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SUPPLEMENTARY MATERIAL TO

Reactions of copper(II) bromide with 2,6-diacetylpyridine bis(phenylhydrazone) (L) – Molecular and crystal structures of L and its mixed-valence complex $[Cu^{II}L_2][Cu^{I}_2Br_4]$

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2,6-diacetylpyridine-bis(phenylhydrazone) ***(L)***

Selected IR bands [wavenumber, cm^{-1}]: 3442(w), 1602(vs), 1563(s), 1508(s), 1491(m), 1454(s), 1435(s), 1363(m), 1329(w), 1293(w), 1247(s), 1165(s), 1141(m), 1090(w), 842(m), 815(m), 755(m), 748(s), 694(m). ^{1}H-NMR [DMSO-d_6, δ / ppm]: 9.51 (2H, *s*, NH), 8.01 (2H, *d*, J = 7.8 Hz, H-2, H-4), 7.76 (1H, *dd*, J = 7.8 Hz, J = 7.8 Hz, H-3), 7.32 (4H, *ddd*, ^3J = 8.0 Hz, ^3J = 1.0 Hz, ^4J = 0.8 Hz, H-11, H-15, H-17, H-21), 7.26 (4H, *ddd*, ^3J = 8.0 Hz, ^3J = 7.2 Hz, ^4J = 1.5 Hz, H-12, H-14, H-18, H-20), 6.81 (2H, *dddd*, ^3J = 7.2 Hz, ^4J = 1.3 Hz, H-13, H-19), 2.44 (6H, *s*, CH_3). ^{13}C-NMR [DMSO-d_6, δ / ppm]: 155.4 (C-1, C-5), 146.1 (C-10, C-16), 142.0 (C-6, C-8), 136.7 (C-3), 129.4 (C-12, C-14, C-18, C-20), 119.8 (C-13, C-19), 117.9 (C-2, C-4), 113.5 (C-11, C-15, C-17, C-21), 11.7 (C-7, C-9).

$[Cu^{II}L_2][Cu^{I}_2Br_4]$ ***(1)***

Anal. Calc. for the black prismatic single crystals of $C_{42}H_{42}Br_4Cu_3N_{10}$: C, 42.14; H, 3.48; N, 11.70. Found: C, 42.34; H, 3.53; N, 11.59 %. Conductivity in DMF, Λ = 134 S cm^2 mol^{-1}. Selected IR bands [$\tilde{\nu}$ / cm^{-1}]: 3446(w), 3272(m), 1597(vs), 1518(m), 1494(s), 1435(m), 1262(s), 1170(m), 750(m), 693(m).

$[Cu^{II}L_2][Cu^{I}_2Br_4]$ ***(1)*** *(from MeOH solution)*

Anal. Calc. for $C_{42}H_{42}Br_4Cu_3N_{10}$: C, 42.14; H, 3.48; N, 11.70 %. Found: C, 42.47; H, 3.29; N, 11.64 %. Selected IR bands [$\tilde{\nu}$ / cm^{-1}]: 3446(w), 3272(m), 1597(vs), 1517(m), 1494(s), 1435(m), 1262(s), 1170(m), 751(m), 693(m).

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TABLE S-I. Crystallographic and refinement details

Crystal data	**L**	$[Cu^{II}L_2][Cu^{I}_2Br_4]$ (**1**)
Chemical formula	$C_{21}H_{21}N_5$	$C_{42}H_{42}Br_4Cu_3N_{10}$
M_r	466.05	1197.11
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	Pbca
Temperature, K	170	170
a / Å	5.3545(2)	21.9263(19)
b / Å	17.3224(6)	16.8642(10)
c / Å	19.3856(7)	23.8799(18)
V / Å^3	1798.07(11)	8830.1(11)
Z	4	8
Radiation type	Cu Kα	Mo Kα
Radiation wavelength	1.54184	0.71073
μ / mm^{-1}	0.615	5.10
Crystal size, mm	0.62 × 0.24 × 0.11	0.49 × 0.35 × 0.14
Data collection		
Absorption correction	Multiscan	Gaussian
T_{min}, T_{max}	0.651, 1	0.258, 0.773
Measured reflections	8671	50087
Independent reflections	3205	9054
Observed [$I > 2\sigma(I)$] reflections	2960	5901
R_{int}	0.058	0.081
$(\sin \theta/\lambda)_{max}$ / Å^{-1}	0.600	0.627
Refinement		
$R[F^2 > 2\sigma(F^2)]$	0.045	0.042
$wR(F^2)$	0.107	0.072
S	1.13	1.01
No. of reflections	3205	9054
No. of parameters	246	536
No. of restraints	0	0
H-atom treatment	Mixed	Constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.20, −0.29	0.71, −0.85
Flack x	0.2(2)	N.A.

TABLE S-II. Decomposition of the Hirshfeld surface of **L** into specific atom–atom contacts, expressed as a percentage of the Hirshfeld surface occupied by such contacts, and calculated enrichment ratios

Observed contact surface area ratio, %			
	Outside Atom		
Inside Atom	C	N	H
C	0.1	0.1	21.1
N	0.1	0.0	7.1
H	14.6	6.1	50.8

Enrichment ratios			
	Outside Atom		
Inside Atom	C	N	H
C	<0.01		
N	0.08	/	
H	1.31	1.31	0.90

Enrichment ratios were not listed when the 'random contacts' were lower than 0.9%, as they are not meaningful (/ written instead).

TABLE S-III. Hydrogen-bond parameters of $[Cu^{II}L_2][Cu^{I}_2Br_4]$ (**1**)

D–H···A	*d*(D–H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠(D–H···A) / °	Symmetry operation on A
N3A–H3A···Br2	0.88	3.01	3.632(4)	129.4	$-x+½, -y+1, z+½$
N3A–H3A···Br4	0.88	3.05	3.735(4)	136.7	$-x+½, -y+1, z+½$
N3B–H3B···Br1	0.88	2.84	3.479(4)	130.6	
N3B–H3B···Br3	0.88	3.10	3.749(4)	132.3	
N5A–H5A···Br3	0.88	2.89	3.659(4)	147.5	
N5B–H5B···Br4	0.88	2.93	3.645(4)	139.7	$-x+½, -y+1, z+½$

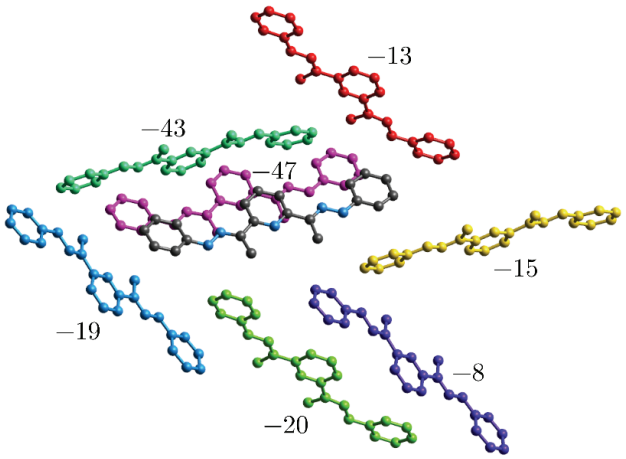

Fig. S-1. Arrangement of molecules and their interaction energies in kJ mol^{-1}. For clarity, only one of two molecular pairs is displayed for every unique interaction. The central molecule is color-coded by element-type, while partner molecules are decorated with different colors.

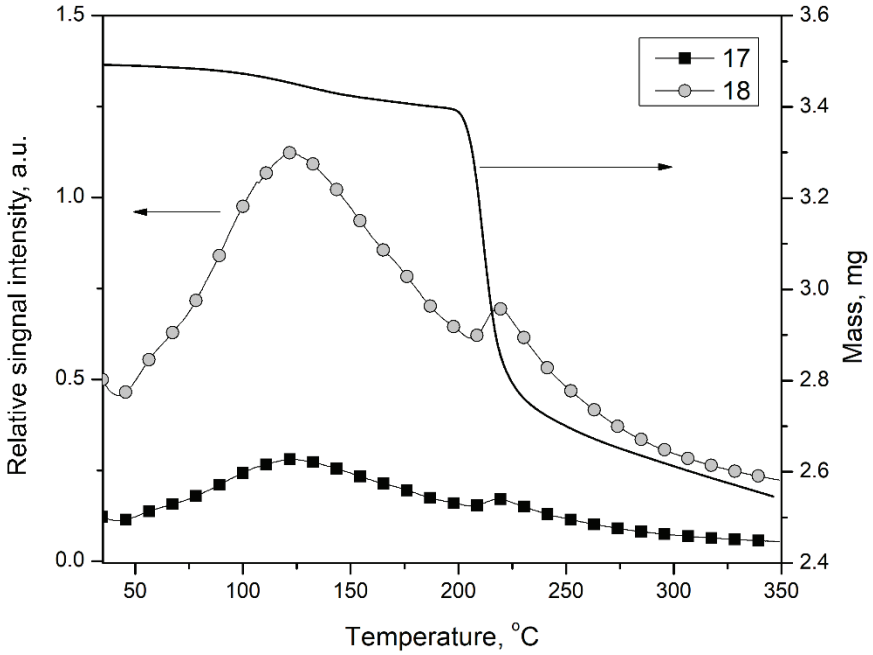

Fig. S-2. TG and MS curves of $[Cu^{II}L_2][Cu^{I}_2Br_4]$ for signals m/z = 17 and 18 in argon.

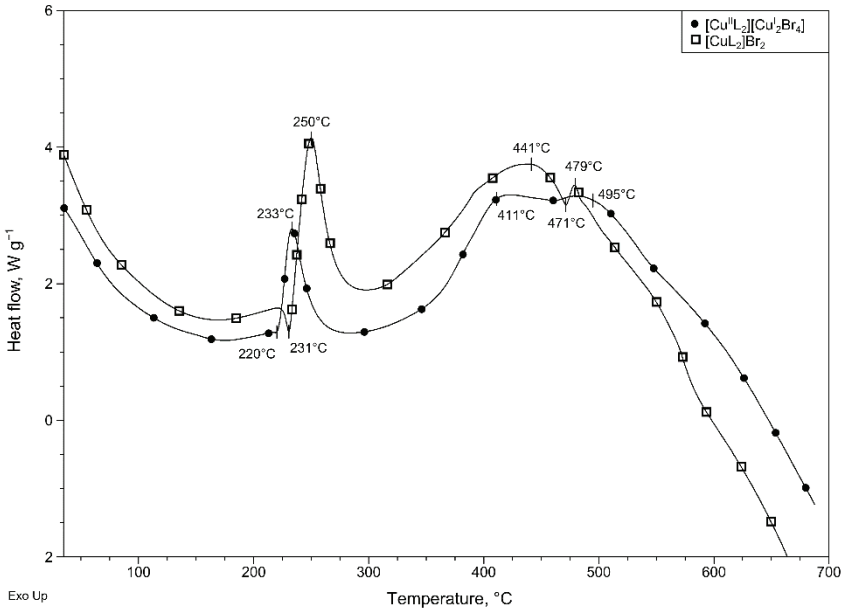

Fig. S-3. DSC curve of $[Cu^{II}L_2][Cu^{I}_2Br_4]$ and $[CuL_2]Br_2$ in nitrogen.

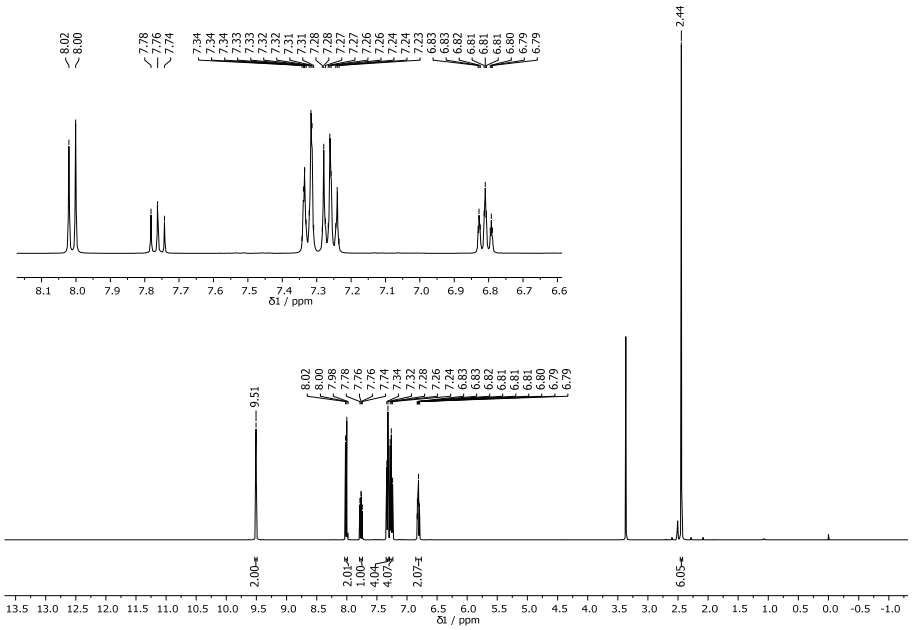

Fig. S-4. ^{1}H-NMR spectrum of **L**.

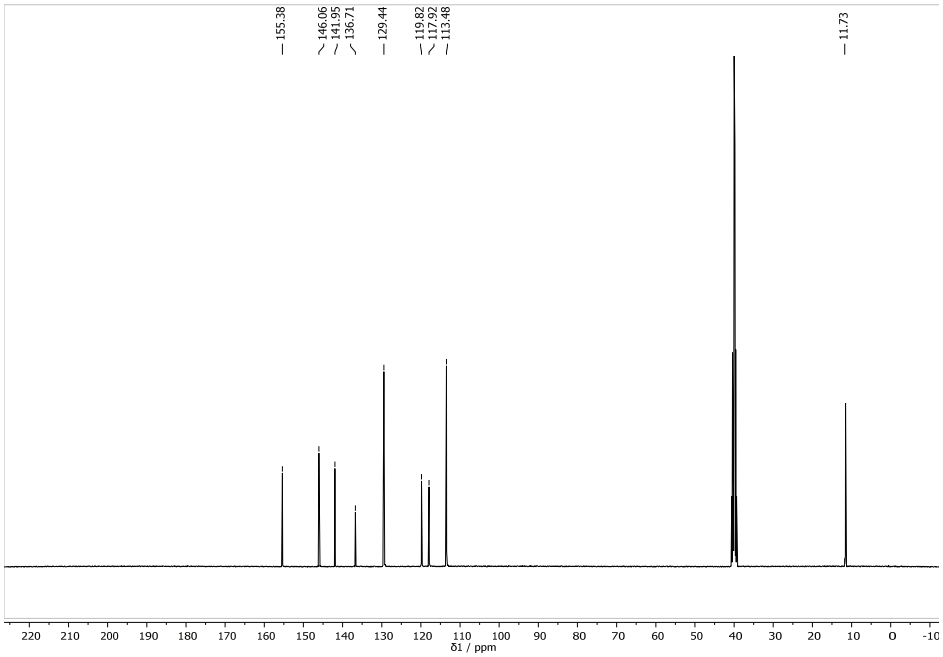

Fig. S-5. ^{13}C-NMR spectrum of **L**.

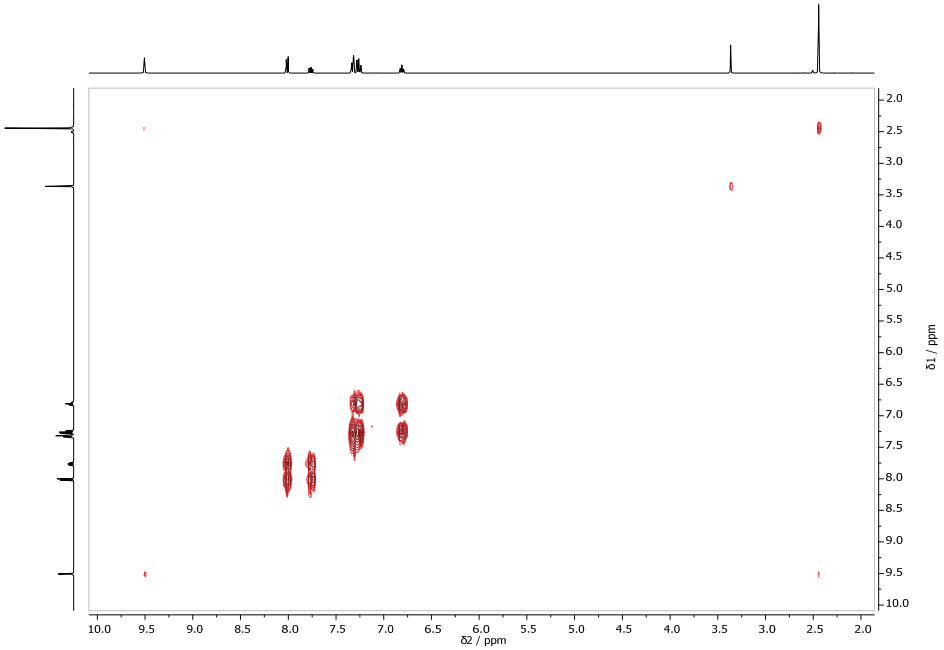

Fig. S-6. Gradient ^{1}H–^{1}H COSY NMR spectrum of **L**.

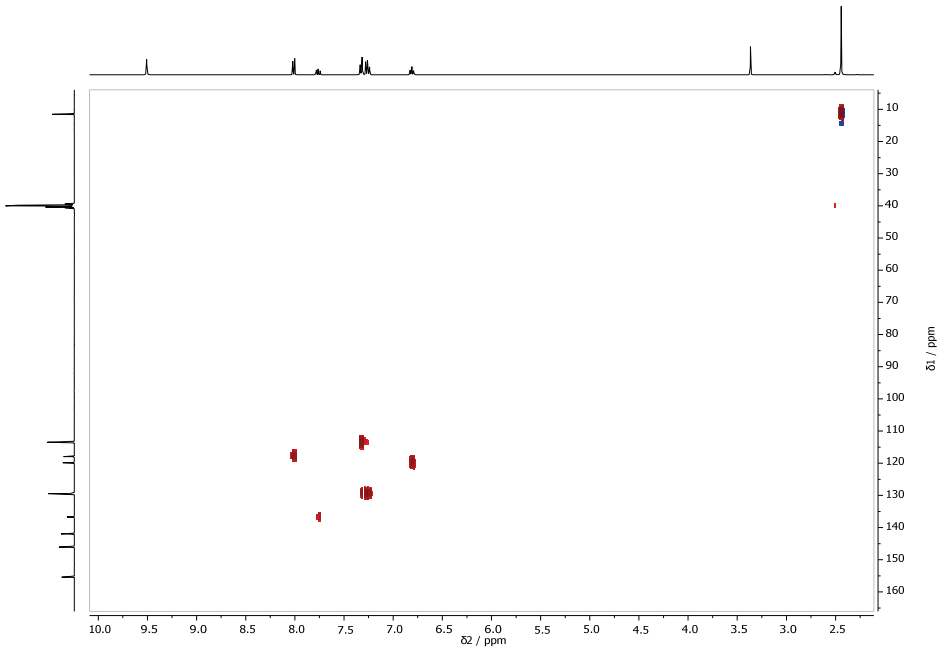

Fig. S-7. HSQC NMR spectrum of **L**.

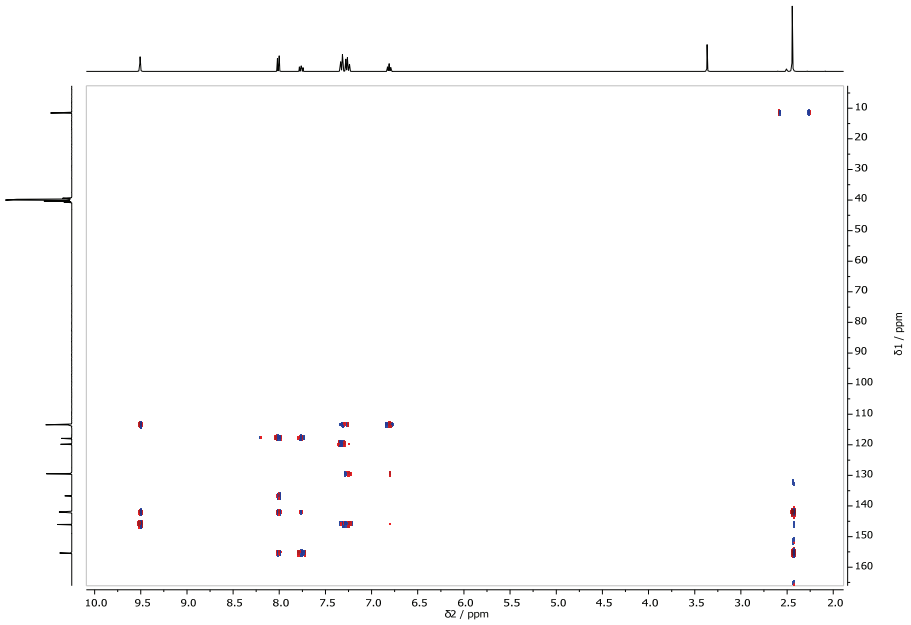

Fig. S-8. ^{1}HMBC NMR spectrum of **L**.