Supplementary data to accompany:

**Monomer, dimer or cyclic helicate? Coordination diversity with hard-soft P,N-donor ligands?**

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Figure S1a. ESI MS of an MeOH solution of [Cu(1)][PF₆] showing m/z 748.2 assigned to [Cu(1)]⁺. The peak envelope at m/z 797.1 is assigned to [Cu(1)(MeOH)(OH)]⁺, oxidation occurring in the mass spectrometer.
Fig. 1b ESI MS of a solution of [Cu(1)]\([PF_6]\) in a 1:1 mixture of MeOH and CH\(_2\)Cl\(_2\); peak assignments: \(m/z\) 740.2 \([1 + 2O + Na]^+\), 756.2 \([1 + 2O + K]^+\), 748.2 \([Cu(1)]^+\), 770.1 \([Cu(1) – H + Na]^+\). The peak at \(m/z\) 792.1 is tentatively assigned to \([Cu(1) – 2H + 2Na]^+\).
Figure S2. ESI MS of an MeCN solution of [Cu(2)][PF₆]: m/z 747.2 corresponds to [Cu(2)]⁺ and m/z 763.1 to [Cu(2 + O)]⁺.
Figure S3   ESI MS of a MeOH solution of [Cu(3)][PF₆]: m/z 715.2 corresponds to [Cu(3)]⁺.

Crystallographic data for 2{[Cu₂(3)₂][PF₆]₂}C₅H₁₂·5H₂O

C₁₈₁H₁₅₈Cu₄F₂₄N₈O₉P₁₂, M = 3607.02, yellow block, monoclinic, space group P₂₁/c, a = 12.9676(14), b = 47.180(5), c = 18.0286(15) Å, β = 128.169(5)°, U = 8671.8(15) Å³, Z = 2, Dc = 1.378 Mg m⁻³, μ(Mo-Kα) = 0.677 mm⁻¹, T = 123 K. Total 70538 reflections, 19083 unique, Rint = 0.0600. Refinement of 12947 reflections (1119 parameters) with I > 2σ (I) converged at final R1 = 0.0831 (R1 all data = 0.1296), wR2 = 0.2258 (wR2 all data = 0.2623), gof = 1.160. CCDC 907594.
Fig. S4 The structure of the [Cu2(3)2]2+ cation in 2{[Cu2(3)2][PF6]2}·C5H12·5H2O (ellipsoids plotted at 40% probability level and H atoms omitted). Selected bond parameters: Cu1-N1A = 2.119(3), Cu1-N1B = 2.120(4), Cu1-P1A = 2.2441(9), Cu1-P1B = 2.2442(9), Cu2-N2A = 2.089(3), Cu2-N2B = 2.138(3), Cu2-P2B = 2.2332(9), Cu2-P2A = 2.2531(9) Å; N1A-Cu1-N1B = 140.15(12), N1A-Cu1-P1A = 83.36(8), N1B-Cu1-P1A = 114.38(9), N1A-Cu1-P1B = 115.00(8), N1B-Cu1-P1B = 83.28(8), P1A-Cu1-P1B = 127.51(4), N2A-Cu2-N2B = 140.74(12), N2A-Cu2-P2B = 119.53(9), N2B-Cu2-P2B = 81.96(8), N2A-Cu2-P2A = 83.69(8), N2B-Cu2-P2A = 110.29(8), P2B-Cu2-P2A = 127.07(4).