A Cap for Copper(I) Ions! Metallosupramolecular Solid and Solution State Structures on the Basis of the Dynamic Tetrahedral \([\text{Cu(phenAr}_2\text{)(py)}_2]^+\) Motif

Supporting Information

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General

All commercial reagents were used without further purification. The purification and drying of the solvents was accomplished according to standard methods. Thin-layer chromatography was performed using thin-layer chromatography plates (Merck, Silica Gel 60 F254). Silica Gel 60 was equally used for column chromatography. Confirmation of the structures of all products was obtained by \(^1\text{H NMR}\) and \(^{13}\text{C NMR}\) spectroscopy (Bruker AC 200 and Avance 400 spectrometer, using the deuterated solvent as the lock and residual protiated solvent as the internal reference). The numbering of carbon atoms of the molecular formulae shown in the experimental section is only used for the assignment of the NMR signals and is not in accordance with the IUPAC nomenclature rules. Melting points were taken using an apparatus of Dr. Tottoli (Büchi) and are uncorrected. Electrospray mass spectra (ESI-MS) were recorded using a ThermoQuest LCQ Deca. The purity of all compounds was checked by thin-layer chromatography on SiO\(_2\) (Merck, silica gel 60 F254). Infrared spectra were recorded on a Perkin Elmer 1750 FT-IR spectrometer.
2,9-Bis(4-bromotetramethylphenyl)-1,10-phenanthroline\(^1\) (603 mg, 1.00 mol), 4-pyridine boronic acid (500 mg, 4.07 mmol), [1,1’-bis(diphenylphosphino)ferrocene]palladium(II) chloride (1:1 complex with dichloromethane, 80 mg, 98 µmol) and Na\(_2\)CO\(_3\) (4.00 g, 37.7 mmol) were dissolved in a mixture of toluene (40.0 mL), THF (10.0 mL) and H\(_2\)O (10.0 mL). After the mixture had been deoxygenated by bubbling through a nitrogen flow for 10 min, it was heated to reflux for 2 days. Then, the mixture was cooled and dichloromethane (100 mL) was added. The organic layer was separated and washed twice with 40 mL of H\(_2\)O. After the solvents had been removed under reduced pressure, the solid residue was purified by chromatography on alumina (dichloromethane, \(R_f = 0.3\)) to afford the product as a white solid, (490 mg, 818 µmol, 82%). mp: >300°C; IR (KBr): \(\tilde{\nu} = 3439, 2993, 2924, 1597, 1541, 1497, 1465, 1409, 1380, 1261, 1218, 1191, 1090, 1014, 870, 853, 823, 802, 640, 579\) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.69\) (m, 4H, 7\(_a\)-H, 7\(_b\)-H), 8.35 (d, \(J = 8.2\) Hz, 2H, 2-H), 7.91 (s, 2H, 1-H), 7.62 (d, \(J = 8.2\) Hz, 2H, 3-H), 7.21 (d, \(J = 4.9\) Hz, 2H, 6\(_a\)-H), 7.09 (d, \(J = 4.9\) Hz, 2H, 6\(_b\)-H), 1.99 (s, 12H, 4-H), 1.90 (s, 12H, 5-H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 161.5, 152.0, 149.7, 149.6, 146.5, 141.6, 139.3, 136.2, 132.6, 131.2, 127.5, 126.5, 125.4, 125.1, 125.0, 18.0\) (2x). Because of sterically hindered rotation C6 and C7 carbons exhibit two signals. ESI-MS: calcd. for [M+H]\(^+\): \(m/z\) 599.3, found: \(m/z\) 599.4; Anal. Calcd. for C\(_{42}\)H\(_{38}\)N\(_4\)•0.5H\(_2\)O: C, 83.00; H, 6.47; N, 9.22; found C, 83.05; H, 6.46; N, 9.17.

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Synthesis of Complexes

Complex 1 (solution state characterization): Ligand Phen1 (4.16 mg, 10.0 µmol) and [Cu(MeCN₄)]PF₆ (3.73 mg, 10.0 µmol) were dissolved in dichloromethane (0.50 mL) affording a slightly yellow solution. Then, 4,4’-bipyridine (BP, 1.56 mg, 10.0 µmol) was added resulting in an intensification of the yellow color. After removal of the solvents the solid residue was analyzed by FTICR-MS, ¹H NMR, ¹³C NMR, and elemental analysis without any further purification. The experimental evidence strongly supports the formation of structures [Cu(Phen1)(BP)]⁺ in solution.

mp: >300°C; IR (KBr): \( \tilde{\nu} = 3450, 2921, 1601, 1509, 1482, 1442, 1411, 1378, 1355, 1147, 1111, 840, 625, 558 \text{ cm}^{-1}; \) ¹H NMR (400 MHz, CD₂Cl₂): \( \delta = 8.72 (d, J = 8.3 \text{ Hz}, 2H, 2\text{-H}), 8.19 (s, 2H, 1\text{-H}), 7.92 (d, J = 8.3 \text{ Hz}, 2H, 3\text{-H}), 7.75 (d, J = 6.1 \text{ Hz}, 4H, a\text{-H}), 7.39 (d, J = 6.1 \text{ Hz}, 4H, b\text{-H}), 6.96 (s, 4H, 5\text{-H}), 2.32 (s, 6H, 6\text{-H}) \) 2.01 (s, 12H, 4\text{-H}); ¹³C NMR (100 MHz, CD₂Cl₂): \( \delta = 160.8, 151.0, 145.6, 144.0, 139.7, 139.5, 137.4, 136.2, 129.1, 128.4, 127.5, 127.2, 122.1, 21.2, 20.4; \) FTICR-MS: calcd. for [Cu(Phen1)(BP)]⁺: m/z 635.2, found: m/z 635.2, calcd. for [Cu₂(Phen1)₂(BP)(PF₆)]⁺: m/z 1261.4, found: m/z 1261.4; Anal. Calcd. for C₄₀H₃₆CuF₆N₄P•0.5MeCN ([Cu(Phen1)(BP)(PF₆)]•0.5MeCN): C, 61.42; H, 4.71; N, 7.86; found C, 61.09; H, 4.46; N, 7.82.
Complex 2 (solution and solid state characterization):

Complex 2 (solution and solid state characterization): Ligand Phen2 (3.88 mg, 10.0 µmol) and [Cu(MeCN)4]PF6 (3.73 mg, 10.0 µmol) were dissolved in a mixture of dichloromethane and acetonitrile (0.50 mL, 19:1) to afford a slightly yellow solution. After addition of 4,4’-bipyridine (BP, 1.56 mg, 10.0 µmol) the yellow color of the solution intensified. After removal of the solvents the solid residue was analyzed by FTICR-MS, 1H NMR, and 13C NMR without any further purification. Single crystals suitable for X-ray analysis suitable for measurement were obtained by slow evaporation of acetonitrile from a 1,2-dichlorobenzene / acetonitrile (4:1) solution of Phen2, BP and [Cu(MeCN)4]PF6 (1:1:1) suitable for X-ray analysis. For the solid state characterization, see the X-ray structural analysis.

mp: >300°C; IR (KBr): υ = 3070, 1602, 1584, 1498, 1412, 1354, 1216, 1124, 1033, 867, 838, 779, 751, 557 cm⁻¹; 1H NMR (400 MHz, CD2Cl2:CD3CN (19:1)): δ = 8.67 (d, J = 8.2 Hz, 2H, 2-H), 8.21 (dd, J = 6.3 Hz, 1.6 Hz, 4H, a-H), 8.15 (s, 2H, 1-H), 7.86 (d, J = 8.2 Hz, 2H, 1-H), 7.45 (dd, J = 6.3 Hz, 1.6 Hz, 4H, b-H), 7.25 (t, J = 7.8 Hz, 2H, 6-H), 7.08 (d, J = 7.8 Hz, 4H, 5-H), 1.92 (s, 12H, 4-H); 13C NMR (100 MHz, CD2Cl2:CD3CN (19:1)): δ = 159.8, 150.7, 145.5, 143.9, 140.0, 138.4, 136.0, 129.3, 128.3, 127.8, 127.1, 126.8, 121.8, 20.0; FTICR-MS: calcd. for [Cu(Phen2)(BP)]⁺: m/z 607.2, found: m/z 607.2, calcd. for [Cu2(Phen2)2(BP)(PF6)]⁺: m/z 1203.3, found: m/z 1203.3, calcd. for [Cu3(Phen2)3(BP)2(PF6)2]⁺: m/z 1958.4, found: m/z 1957.5; Anal. Calcd. for C38H32CuF6N4P•C8H4Cl2 ([Cu(Phen2)(BP)(PF6)]•1,2-dichlorobenzene): C, 58.71; H, 4.03; N, 6.22; found C, 58.38; H, 3.64; N, 6.30.
Complex 3c (solution state characterization): 2,9-Dimesitylphenanthroline (Phen1, 4.16 mg, 10.0 µmol) and [Cu(MeCN)4]PF6 (3.73 mg, 10.0 µmol) were dissolved in dichloromethane (0.50 mL) affording a yellowish solution. Then, 1,3,5-trimethyl-2,4,6-tris(4-pyridinylethynyl)benzene2 (TP, 2.82 mg, 6.66 µmol) was added whereupon the yellow color intensified. After removal of the solvent the solid residue was analyzed by FTICR-MS, 1H NMR, 13C NMR, DOSY and elemental analysis without any further purification.

mp: >300 °C; IR (KBr): ν = 2919, 2207, 1606, 1492, 1481, 1379, 1357, 1214, 1148, 1111, 870, 841, 558 cm^{-1}; 1H NMR (400 MHz, CD2Cl2): δ = 8.72 (d, J = 8.3 Hz, 12H, 2×H), 8.19 (s, 12H, 1×H), 7.93 (d, J = 8.3 Hz, 12H, 3×H), 7.65 (d, J = 6.3 Hz, 24H, a×H), 7.28 (d, J = 6.3 Hz, 24H, b×H), 6.97 (s, 24H, 5×H), 2.78 (s, 36H, c×H), 2.36 (s, 36H, 6×H) 2.01 (s, 72H, 4×H); 13C NMR (100 MHz, CD2Cl2): δ = 160.8, 150.0, 144.9, 144.0, 139.8, 139.5, 137.4, 136.1, 132.5, 129.1, 128.4, 127.5, 127.2, 126.2, 121.0, 95.0, 92.5, 21.2, 20.6/20.4; FTICR-MS: calcd. for [Cu(Phen1)(TP)]+: m/z 902.3, found: m/z 902.4, calcd. for [Cu3(Phen1)3(TP)2(PF6)]2+: m/z 1216.2, found: m/z 1215.9, calcd. for [Cu2(Phen1)2(TP)(PF6)]+: m/z 1528.7, found: m/z 1528.5, calcd. for [Cu4(Phen1)4(TP)4(PF6)2]2+: m/z 1740.4, found: m/z 1740.1, calcd. for [Cu4(Phen1)4(TP)4(PF6)2]2+: m/z 1952.2, found: m/z 1951.7, calcd. for [Cu6(Phen1)6(TP)6(PF6)3]2+: m/z 2053.0, found: m/z 2053.2, calcd. for [Cu5(Phen1)5(TP)5(PF6)3]2+: m/z 2264.7, found: m/z 2264.8, calcd. for [Cu6(Phen1)6(TP)6(PF6)3]2+: m/z 2577.2, found: m/z 2577.2; Anal. Calcd. for C300H252Cu3F60N24P6•2CH2Cl2 ([Cu6(Phen1)6(TP)6(PF6)6]•2CH2Cl2): C, 64.61; H, 4.60; N, 5.99; found C, 64.46; H, 4.24; N, 5.96.

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Complex 3n: Single crystals suitable for X-ray analysis suitable for measurement were obtained by slow evaporation of acetonitrile from a 1,2-dichlorobenzene / acetonitrile solution of Phen1, TP and [Cu(MeCN)₄]PF₆ (6:4:6) suitable for X-ray analysis. For the solid state characterization, see the X-ray structural analysis.

Complex 4 (solid state characterization):

2,9-Dimesityl-[1,10]-phenanthroline (Phen1, 3.88 mg, 10.0 µmol) and [Cu(MeCN)₄]PF₆ (5.59 mg, 15.0 µmol) were dissolved in a mixture of 1,2-dichlorobenzene and acetonitrile (10.0 mL, 9:1) to afford a slightly yellow solution. Then, meso-tetra(4-pyridyl)porphyrin (TPP, 3.09 mg, 5.00 µmol) was added, and the mixture was heated to reflux for 30 minutes. The solution was put aside, and after slow evaporation of acetonitrile, dark red crystals were obtained.

mp: >300 °C; IR (KBr): ν = 3438, 2916, 1601, 1543, 1481, 1456, 1415, 1378, 1349, 1325, 1304, 1208, 1137, 1125, 1084, 1061, 1032, 999, 893, 855, 798, 757, 716, 625, 494 cm⁻¹.
Complex 5 (solution and solid state characterization):

Ligand Phen3 (5.99 mg, 10.0 µmol) and [Cu(MeCN)4]PF6 (3.73 mg, 10.0 µmol) were dissolved in dichloromethane (0.50 mL) to afford a yellow solution. After removal of the solvent, the solid residue was analyzed by FTICR-MS, 1H NMR, 13C NMR, DOSY, and elemental analysis without any further purification. Crystals for X-ray structure analysis were obtained from diethylether diffusion into a solution of 5 in 1,2-dichlorobenzene.

mp: >300°C; IR (KBr): ν = 2964, 1607, 1585, 1504, 1416, 1385, 1356, 1262, 1098, 1019, 876, 843, 804, 577, 558 cm⁻¹; 1H NMR (400 MHz, acetone-d6): δ = 9.01 (d, J = 8.3 Hz, 12H, 2-H), 8.46 (s, 12H, 1-H), 8.36-8.39 (m, 12H, 7a-H), 8.18-8.20 (m, 12H, 7b-H), 8.01(dd, J = 8.3 Hz and 2.0 Hz, 12H, 3-H), 7.29-7.31 (m, 12H, 6a-H), 7.12-7.21 (m, 12H, 6b-H), 1.79 (s, 72H, 4-H) 1.61 (s, 72H, 5-H); 13C NMR (100 MHz, acetone-d6): δ = 161.1, 153.3, 153.1, 153.4, 149.9, 145.1, 141.9, 140.0, 139.2, 132.9, 131.4, 129.9, 128.3, 126.9, 126.6, 18.8, 18.7; ESI-MS: calcd. for [M-6(PF6)6]+: m/z 662.3, found: m/z 662.6, calcd. for [M-5(PF6)5]+: m/z 823.8, found: m/z 823.6, calcd. for [M-4(PF6)4]+: m/z 1066.0, found: m/z 1066.8, calcd. for [M-3(PF6)3]+: m/z 1469.6, found: m/z 1469.1; Anal. Calcd. for C252H228Cu6F36N24P6•6CH2Cl2•2CH3CN ([Cu6(Phen3)6(PF6)6]•6CH2Cl2•2CH3CN): C, 57.89; H, 4.56; N, 6.70; found C, 57.55; H, 4.62; N, 6.74.
Figure S1. Top view of X-ray structure of complex 2. Carbon: gray; Nitrogen: blue; Copper: green. Solvate molecules, anions and hydrogen were omitted for clarity.

Figure S2. Side view of X-ray structure of complex 2 (right-handed helix). Carbon: gray; Nitrogen: blue; Copper: green. Solvate molecules, anions and hydrogen were omitted for clarity.
**Figure S3.** Crystal packing of complex 2. Carbon: gray; Nitrogen: blue; Copper: green. Solvate molecules, anions and hydrogen were omitted for clarity.

**Figure S4.** Top view of HyperChem® structure of cage 3c. Carbon: cyan; Nitrogen: blue; Copper: green; Hydrogen: white.
**Figure S5.** X-ray structure of complex 4. Carbon: gray; Nitrogen: blue; Copper: green. Ligand Phen1, solvate molecules, anions and hydrogen were omitted for clarity.

**Figure S6.** X-ray structure of complex 4. Carbon: gray; Nitrogen: blue; Copper: green. Solvate molecules, anions and hydrogen were omitted for clarity.
**Figure S7.** $^1$H NMR spectrum of Phen3.

**Figure S8.** $^{13}$C NMR spectrum of Phen3.
Figure S9. FTICR-MS spectrum of complex 1.

Figure S10. $^1$H NMR spectrum of complex 1.
Figure S11. $^{13}$C NMR spectrum of complex 1.

Figure S12. FTICR-MS spectrum of complex 2.
Figure S13. $^1$H NMR spectrum of complex 2.

Figure S14. $^{13}$C NMR spectrum of complex 2.
Figure S15. FTICR-MS spectrum of complex 3c; X = PF$_6^-$.

Figure S16. $^1$H NMR spectrum of complex 3c.
Figure S17. $^{13}$C NMR spectrum of complex 3c.

Figure S18. $^{31}$P NMR spectrum of complex 3c.
Figure S19. $^{19}$F NMR spectrum of complex 3c.
Figure S20. DOSY spectrum of complex 3c.
**Figure S21.** ESI-MS spectrum of complex 5.

**Figure S22.** $^1$H NMR spectrum of complex 5.
**Figure 23.** $^{13}$C NMR spectrum of complex 5.

**Figure S24.** $^{31}$P NMR spectrum of complex 5.
Figure S25. $^{19}$F NMR spectrum of complex 5.
Figure S26. DOSY spectrum of complex 5.