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PAPER

The solution stability of copper(I) and silver(I) complexes with *N*-heterocyclic carbenes

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SUPPLEMENTARY INFORMATION

1. X-ray diffraction studies (with Table 1 and Figures S1, S2 and S3)
2. ^{1}H NMR spectra of $[Cu^{I}(LH)]^{2+}$ and $[Cu^{I}(LH)]^{2+}$ (with Figures S4 and S5)

1. X-ray crystallographic studies

Diffraction data for **[LH$_3$]Br$_3$·7.7H$_2$O** and **[Cu^I(LH)](ClO$_4$)$_2$** have been collected at ambient temperature by means of Bruker-Axs CCD-based diffractometer. Diffraction data for **[Ag^I(LH)](NO$_3$)$_2$·5H$_2$O** have been collected at ambient temperature by means of an Enraf-Nonius CAD4 four circle diffractometer equipped with a punctual detector (scintillation counter). Both diffractometers work with graphite-monochromatized MoKα X-radiation (λ = 0.71073 Å). Data reductions (including intensity integration, background, Lorentz and polarization corrections) for intensities collected with the conventional diffractometer were performed with the WinGX package;[1] absorption effects were evaluated with the psi-scan method,[2] and absorption correction was applied to the data. Frames collected by the CCD-based system were processed with the SAINT software,[3] and intensities were corrected for Lorentz and polarization effects; absorption effects were empirically evaluated by the SADABS software[4] and absorption correction was applied to the data.

All crystal structures were solved by direct methods (SIR 97)[5] and refined by full-matrix least-square procedures on F^2 using all reflections (SHELXL 97).[6] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms belonging to the tris-benzimidazolium cages were placed at calculated positions with the appropriate AFIX instructions and refined using a riding model.

Several kinds of disorder affect two of the studied crystal structures. In particular, the crystalline hydrate salt [**LH$_3$**]Br$_3$·7.7H$_2$O has the three bromide counterions and the not stoichiometric water solvent molecules placed on partly populated atom sites; some of them are mutually exclusive. The [Cu^I(**LH**)](ClO$_4$)$_2$ is characterized by positional disordered affecting the Cu^I species. The copper(I) results disordered over two alternative positions with very different occupancies: 0.93(1) vs. 0.07(1). This means that also the atoms forming the cage should be disordered over alternative positions corresponding to the two geometrical arrangements suitable to satisfy the bonding requirements of the two Cu atom sites. However, the secondary arrangement occurs only in 7% of the unit cells forming the crystal and the features of the cage in this minority portion of the crystal cannot be characterized through X-ray diffraction analysis. Interestingly, a similar disordered for the metal species and a proposed but unresolved disordered for the cage have been detected in the [Ag^I(**NH**)]$^{2+}$ complex obtained from the tris-imidazolium cage,[7] whereas it does not occur in our [Ag^I(**LH**)]$^{2+}$ complex obtained from the tris-benzimidazolium cage.

Crystal data for the three molecular complexes are shown in Table S1. ORTEP views for the three molecular cages are shown in Figure S1, S2, S3.

Table S1. Crystal data for investigated crystals

	$[LH_3]Br_3 \cdot 7.7H_2O$	$[Cu^I(LH)](ClO_4)_2$	$Ag^I(LH)](NO_3)_2 \cdot 5H_2O$
Formula	$C_{45}H_{60.4}Br_3N_6O_{7.7}$	$C_{90}H_{86}Cl_4Cu_2N_{12}O_{16}$	$C_{45}H_{53}AgN_8O_{11}$
M [g/mol]	1048.38	1860.60	989.74
dimension[mm]	0.30x0.15x0.05	0.30x0.25x0.18	0.70x0.50x0.40
colour	colourless	colourless	colourless
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*C* 2/*m* (no. 12)	*P* 2_1/*n* (no. 14)	*Ibmm* (no. 74)
a [ ]	21.808(2)	15.002(1)	15.243(7)
b [ ]	17.048(2)	25.618(1)	17.179(8)
c [ ]	15.933(2)	21.941(1)	17.400(6)
β [°]	120.49(1)	97.80(1)	90.00
V [^{3}]	5104.7(9)	8354.2(1)	4556.3(28)
Z	4	4	4
ρ_{calcd} [g/cm^3]	1.364	1.479	1.443
μ Mo K_α [mm-^{1}]	2.424	0.714	0.511
F(000)	2156	3856	2056
θ range [°]	2-25	2-25	2-25
Measured refl.	20614	79425	4231
Unique refl.	4666	14809	2163
R_{int}	0.0409	0.0162	0.0332
min/max transmission	0.72/0.98	0.76/0.98	0.73/0.78
Strong data (I_0>2σ(I_0))	3442	10539	1503
Refined parameters	327	1136	170
R1, *wR2* (strong data)	0.0716, 0.2118	0.0744, 0.2214	0.0914, 0.2487
R1, *wR2* (all data)	0.0909, 0.2331	0.0989, 0.2482	0.1151, 0.2719
GOF	1.064	1.025	1.147
Max/min residuals [e $^{-3}$]	0.99/-0.31	1.29/-0.56	0.84/-0.78

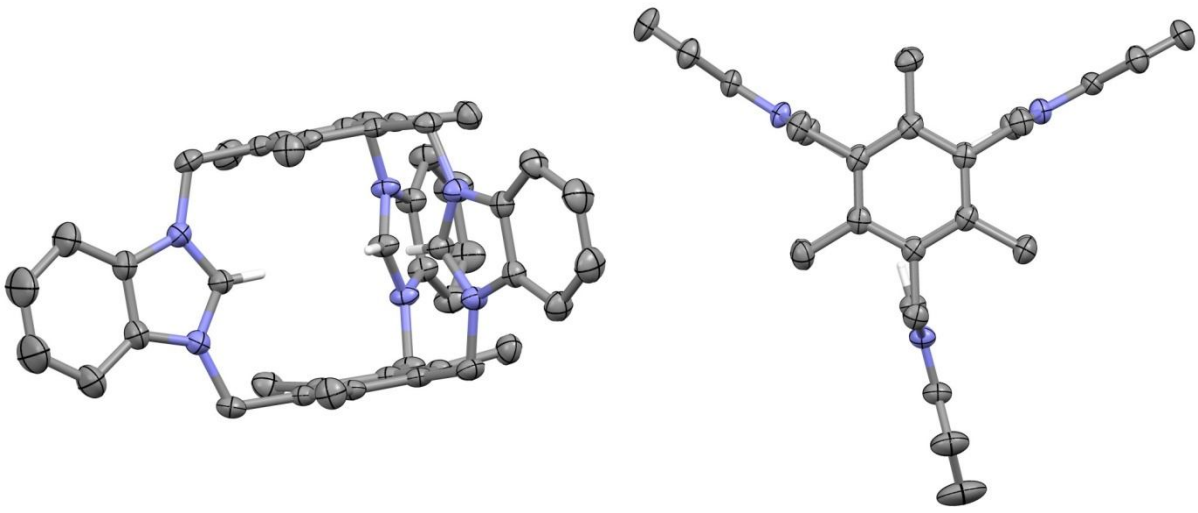

Figure S1. Lateral and top ORTEP views of the $[LH_3]^{3+}$ molecular cage: ellipsoids are drawn at the 30% probability level; only H atoms belonging to the imidazolium moieties are shown; bromide counterions and water solvent molecules have been omitted for clarity.

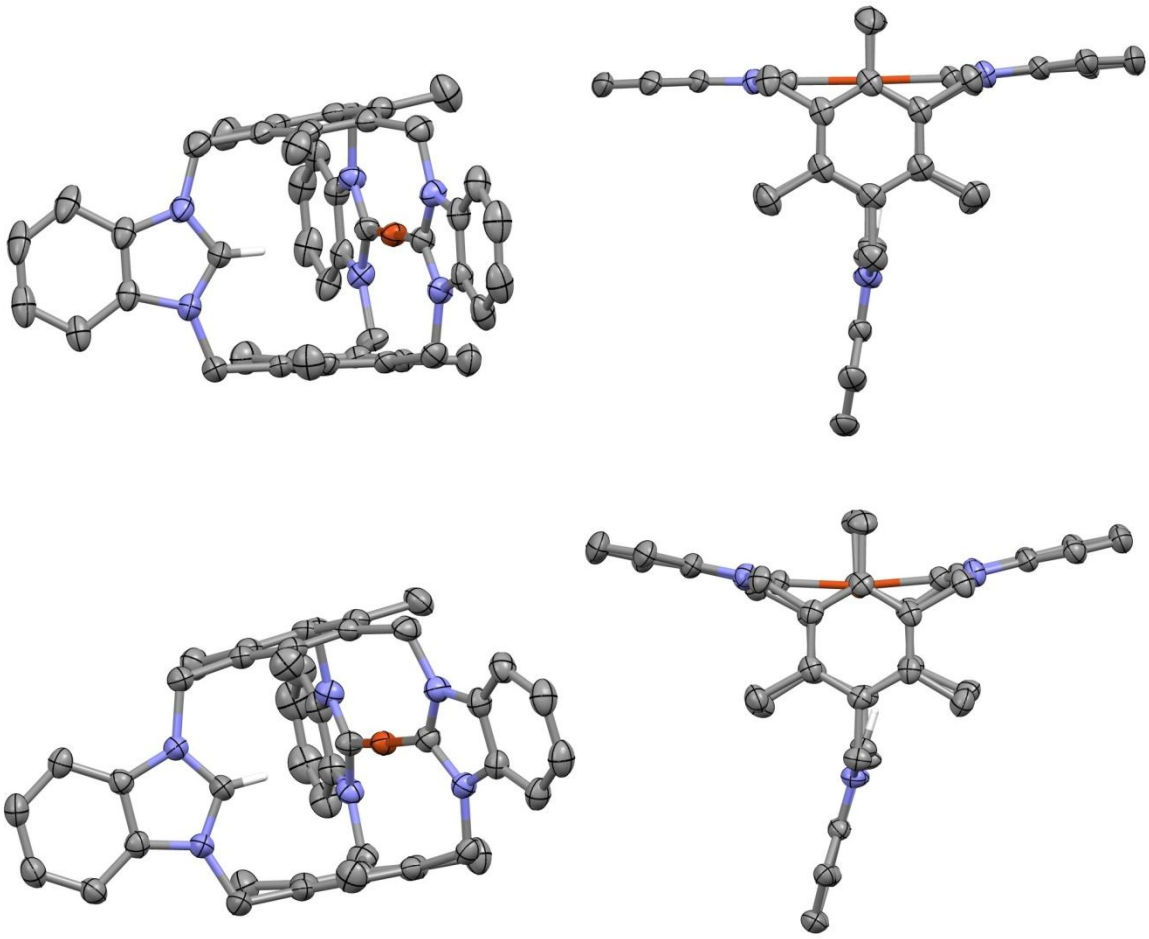

Figure S2. Lateral and top ORTEP views of the two not symmetrically equivalent $[Cu^{I}(LH)]^{2+}$ cation molecular complexes forming the crystal: ellipsoids are drawn at the 30% probability level; only H atoms belonging to the imidazolium moiety is shown; perchlorate counterions have been omitted for clarity.

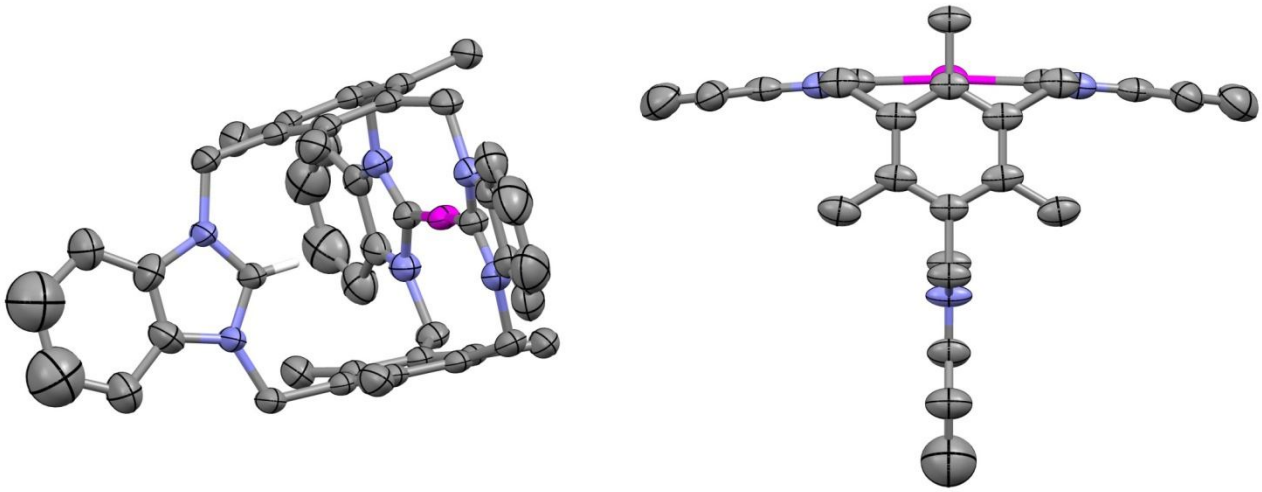

Figure S3. Lateral and top ORTEP views of the $[Ag^{I}(LH)]^{2+}$ cation molecular complex: ellipsoids are drawn at the 30% probability level; only H atoms belonging to the imidazolium moiety is shown; nitrate counterions and water solvent molecules have been omitted for clarity.

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2. ^{1}H NMR spectra

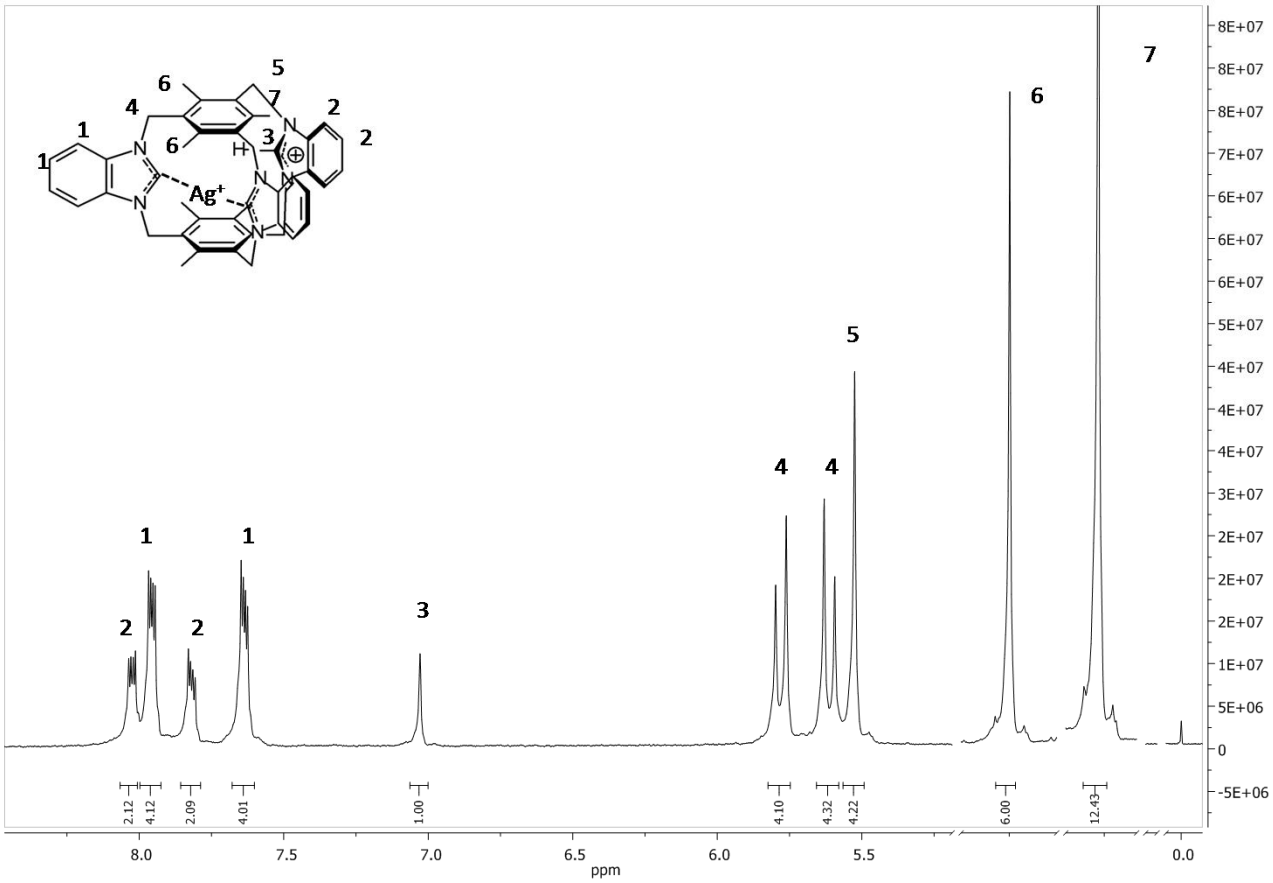

Figure S4. ^{1}H-NMR spectrum of $[Ag^{I}(\mathbf{LH})]^{2+}$ complex in CD_3CN. Splitting of 1-7 proton signals indicates the three benzo-heterocyclic moieties are not equivalent, as expected from the circumstance that two are bound to the Ag^{I} as carbenes, whereas the third one exhibits an imidazolium nature (signal 3).

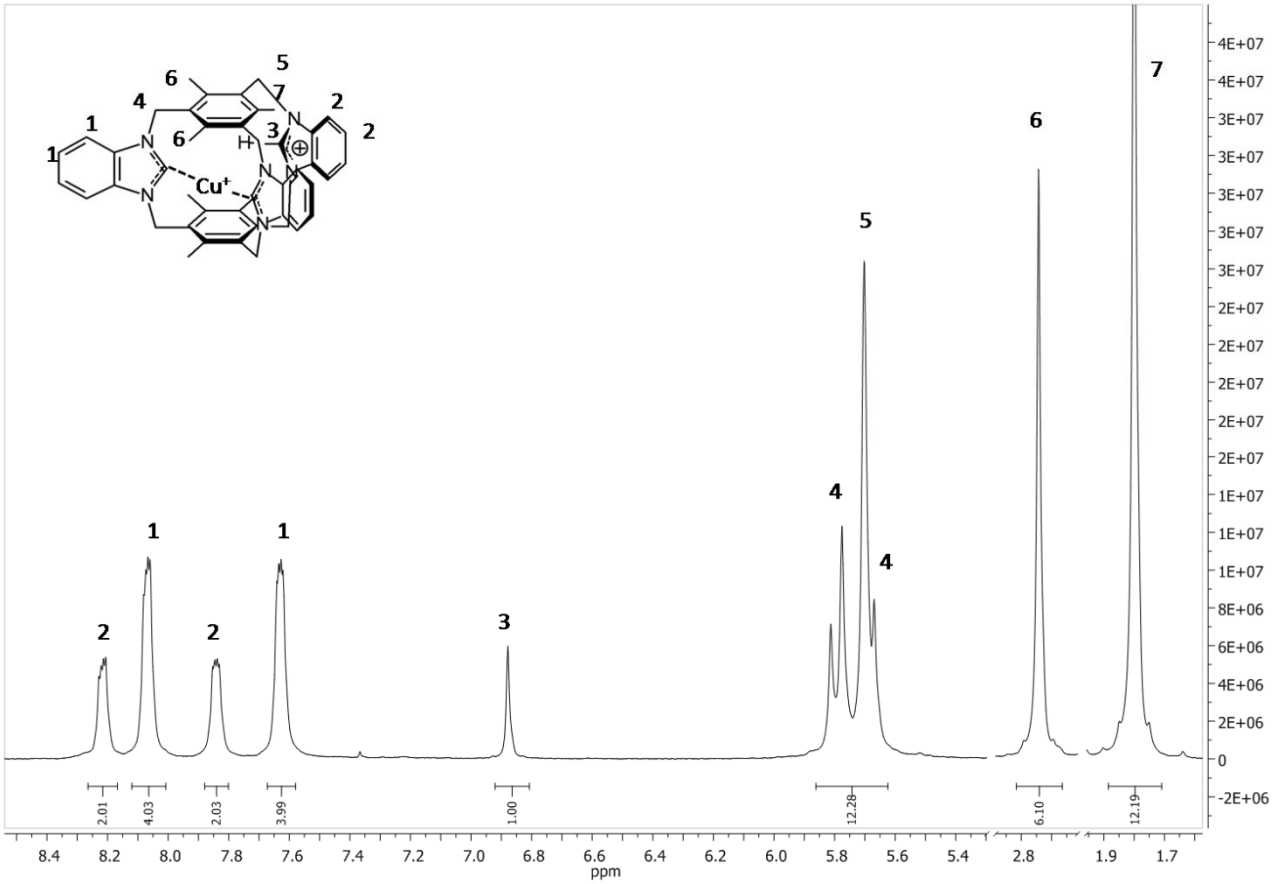

Figure S5. ^{1}H-NMR spectrum of $[Cu^{I}(\mathbf{LH})]^{2+}$ complex in DMSO-d_6. Splitting of 1-7 proton signals indicates the three benzo-heterocyclic moieties are not equivalent, as expected from the circumstance that two are bound to the Cu^{I} as carbenes, whereas the third one exhibits an imidazolium nature (signal 3).