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Cu^I and Ag^I scorpionate-like complexes based on sterically hindered tris(6-methyl-2-pyridyl)phosphine oxide

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§1. Materials and Instrumentation

Tris(6-methyl-2-pyridyl)phosphine oxide (L) was synthesized following the described procedure [S1]. $[Cu(CH_3CN)_4]PF_6$ (≥99%, Acros) and $AgClO_4$ (97%, Alfa Aesar) were used as purchased. All the solvents (MeCN, hexane) prior to use were purified by common protocols.

Powder X-ray diffraction (PXRD) patterns were recorded on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation, Ni – filter, 3–35° 2θ range, 0.03° 2θ step, 5s per point).

FT-IR spectra were collected on a Bruker Vertex 80 spectrometer. The CHN microanalysis was performed on a MICRO cube analyzer.

Emission and excitation spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) equipped with a cooled PC177CE-010 photon detection module and an R2658 photomultiplier. The emission decays were recorded on the same instrument. The absolute PLQYs were determined at 298 K using a Fluorolog 3 Quanta-phi integrating sphere.

§2. Synthetic procedures and characterization data

$[CuL(MeCN)]PF_6$ (**1**).

The mixture of $[Cu(CH_3CN)_4]PF_6$ (25 mg, 0.067 mmol) and L (22 mg, 0.068 mmol) in MeCN (1 mL) was stirred at room temperature for 20 min. To the resulting solution, diethyl ether (3 mL) was then added and the precipitate formed was centrifuged and dried in air. Orange powder. Yield: 31 mg (81%). FT-IR (KBr, cm^{-1}): 406 (w), 457 (w), 491 (s), 559 (m), 591 (s), 664 (w), 697 (m), 731 (m), 742 (s), 778 (m), 800 (s), 843 (vs), 940 (w), 999 (w), 1040 (w), 1095 (w), 1146 (s), 1166 (m), 1229 (m), 1264 (w), 1351 (m), 1368 (m), 1381 (m), 1449 (m), 1488 (m), 1557 (w), 1590 (m), 1938 (vw), 2009 (vw), 2273 (vw), 2488 (vw), 2927 (m), 2956 (w), 3025 (w), 3066 (w). Anal. Calc. for $C_{20}H_{21}CuF_6N_4OP_2$ (572.89): C, 41.9; H, 3.7; N, 9.8. Found: C, 41.5; H. 3.4; N, 9.7.

$[AgL(MeCN)]ClO_4$ (**2**).

The mixture of $AgClO_4$ (25 mg, 0.121 mmol) and L (39 mg, 0.121 mmol) in MeCN (1 mL) was stirred at room temperature for 20 min. To the resulting solution, diethyl ether (3 mL) was then added and the precipitate formed was centrifuged and dried in air. Off-white powder. Yield: 51 mg (74%). FT-IR (KBr, cm^{-1}): 404 (w), 490 (s), 551 (w), 591 (s), 623 (m), 695 (m), 741 (m), 802 (s), 871 (m), 998 (m), 1041 (m), 1093 (vs), 1148 (m), 1166 (s), 1208 (m), 1222 (s), 1260 (m), 1368 (w), 1379 (w), 1447 (vs), 1558 (m), 1587 (s), 2008 (vw), 2284 (w), 2312 (vw), 2929 (w), 2963 (vw), 2994 (w), 3065 (w). Anal. Calc. for $C_{20}H_{21}AgClN_4O_5P$ (571.70): C, 42.0; H, 3.7; N, 9.8. Found: C, 41.6; H. 3.5; N, 9.5.

§3. Powder X-ray diffraction data

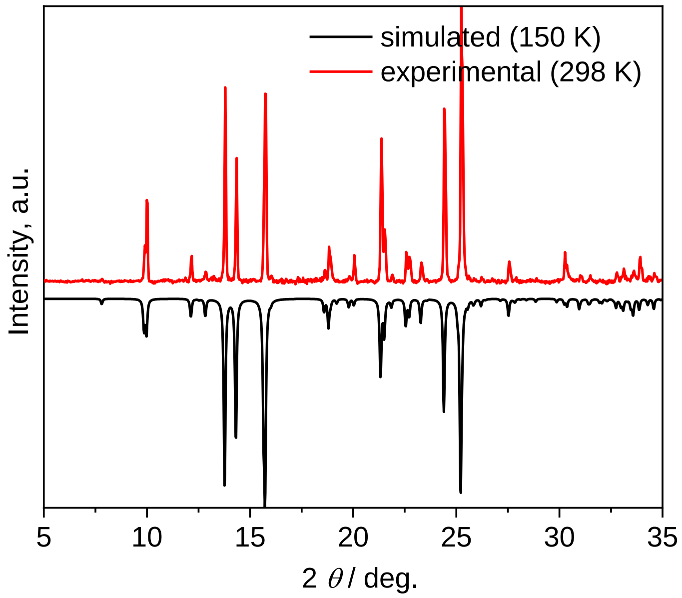


Figure S1. Experimental and simulated PXRD patterns of **1**.

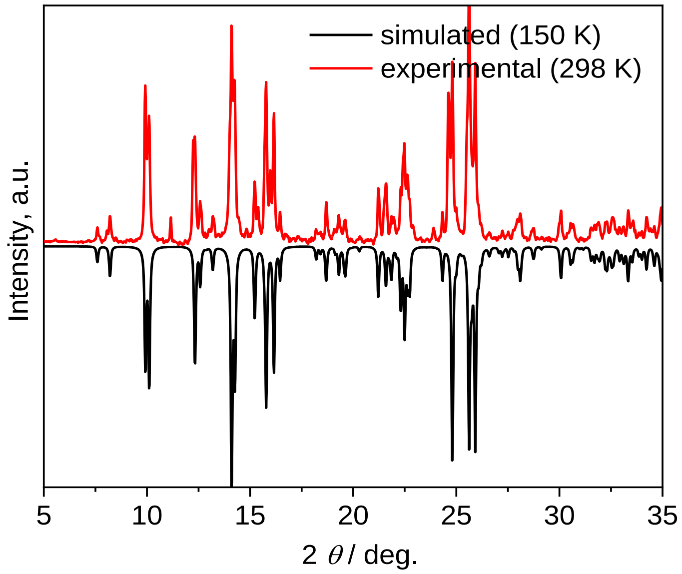


Figure S2. Experimental and simulated PXRD patterns of **2**.

§4. FT-IR spectra

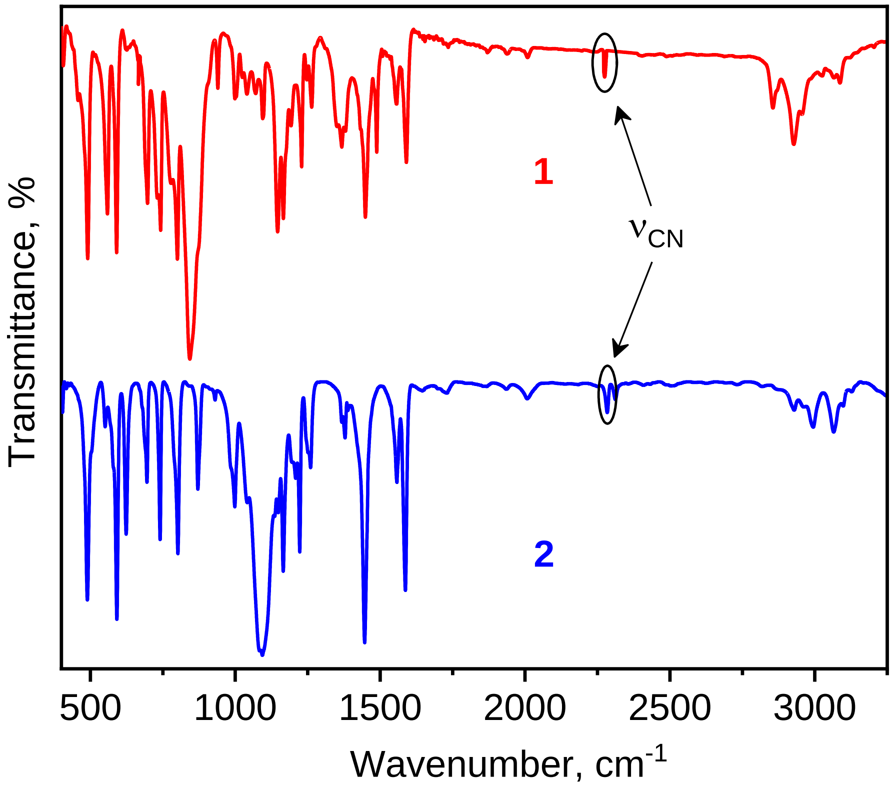


Figure S3. FT-IR spectra for **1** and **2** in the 400–3250 cm^{-1} region.

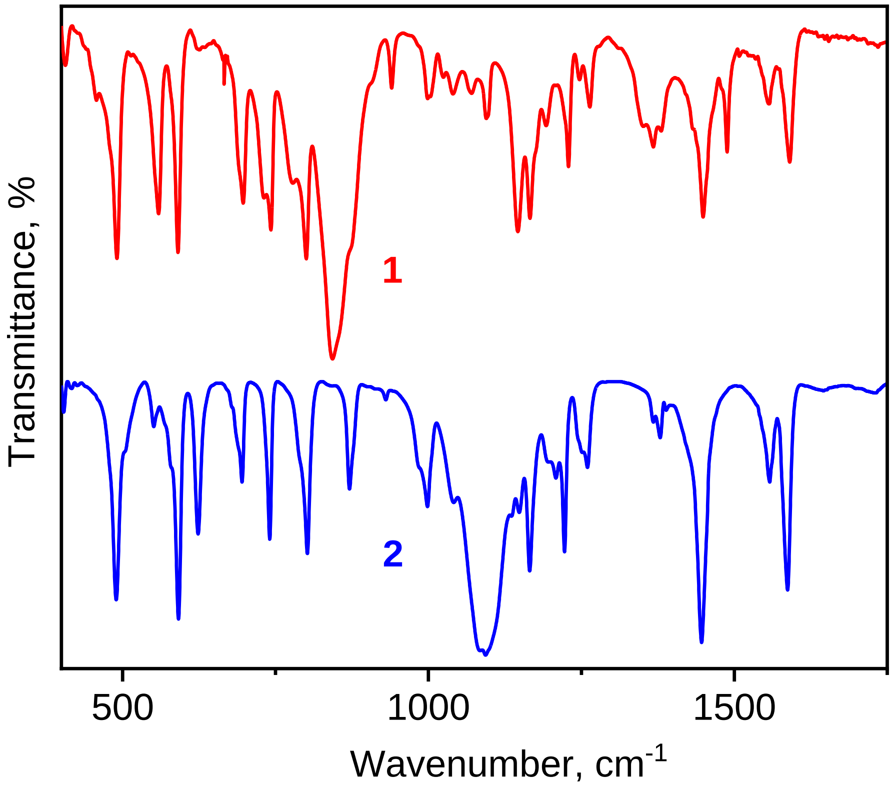
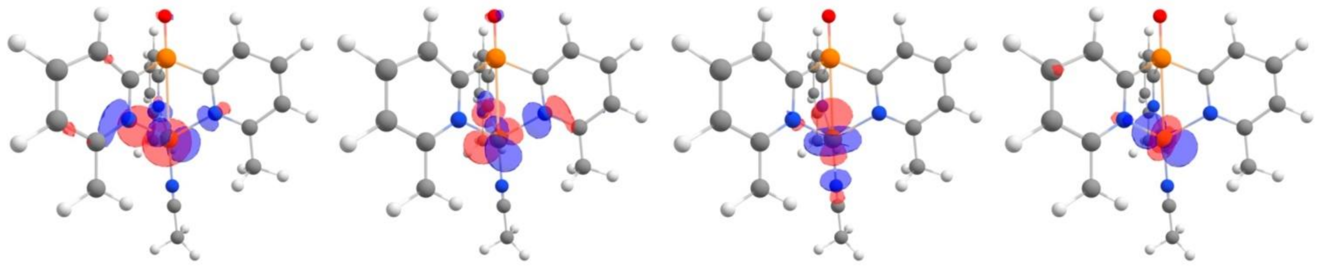


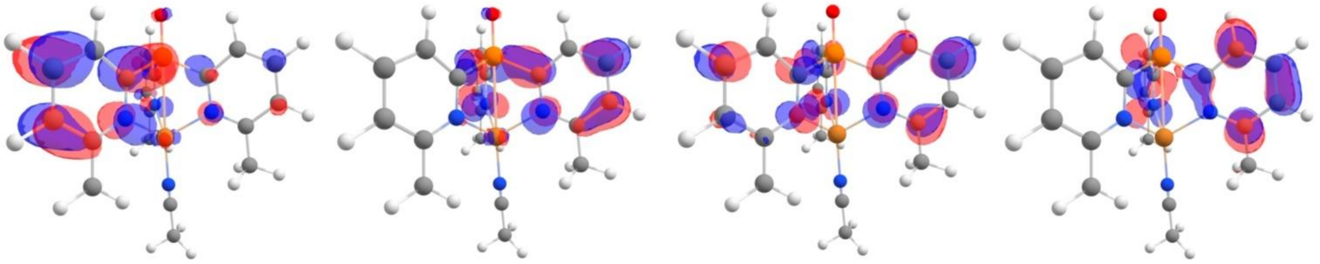
Figure S4. FT-IR spectra for **1** and **2** in the fingerprint region.

§5. Computational details

DFT computations were performed using Gaussian 09 program [S2]. The structures of the S_0 were fully optimized using PBE0 hybrid functional [S3] coupled with the def2-TZVP basis set [S4]. There are no imaginary frequencies were found in all optimized structures.

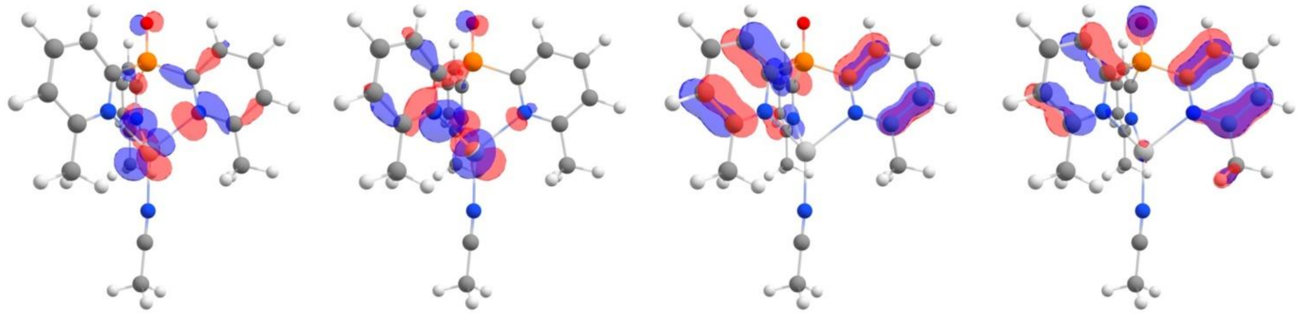


HOMO (–8.918 eV) **HOMO-1** (–8.973 eV) **HOMO-2** (–9.418 eV) **HOMO-3** (–9.756 eV)

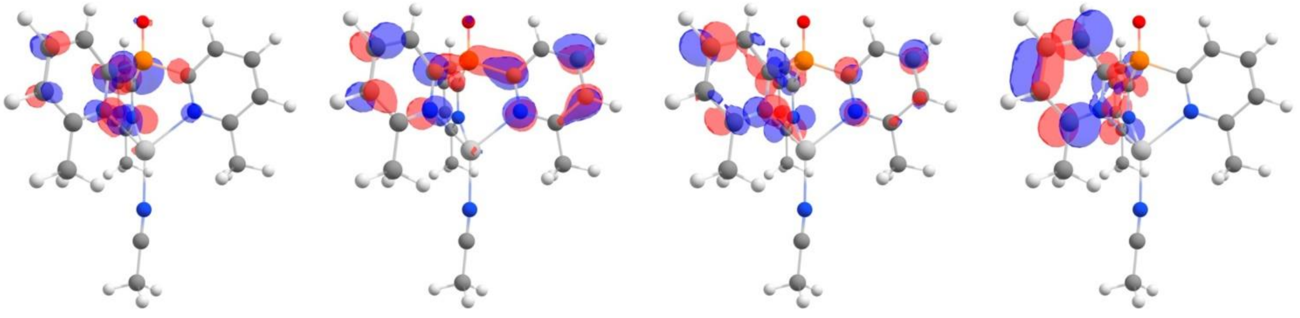


LUMO (–4.518 eV) **LUMO+1** (–4.430 eV) **LUMO+2** (–3.823 eV) **LUMO+3** (–3.721 eV)

Figure S5. Frontier orbitals (isovalue of 0.03) in the ground state for cationic part $[CuL(MeCN)]^+$ of **1** computed at the PBE0/def2TZVP level of theory.



HOMO (–5.448 eV) **HOMO-1** (–5.592 eV) **HOMO-2** (–5.630 eV) **HOMO-3** (–5.800 eV)



LUMO (–1.649 eV) **LUMO+1** (–1.569 eV) **LUMO+2** (–1.482 eV) **LUMO+3** (–1.251 eV)

Figure S6. Frontier orbitals (isovalue of 0.03) in the ground state for cationic part $[AgL(MeCN)]^+$ of **2** computed at the PBE0/def2TZVP level of theory.

§6. References

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S3. (*a*) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158; (*b*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

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