SUPPORTING INFORMATION

Impact of High Pressure on Metallophilic Interactions and Its Consequences for Spectroscopic Properties of a Model Tetranuclear Silver(I)-Copper(I) Complex in the Solid State

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Table 1S. Selected X-ray data collection, processing and refinement parameters for all presented crystal structures.[#]

Pressure, P / GPa	0.0 ¶	0.45(1)	0.98(1)	1.57(2)	2.17(1)	2.71(4)	3.47(4)
Moiety formula	$C_{84}H_{68}N_4P_4Cu_2Ag_2$						
Moiety formula mass, M_r / a.u.	1600.2						
Crystal system	triclinic						
Space group	$P\bar{1}$ (no. 2)						
a / Å	12.8027(10)	12.6977(8)	12.4481(6)	12.2670(6)	12.1122(12)	11.951(4)	11.786(4)
b / Å	14.2789(12)	14.2150(19)	14.0795(15)	14.0055(15)	13.942(3)	13.915(6)	13.810(6)
c / Å	22.3067(17)	22.2188(18)	21.8460(12)	21.5659(15)	21.376(3)	21.273(7)	21.198(8)
α / °	75.886(2)	75.902(9)	76.218(7)	76.268(7)	76.215(13)	75.84(3)	75.41(4)
β / °	81.359(2)	81.520(6)	81.655(4)	81.720(5)	81.687(10)	81.51(3)	81.41(3)
γ / °	66.609(2)	66.740(9)	66.768(7)	66.563(7)	66.296(13)	66.08(3)	66.28(4)
V / Å^3	3623.2(5)	3567.6(7)	3411.4(5)	3297.2(5)	3205.1(9)	3131(2)	3053(2)
Z	2						
T / K	RT §						
F_{000}	1624						
d_{calc} / g·cm^{-3}	1.467	1.490	1.558	1.612	1.658	1.697	1.741
θ range	1.59° – 20.18°	3.24° – 33.11°	3.31° – 32.81°	3.36° – 33.95°	3.66° – 31.28°	3.44° – 33.65°	3.49° – 33.48°
$(\sin\theta/\lambda)_{max}$ / Å^{-1}	0.49	0.62	0.62	0.79	0.61	0.79	0.78
Wavelength, λ / Å	0.71073 ¥	0.3738 ¥					
Absorption coefficient, μ / mm^{-1}	1.248	1.267	1.325	1.371	1.411	1.444	1.481
Crystal color & shape	orange prism						
Crystal size / mm^3	0.12×0.06×0.04	0.05×0.04×0.02					
No. of reflections collected / unique	27928 / 6926	4385 / 3654	4693 / 3987	4960 / 4264	3693 / 3086	4720 / 4076	4543 / 3948
Completeness	> 99%	24.2%	25.0%	15.9%	23.9%	16.4%	16.5%
R_{int}	10.17%	3.24%	2.54%	2.85%	3.34%	4.80%	5.28%
No. of reflections with $I > n \cdot \sigma(I)$ ‡	3541	1791	2304	1927	1373	716	587
No. of parameters / restraints	865 / 0	866 / 1770	866 / 1781	866 / 1781	865 / 1783	865 / 1785	865 / 1794
$R[F]$ $(I > n \cdot \sigma(I))$ ‡	3.93%	7.11%	8.78%	9.03%	7.21%	8.40%	8.25%
$\varrho_{res}^{min/max}$ / e·Å^{-3}	−0.86 / +0.76	−0.25 / +0.35	−0.68 / +0.66	−0.31 / +0.32	−0.17 / +0.25	−0.22 / +0.21	−0.11 / +0.16
CCDC code	1834267	1834272	1834271	1834266	1834268	1834269	1834270

[#] All raw data are available under the following DOI: 10.18150/repod.5075600. ¶ Ambient-pressure data set measured on a laboratory diffractometer. § Room temperature. ‡ n = 2 and 3 for *SHELX* and *JANA* programs, respectively; refinement always done on all data. ¥ 0.71073 Å for laboratory diffractometer with Mo X-ray source, 0.3738 Å for synchrotron source (ESRF ID27 high-pressure beamline; see main text for details).

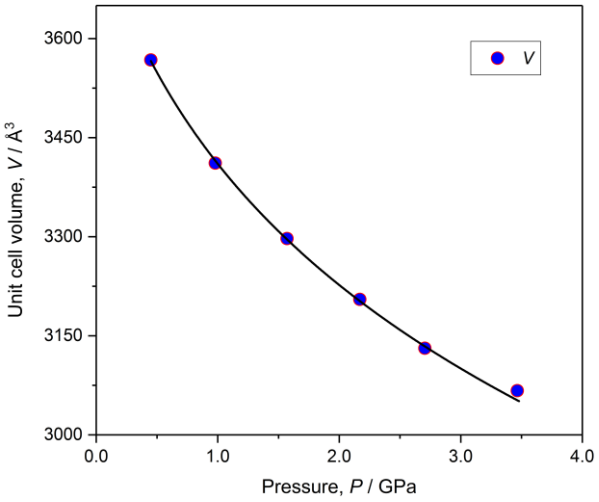


Figure 1S. Pressure-induced evolution of the unit cell volume of the **$Ag_2Cu_2L_4$** crystal structure. Solid black line denotes the Birch-Murnaghan equation-of-state fit.

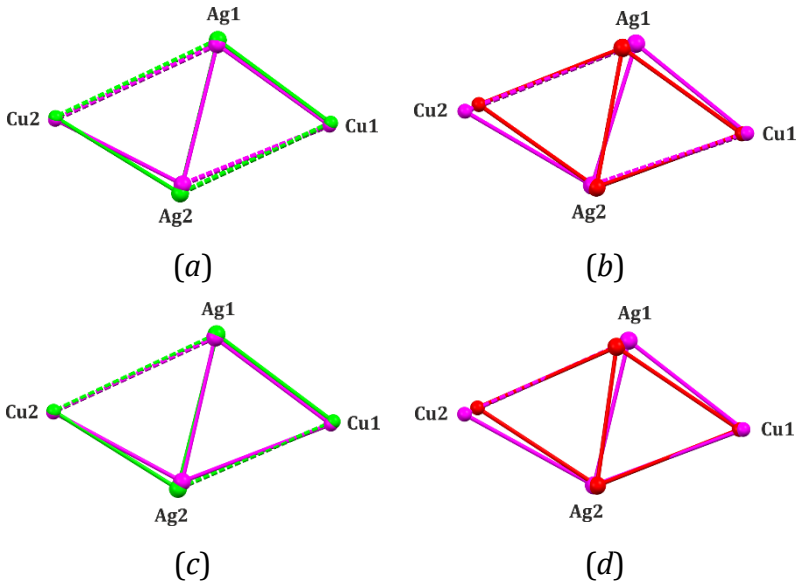


Figure 2S. Overlay of metal cores (top panels): (*a*) ambient pressure (green) *vs.* 3.47 GPa (magenta), (*c*) 3.47 GPa (magenta) *vs.* excited state (red). Bottom panels (*c*,*d*) are the same as Figure 4.

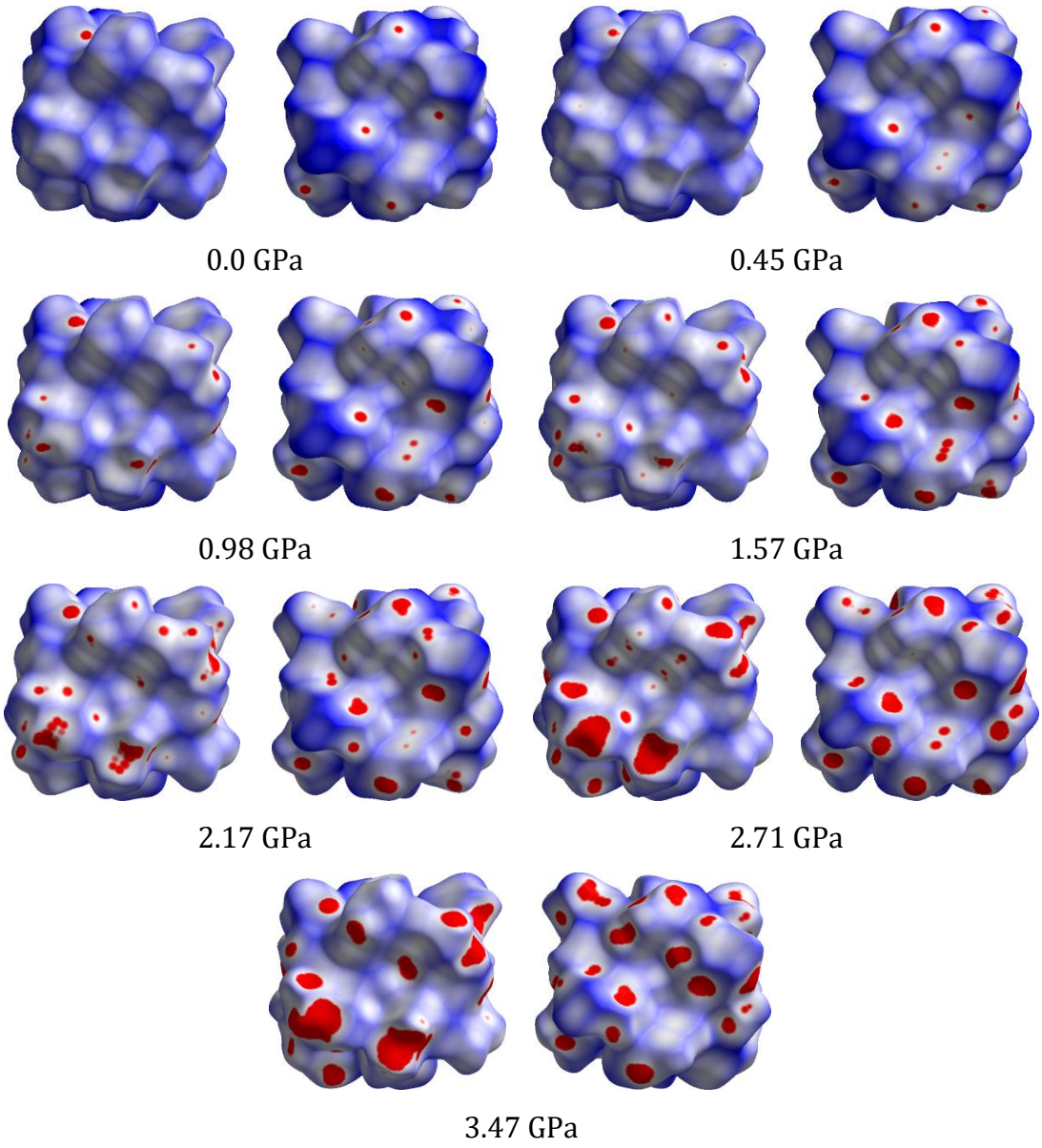


Figure 3S. Hirshfeld surfaces generated for various pressure-point geometries of **$Ag_2Cu_2L_4$** at ambient pressure: Cu1 (left panels) and Cu2 (right panels) sides of the complex molecule (views along Cu···Cu direction).

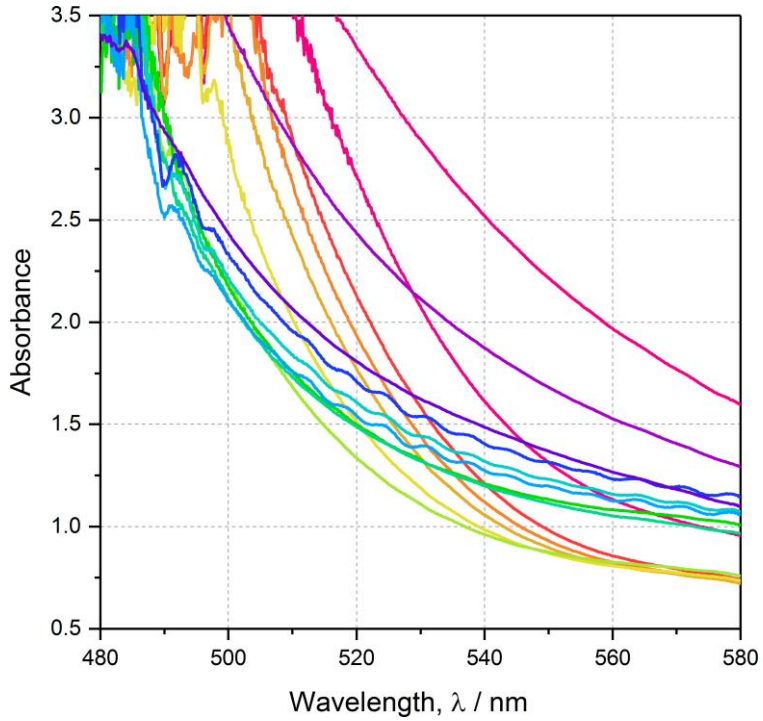
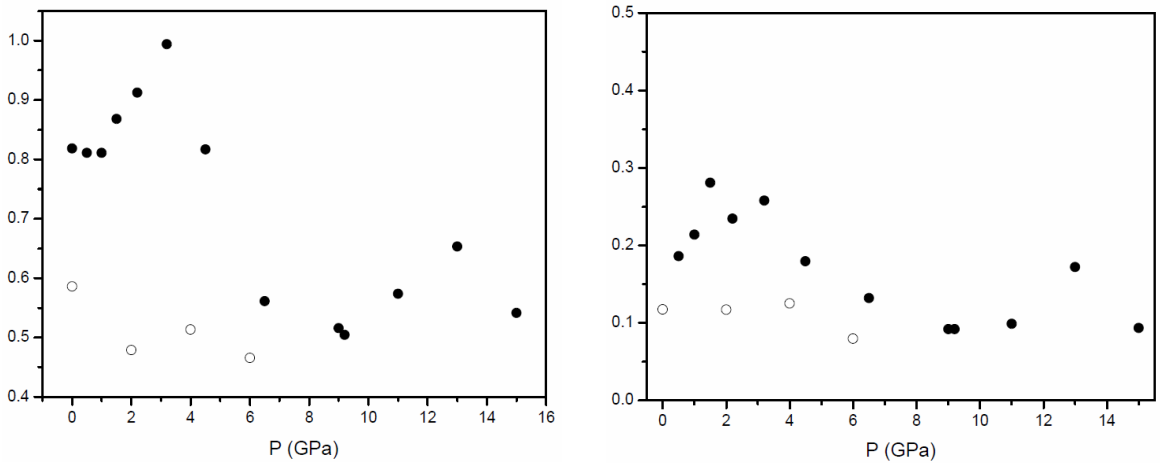


Figure 4S. All absorption spectra (colors and trends are the same as in Figure 6). Raw data are available under the following DOI: 10.18150/repod.5075600.



(a) (b)

Figure 5S. Lifetimes (all given in μs) determined in the spectroscopic experiment: (a) longer litefime τ_l (same as Figure 7a); (b) shorter lifetime τ_s. Numerical values are given in Table 2S. Full symbols denote compression, empty ones denote decompression.

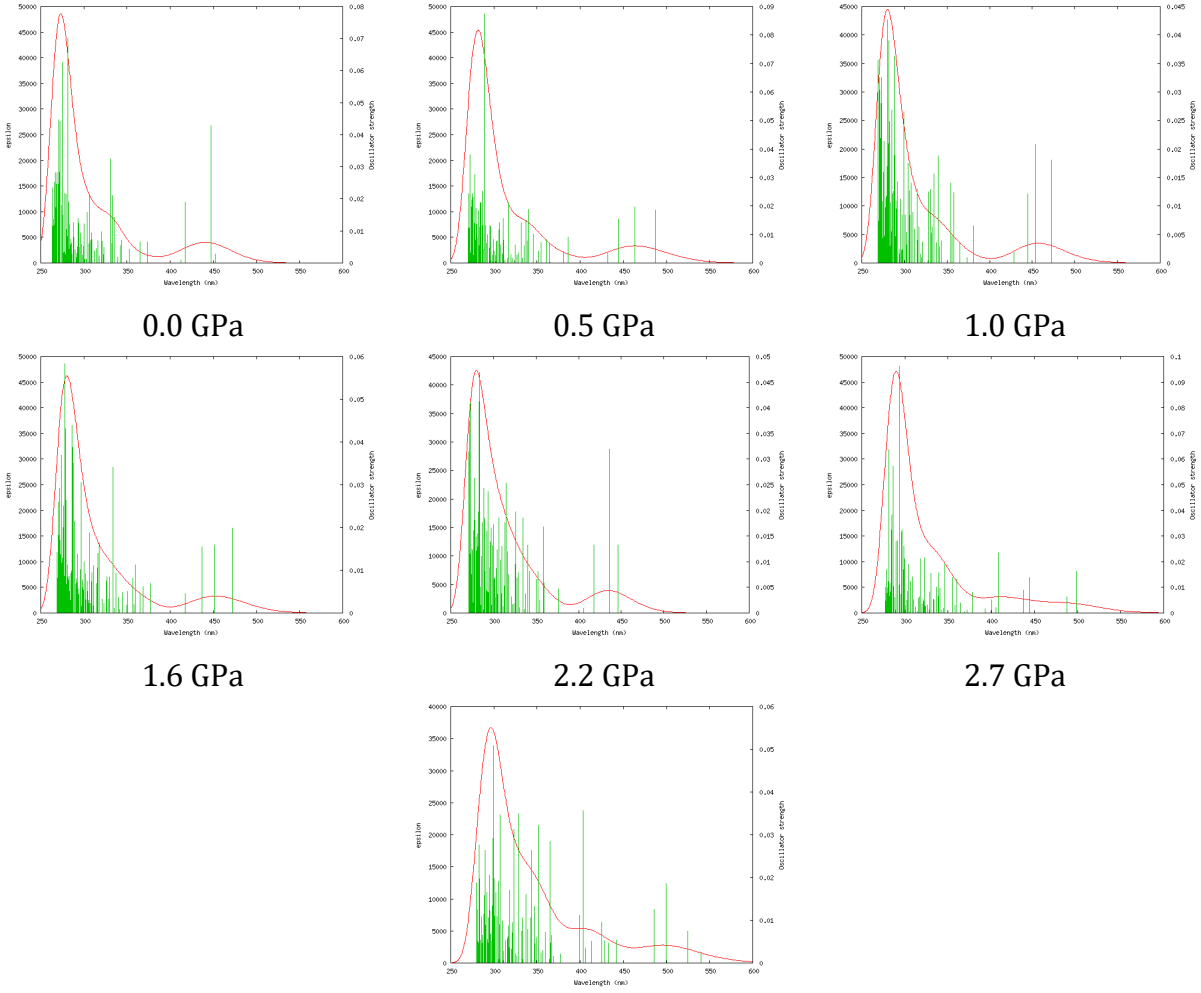


Figure 6S. Theoretical UV-Vis spectra (DTF(PBE0)/LANL2DZ level of theory) calculated for the **$Ag_2Cu_2L_4$** complex solid state geometries in the analyzed pressure range.

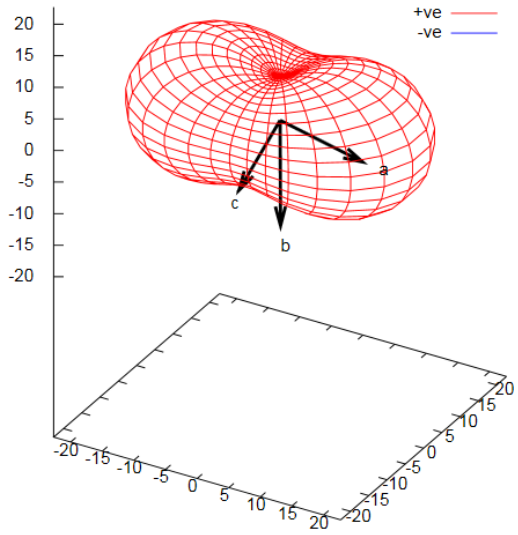


Figure 7S. Compressibility tensor visualized in the form of a compressibility indicatrix as implemented in the *PASCAL* server.[73]

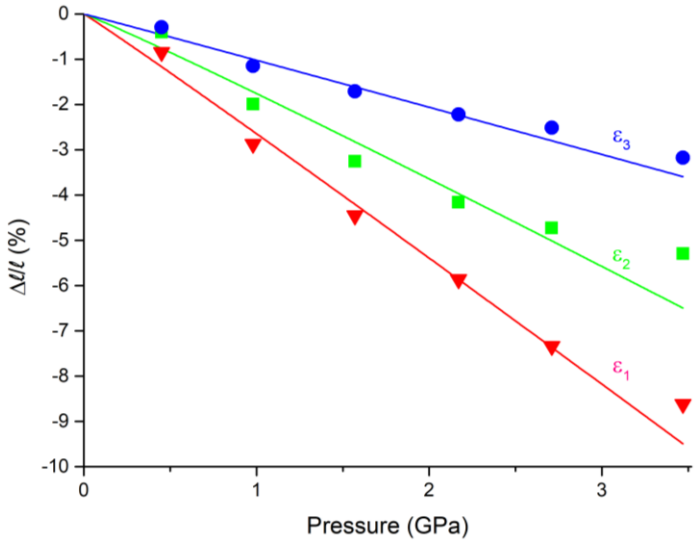


Figure 8S. Relative linear strain along the principal axes of strain ellipsoids:

$$\mathbf{x}_1 = 0.9707 \cdot \mathbf{a} - 0.2049 \cdot \mathbf{b} + 0.1255 \cdot \mathbf{c};$$
$$\mathbf{x}_2 = 0.5355 \cdot \mathbf{a} - 0.2053 \cdot \mathbf{b} - 0.8192 \cdot \mathbf{c};$$
$$\mathbf{x}_3 = 0.1465 \cdot \mathbf{a} - 0.9735 \cdot \mathbf{b} + 0.1757 \cdot \mathbf{c}.$$

Experimental data, calculated using the *PASCAL* server,[73] are shown as scatter points. The corresponding solid lines were drawn using an empirical fit in the form of $\Delta l/l = \lambda \cdot P^{\nu}$.

Table 2S. Luminescence lifetimes obtained from the least-squares fit to the recorded decays measured at various pressure. τ_l and τ_s denote longer and shorter lifetime, respectively.

Pressure, P / GPa	τ_l / μs	τ_s / μs
0.0	0.82 [a]	
0.5	0.81	0.19
1.0	0.81	0.21
1.5	0.87	0.28
2.2	0.91	0.23
3.2	0.99	0.26
4.5	0.82	0.18
6.5	0.56	0.13
9.0	0.50	0.09
9.2	0.50	0.09
11.0	0.57	0.10
13.0	0.65	0.17
15.0	0.54	0.09

[a] Mono-exponential fit was sufficient in this case (ambient pressure).