Structure, EPR/ENDOR and DFT characterisation of a [Cu$^{II}$(en)$_2$](OTf)$_2$ complex.

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Electronic Supplementary Information

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<table>
<thead>
<tr>
<th>Table S1. X-ray data for <a href="OTf">Cu(en)$_2$</a>$_2$ 1</th>
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<tr>
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<td>$b$/Å</td>
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<td>$c$/Å</td>
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<td>$\alpha$/°</td>
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<tr>
<td>$\beta$/°</td>
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<td>$\gamma$/°</td>
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<td>$V$/Å$^3$</td>
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2. Computational data

All calculations were performed using the Gaussian 09 program. The structure of [Cu(en)₂(OTf)₂] was optimised without geometry restraints using the unrestricted B3LYP hybrid functional, employing the 6-31+G(d,p) basis set on all atoms. The geometry optimisation was followed by a frequency calculation to ascertain the nature of the stationary point (minimum vs. saddle point). TD-DFT calculations were performed on the optimised geometry.

Cartesian coordinates of [Cu(en)₂](OTf)₂ 1.

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**TD-DFT calculated excited state:**

Multiplicity and symmetry: 2.001-A

Energy: 2.3134 eV, 535.95 nm

Oscillator strength: f=0.0000

S^2: 0.751

Principal Orbital contributions:

- 107B -> 122B: 38.7%
- 110B -> 122B: 50.7%
- 112B -> 122B: 1.5%
- 119B -> 122B: 3.1%
- 121B -> 122B: 3.6%
**Fig S1a:** Molecular orbital 107B of [Cu(en)$_2$](OTf)$_2$

**Fig S1b:** Molecular orbital 110B of [Cu(en)$_2$](OTf)$_2$
**Fig S1c;** Molecular orbital 122B of [Cu(en)₂](OTf)₂
3. Additional X-band CW and pulsed EPR and ENDOR data.

**Fig S2:** CW EPR spectrum (298 K) of [Cu(en)$_2$](OTf)$_2$ dissolved in acetonitrile:tetrahydrofuran (1:1). a) experimental and a’ simulation.

**Fig S3:** Field Sweep Echo Detected EPR spectrum (10 K) of [Cu(en)$_2$](OTf)$_2$ a) experimental and a’) simulation.
**Fig S4** Pulsed Davies ENDOR spectra of [Cu(en)$_2$(OTf)$_2$] recorded at a) 350 mT and b) 288 mT. Corresponding simulations are shown in a’,b’. The spectra were taken at 10 K, with a repetition rate of 333 kHz. The pulse sequence $\pi$-T-$\pi$/2-τ-$\pi$-τ-echo using mw pulse lengths of $t_\pi = 256$ ns, $t_{\pi/2} = 128$ ns, and an interpulse time $\tau$ of 820 ns was used. An rf $\pi$ pulse of variable frequency and a length of 8 μs was applied during time T of 10 μs.
**Fig S5:** Schematic illustration of the Cu(II) complexes referenced in Table 3 (main text).