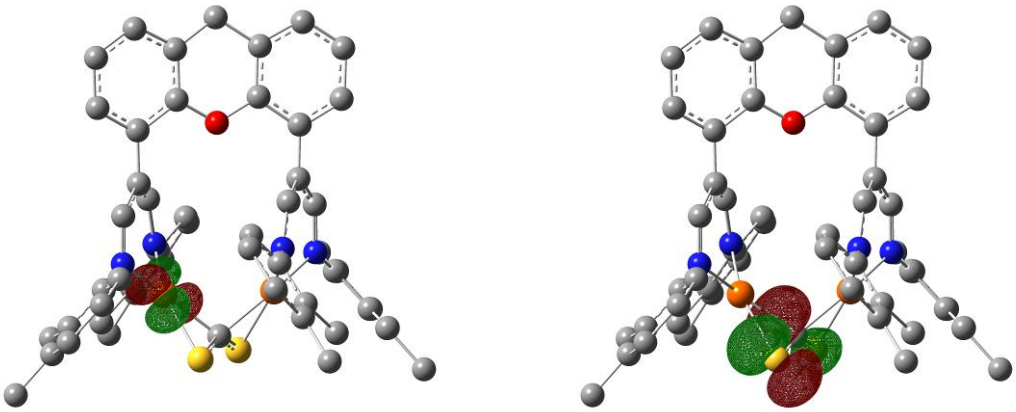

Figure S4. Interaction of the Cu d orbital and the C=S π* orbital.

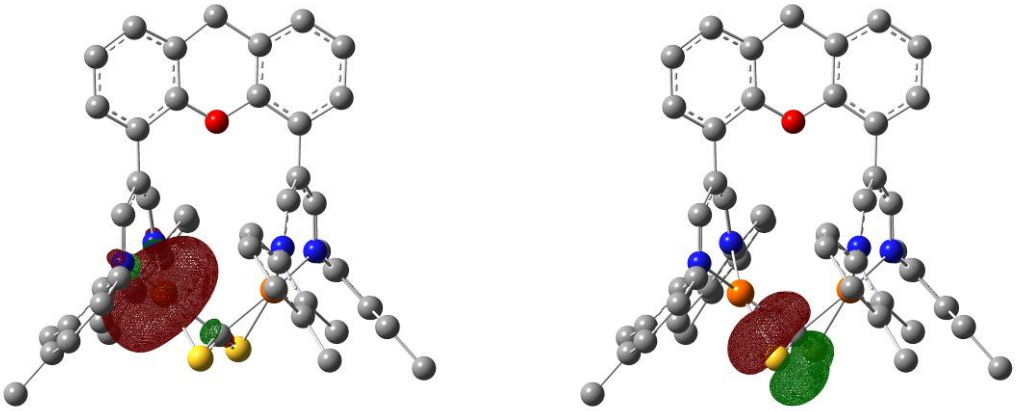

Figure S5. Interaction of the Cu s orbital and the C=S π orbital.

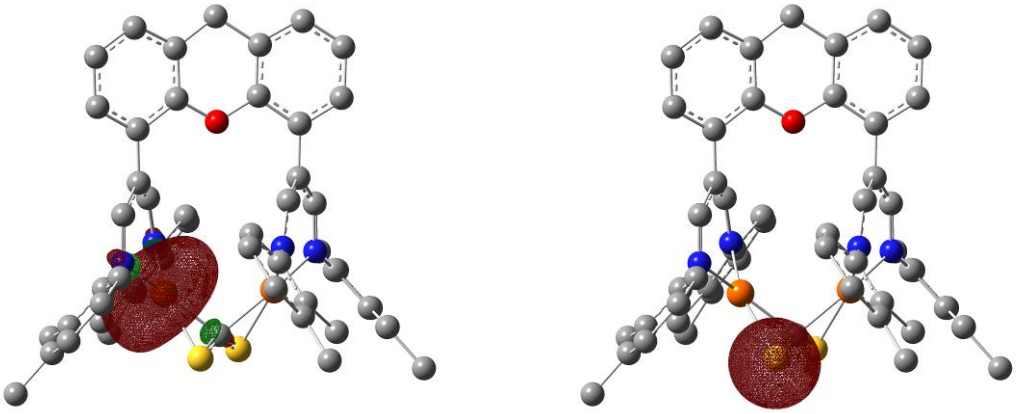

Figure S6. Interaction of the Cu s orbital and the S lone pair.