

Electronic Supplementary Information

Copper(I) complexes of a non-innocent quadridentate ligand

Gojko Buncic, Jonathan M. White, Zhiguang Xiao, Anthony G. Wedd, and Paul S. Donnelly*

Experimental

N,N'-bis[2-(2-pyridinyl)ethyl]-1,2-phenylenediamine (**H₂L**)

Glacial acetic acid (1.0 mL, 18.4 mmol) was added to 1,2-phenylenediamine (1.0 g, 9.2 mmol) in methanol (10 mL) followed by 2-vinylpyridine (1.7 mL, 15.6 mmol). The resulting mixture was stirred at reflux under nitrogen for 12 h. After cooling, the mixture was poured over ice and a solution of NaOH (0.8 g, 20 mmol) in water (10 mL) was added. The aqueous phase was extracted using dichloromethane. Organic phases were dried over magnesium sulphate and concentrated to give a dark brown oily crude product (2.5 g). Purification by column chromatography (ethyl acetate / pentane, 50 - 100 % gradient), followed by drying under high vacuum 2 h, gave light red oil (1.0 g, 40 %). ¹H NMR (500 MHz, dms_o-d₆): δ(ppm) 8.50 (ddd, ³J_{HH} = 4.9 Hz, ⁴J_{HH} = 1.9 Hz, ⁵J_{HH} = 0.9 Hz, 2H), 7.70 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.9 Hz, 2H), 7.32 (dt, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.0 Hz, 2H), 7.22 (ddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 4.9 Hz, ⁴J_{HH} = 1.2 Hz, 2H), 6.60 - 6.53 (m, 4H), 4.60 (t, ³J_{HH} = 5.7 Hz, 2H), 3.41 - 3.35 (m, 4H), 3.04 (t, ³J_{HH} = 7.2 Hz, 4H). ¹³C NMR (125.7 MHz, dms_o-d₆): δ 159.71, 149.01, 136.41, 136.21, 123.18, 121.39, 117.52, 109.89, 43.45, 37.08. ESI MS. (^{m/z}) found 319.1924; calc. for [M+H]⁺ 319.1923. Elem. Anal. found C, 75.30; H, 6.85; N, 17.69; calc. for {C₂₀H₂₂N₄} C, 75.44; H, 6.96; N, 17.60.

N,N'-bis[2-(2-pyridinyl)ethyl]-1,2-phenylenediamine copper(I) tetrafluoroborate, [Cu^I(H₂L)]BF₄.

Tetrakis(acetonitrile) copper(I) tetrafluoroborate (49 mg, 0.16 mmol) was added to a solution of H₂L (50 mg, 0.16 mmol) treated by freeze-pump-thaw cycles (5 x) in dry N,N-dimethylformamide (0.5 mL), under nitrogen. The resulting green solution contained a small quantity of dark red-brown precipitate and was frozen in liquid dinitrogen. Degassed diethyl ether (10 mL) was added via cannula and the mixture allowed to stand under dinitrogen. The mixture was allowed to stand under dinitrogen for 4 days to give revealed dark brown crystals. These were washed with deoxygenated ethanol (2 x) and dried under high vacuum (39 mg, 52 %). From a separate preparation, yellow crystals were isolated, washed with degassed ethanol, dried under high vacuum and dissolved in degassed d₆-dimethyl sulfoxide. ¹H NMR (500 MHz, dms_o-d₆): δ(ppm) 8.41 (ddd, ³J_{HH} = 5.3 Hz, ⁴J_{HH} = 1.7 Hz, ⁵J_{HH} = 0.8 Hz, 2H), δ 7.90 (td, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.8 Hz, 2H), 7.50 (d, ³J_{HH} = 7.8 Hz, 2H), 7.39 (ddd, ³J_{HH} = 7.6 Hz, ³J_{HH} = 5.3 Hz, ⁴J_{HH} = 1.3 Hz, 2H), 7.24-7.20 (m, 2H), 7.09-7.05 (m, 2H), δ 5.71 (bs, 2H), 3.40-3.33 (m, 4H), 3.03-2.96 (m, 4H). ESI MS. (^{m/z}) found 381.1217; calc. for {[C₂₀N₄H₂₀Cu]⁺} 381.1140. Elem. Anal. found C, 49.56; H, 4.80; N, 11.26; calc. for {[C₂₀H₂₂N₄CuBF₄].H₂O} C, 49.35; H, 4.97; N, 11.51.

***N,N'*-bis[2-(2-pyridinyl)ethyl]-*o*-benzosemiquinonediiimide copper(II) tetrafluoroborate,
[Cu^{II}L^{•-}]BF₄.**

This complex is prepared by aerial oxidation of the Cu^I complex that is prepared in situ (see above). Tetrakis(acetonitrile) copper(I) tetrafluoroborate (20 mg, 0.06 mmol) was added to a solution of H₂L (20 mg, 0.06 mmol) in dry N,N-dimethylformamide (2 mL). The resulting dark green solution was frozen in liquid nitrogen and diethyl ether (20 mL) was added and the mixture was left to stand under an atmosphere of dinitrogen. Dark green crystals were isolated after standing for one week by decanting off the solution under nitrogen followed by drying under high vacuum for 5 minutes (17 mg, 56 %). ¹H NMR (500 MHz, CD₃OD): δ (ppm) 8.74 (dd, ³J_{HH} = 5.4 Hz, ⁴J_{HH} = 0.9 Hz, 2H), 8.04 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.7, 2H), 7.68 (d, ³J_{HH} = 7.9 Hz, 2H), 7.58-7.53 (m, 2H), 7.51 (ddd, ³J_{HH} = 7.4 Hz, ³J_{HH} = 5.7 Hz, ⁴J_{HH} = 1.5 Hz, 2H), 7.41-7.37 (m, 2H), 4.18 (bs, 3H), 3.56 (bs, 2H), 2.41 (bs, 1H). ¹³C NMR (125.7 MHz, dms_o-*d*₆): δ 159.98, 151.68, 150.61, 140.44, 126.93, 125.16, 124.82, 119.50, 48.95, 37.57. ESI MS. (^{m/z}) found 379.1007; calc. for {[C₂₀N₄H₂₀Cu]⁺} 379.0984. The dark green crystals of this Cu^{II} complex of this a π-radical anionic ligand ([Cu^{II}L^{•-}]BF₄) are unstable over time and with continued exposure to air. The green crystals decompose to a unidentified brown material, as a consequence obtaining satisfactory elementary analysis of this material proved challenging.

Table S1. Summary of Crystal and Structural Refinement Data for $([\text{Cu}^{\text{II}}\text{L}^{\cdot-}]\text{BF}_4)_2 \cdot (\text{CH}_3)_2\text{NCHO}$ and $[\text{Cu}^{\text{I}}(\text{H}_2\text{L})]\text{BF}_4$.

Crystal	$([\text{Cu}^{\text{II}}\text{L}^{\cdot-}]\text{BF}_4)_2 \cdot (\text{CH}_3)_2\text{NCHO}$	$[\text{Cu}^{\text{I}}(\text{H}_2\text{L})]\text{BF}_4$
Chemical formula	$\text{C}_{43}\text{H}_{47}\text{N}_9\text{Cu}_2\text{B}_2\text{F}_8\text{O}$	$\text{C}_{20}\text{H}_{22}\text{N}_4\text{CuBF}_4$
M_w	1006.60	468.77
Crystal System	Monoclinic	Orthorombic
Temperature / K	130(2)	130(2)
Space group	$P 2_1/c$	Pbca
$a / \text{Å}$	8.8006(10)	15.8810(3)
$b / \text{Å}$	28.0293(4)	14.7548(3)
$c / \text{Å}$	17.9337(3)	17.2786(3)
$a / ^\circ$	90.00	90.00
$b / ^\circ$	100.8580(10)	90.00
$g / ^\circ$	90.00	90.00
$V / \text{Å}^3$	8344.59(11)	4048.74(13)
Z	4	8
Independent Reflections	8496	3638
R_{int}	0.0278	0.0270
$R (I > 2s(I))$	0.0412	0.0453
wR (all data)	0.1093	0.1218
Goodness-of-fit on F^2	1.035	1.025

Table S2. Selected bond lengths (Å) and angles (deg) for $[\text{Cu}^{\text{II}}\text{L}^{\bullet}]\text{BF}_4)_2 \cdot (\text{CH}_3)_2\text{NCHO}$ and $[\text{Cu}^{\text{I}}(\text{H}_2\text{L})]\text{BF}_4$.

	$[\text{Cu}^{\text{II}}\text{L}^{\bullet}]\text{BF}_4)_2 \cdot (\text{CH}_3)_2\text{NCHO}$	$[\text{Cu}^{\text{I}}(\text{H}_2\text{L})]\text{BF}_4$
C5-C6	1.428(4)	1.386(5)
C4-C5	1.366(4)	1.382(6)
C3-C4	1.409(4)	1.386(6)
C2-C3	1.363(4)	1.390(6)
C1-C2	1.422(4)	1.387(5)
C1-C6	1.450(3)	1.398(5)
C6-N2	1.335(3)	1.451(5)
C1-N1	1.339(3)	1.451(4)
N2-Cu1	1.928(2)	2.100(3)
N1-Cu1	1.933(2)	2.087(3)
N2-Cu1-N3	96.67(8)	102.14(14)
N2-Cu1-N1	83.77(9)	84.35(12)
N1-Cu1-N4	94.40(8)	100.84(11)
N3-Cu1-N4	98.24(8)	116.38(11)

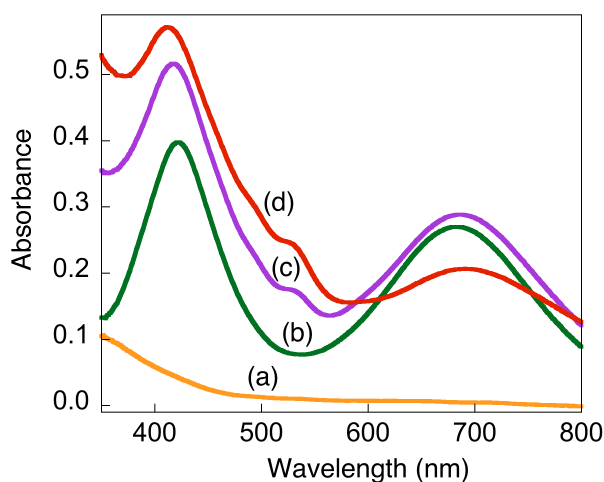


Figure S1. Solution absorption spectra of mixtures containing the ligand H_2L (100 μM) and $\text{Cu}(\text{I})$ (50 μM) under different conditions: (a) upon anaerobic addition of $[\text{Cu}^{\text{I}}(\text{MeCN})_4]^+$ into H_2L in DMSO; (b) as for solution (a) but in Mops buffer (50 mM; pH 7.0) or after aerobic oxidation of solution (a) in DMSO; (c) solution (b) in Mops buffer recorded after 5h; (d) solution (b) in Mops buffer recorded after 8h.

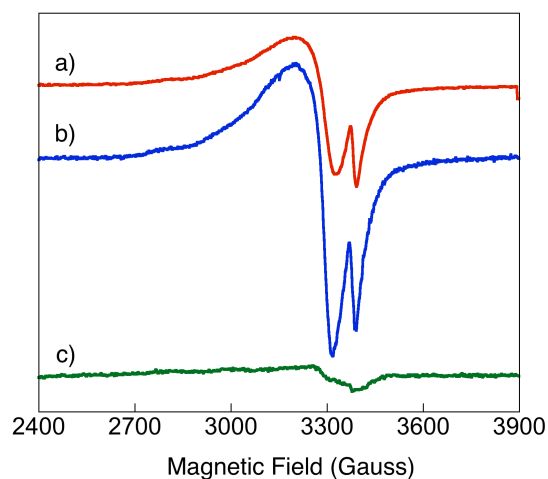


Figure S2. EPR spectra of powdered $[\text{Cu}^{\text{II}}\text{L}^{\cdot-}]\text{BF}_4$ at (a) room temperature and (b) at 77 K; (c) EPR spectrum of frozen solution dissolved in DmsO (0.5 – 1 mM) at 77 K.

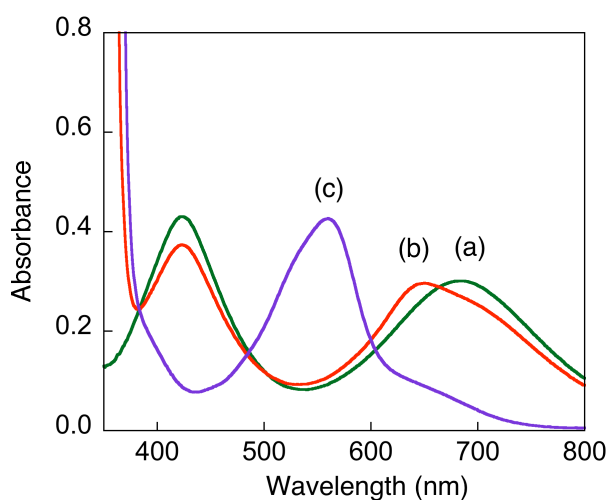


Figure S3. Solution spectra of: (a) $[\text{Cu}^{\text{II}}\text{L}^{\cdot-}]^+$ produced upon addition of $[\text{Cu}^{\text{I}}(\text{MeCN})_4]^+$ (50 μM) into H_2L (100 μM) in Mops buffer (50 mM; pH 7.0); (b) as solution (a) but containing additional Bca (1250 μM); (c) a control of solution (b) with H_2L absent.

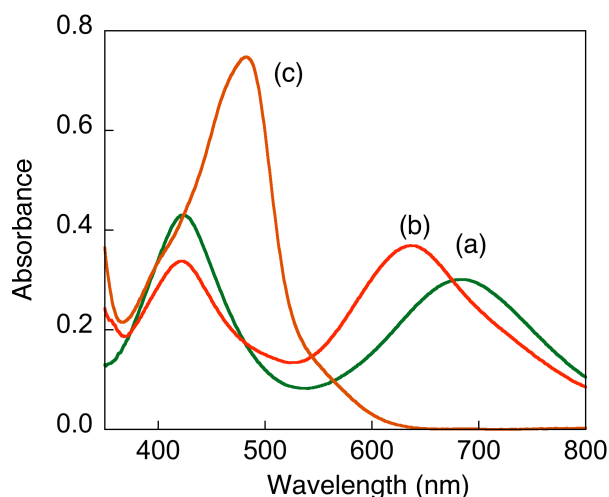


Figure S4. Solution spectra of: (a) $[\text{Cu}^{\text{II}}\text{L}^{\cdot-}]^+$ produced upon addition of $[\text{Cu}^{\text{I}}(\text{MeCN})_4]^+$ ($50\ \mu\text{M}$) into H_2L ($100\ \mu\text{M}$) in Mops buffer ($50\ \text{mM}$; $\text{pH}\ 7.0$); (b) as solution (a) but containing additional Bcs ($125\ \mu\text{M}$); (c) a control of solution (b) with H_2L absent. The solution (c) remained unchanged after addition of ligand H_2L ($100\ \mu\text{M}$).

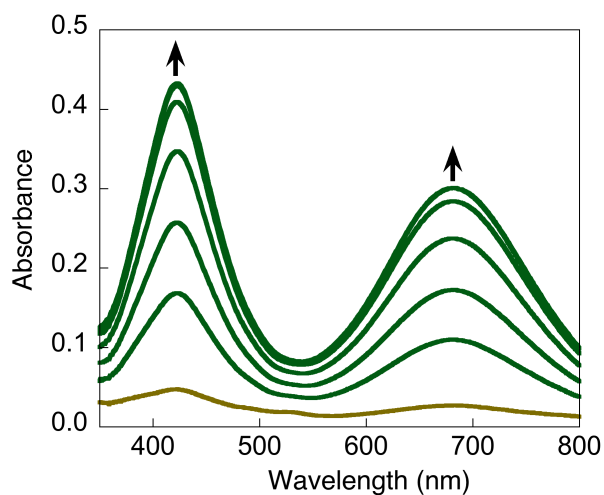


Figure S5. Solution spectra of a mixture containing glycine ($12.5\ \text{mM}$) and $\text{Cu}(\text{II})$ ($50\ \mu\text{M}$) in Mops buffer ($50\ \text{mM}$; $\text{pH}\ 7.0$) monitored every 3 min following addition of H_2L ($100\ \mu\text{M}$).

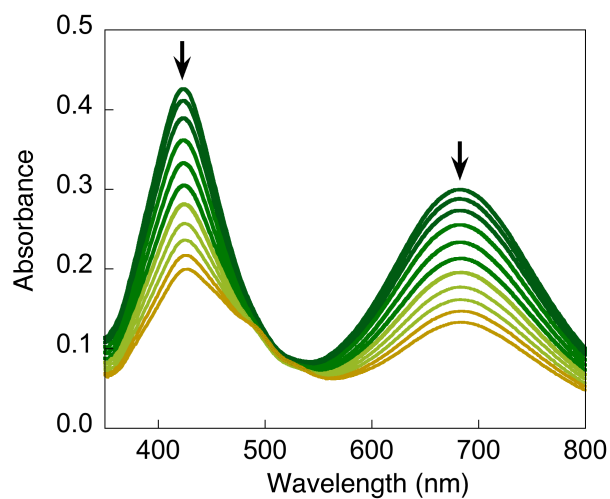


Figure S6. Solution spectra of a mixture containing H_2L ($100 \mu\text{M}$) and $\text{Cu}(\text{II})$ ($50 \mu\text{M}$) in Mops buffer (50 mM ; $\text{pH } 7.0$) titrated with a solution of H_2Edta (88.1 mM). (Each titration corresponds to adding 17.6 equivalents of H_2Edta relative to $\text{Cu}(\text{II})$ or 8.8 equivalents relative to H_2L).