

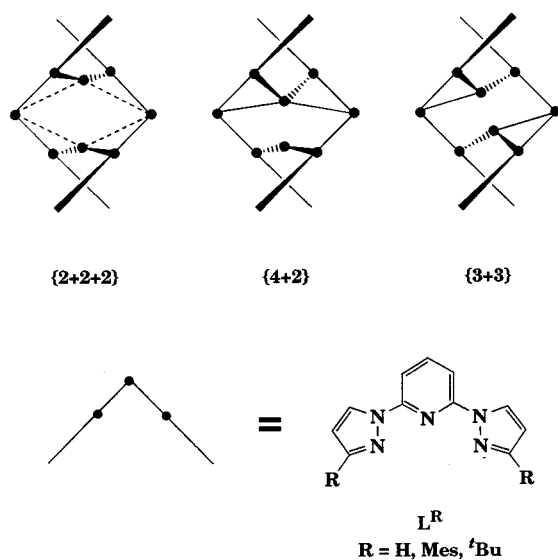
Structural variations in dicopper(I) double helicate complexes

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The helical dimers $[\{\text{Cu}(\mu\text{-L}^{\text{R}})\}_2]^{2+}$ exhibit three different solid state structures when $\text{R} = \text{H}$, Mes or ^tBu; the latter complex, which is a unique example of a {3+3} double helicate, retains this structure in solution.

The Cu(I) co-ordination chemistry of meridional tris(imine) ligands is characterised by the formation of dimeric double helical complexes.¹ Two such classes of $[\{\text{Cu}(\mu\text{-L})\}_2]^{2+}$ compounds have been well studied to date, where L is a terpyridine^{2,3} or 2,6-bis(imidazol-2-yl)pyridine^{4,5} derivative. The co-ordination geometry at Cu in these helicates has been described as 'variable',³ depending on whether the ligand central pyridine moieties are co-ordinated to one Cu ion in a {4+2} connectivity² or symmetrically semi-bridge both metal centres to form a {2+2+2} helix (Chart 1).^{3–5} We describe here a series of complexes $[\{\text{Cu}(\mu\text{-L}^{\text{R}})\}_2]^{2+}$ [$\text{R} = \text{H}$, Mes (mesityl), ^tBu], which between them exhibit all of the three possible molecular structures for a dinuclear double helicate containing a tridentate ligand (Chart 1); one of these is a very unusual example of a helical structure constructed about 3-co-ordinate metal centres.⁶



Complexation of $[\text{Cu}(\text{NCMe})_4]\text{X}$ ($\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$) with 1 molar equivalent of L^{R} ($\text{R} = \text{H}, \text{Mes}, {}^t\text{Bu}$)^{7,8} in MeOH under N_2 yields moderately air-sensitive yellow-orange solutions, from which yellow crystalline products analysing as $[\{\text{CuL}^{\text{R}}\}_n]\text{X}_n$ ($\text{R} = \text{H}$, 1X_n ; $\text{R} = \text{Mes}$, 2X_n ; $\text{R} = {}^t\text{Bu}$, 3X_n) can be isolated in moderate yields upon concentration and addition of Et_2O .[†] IR spectroscopy on these products demonstrated the presence of L^{R} and X^- only, while FAB mass spectrometry in all cases afforded highest molecular ions corresponding to $[\{\text{CuL}^{\text{R}}\}_2]^+$

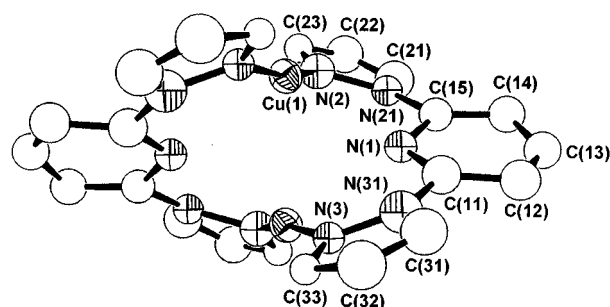


Fig. 1 View of the $[\{\text{Cu}(\mu\text{-H})\}_2]^{2+}$ dication in the crystal structure of $1[\text{PF}_6]_2$. For clarity, all H atoms have been omitted.

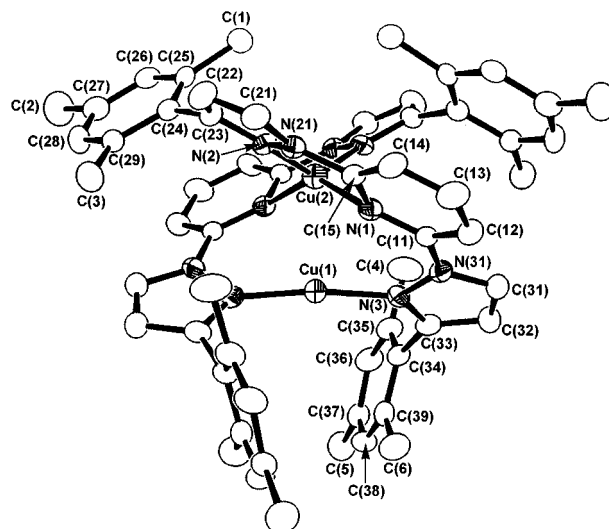


Fig. 2 View of the $[\{\text{Cu}(\mu\text{-L}^{\text{Mes}})\}_2]^{2+}$ dication in the crystal structure of $2[\text{BF}_4]_2 \cdot 2(\text{CH}_3)_2\text{CO}$. For clarity, all H atoms have been omitted. Selected bond distances (Å) and angles ($^\circ$): Cu(1)–N(3) 1.863(6), Cu(2)–N(1) 2.221(6), Cu(2)–N(2) 1.956(6); N(3)–Cu(1)–N(3') 172.1(4), N(1)–Cu(2)–N(1') 143.2(3), N(1)–Cu(2)–N(2) 79.7(2), N(1)–Cu(2)–N(2') 114.0(2), N(2)–Cu(2)–N(2') 137.6(3).

(1X_n , $m/z = 485$; 2X_n , $m/z = 1022$; 3X_n , $m/z = 773$). The resultant formulation of 1X_n – 3X_n as dimeric complexes (*i.e.* $n = 2$) was confirmed by the structure determinations described below.

Crystals of $1[\text{PF}_6]_2$ suffer from twinning; however, two partial X-ray analyses showed that this complex adopts the previously observed^{3,4} {2+2+2} helical structure (Chart 1, Fig. 1), containing two near-linear Cu(I) ions.[‡] Full X-ray structure analyses were achieved on crystals of $2[\text{BF}_4]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ and $3[\text{PF}_6]_2$.^{§¶} While the 2^{2+} dication exhibits a {4+2} helical structure (Chart 1, Fig. 2), 3^{2+} adopts a unique¹ {3+3} structure in the crystal (Chart 1, Fig. 3). The structure of 2^{2+} con-

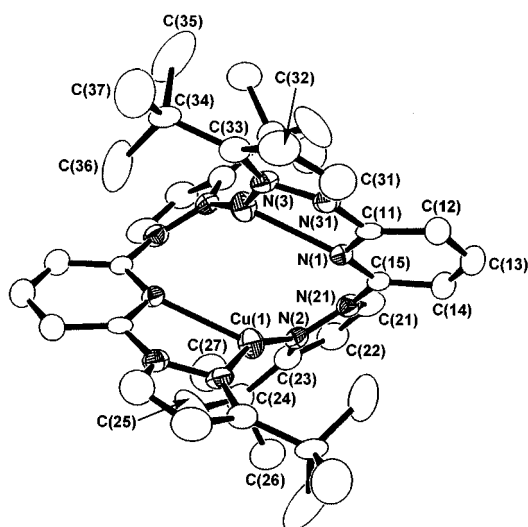


Fig. 3 View of the $[\{\text{Cu}(\mu\text{-L}^{\text{tBu}})\}_2]^{2+}$ dication in the crystal structure of $3[\text{PF}_6]_2$. For clarity, all H atoms have been omitted. Selected bond distances (Å) and angles ($^\circ$): Cu(1)–N(1) 2.293(4), Cu(1)–N(2) 1.929(6), Cu(1)–N(3') 1.902(6); N(1)–Cu(1)–N(2) 79.1(2), N(1)–Cu(1)–N(3') 119.8(2), N(2)–Cu(1)–N(3) 159.2(2).

tains distinct 2- and 4-co-ordinate Cu(I) centres. While Cu(1) is almost perfectly linear, the geometry at Cu(2) is severely flattened, the dihedral angle between the planes of the two ligands [Cu(2), N(1), N(2)] and [Cu(2), N(1'), N(2')] being $47.9(2)^\circ$ (*cf.* 90° for an 'ideal' tetrahedron⁹). The distance Cu(1)⋯Cu(2) = 2.584(2) Å, while Cu(1)⋯N(1) = 2.825(6) Å, which is too long to be considered semi-bridging. There is a weak intramolecular stacking interaction between the phenyl ring C(24)–C(29) and pyridyl group [N(1), C(11)–C(15)], which lie 3.5 Å apart. In 3^{2+} , the 3-co-ordinate geometry at Cu(1) is distorted by the bite of the L^{tBu} chelate; however, the Cu ions are essentially planar, the sum of N–Cu(1)–N angles being 358.1° . The Cu(1)⋯N(1') distance is 2.699(4) Å, while the Cu(1)⋯Cu(1') distance of 2.915(2) Å is the longest yet recorded for a complex of this type.^{2–4}

The ^1H NMR spectra of $1[\text{BF}_4]_2\text{-}3[\text{BF}_4]_2$ in $(\text{CD}_3)_2\text{CO}$ at 293 K show a plane of symmetry or C_2 axis bisecting the pyridyl moieties of the complexed ligands, which is inconsistent with the crystal structures of 2^{2+} and 3^{2+} and demonstrates the fluxional nature of the compounds in solution.^{2,5} In contrast to uncomplexed L^{Mes} , $2[\text{BF}_4]_2$ displays 3 distinct methyl resonances, reflecting hindered rotation of the mesityl substituents. Solvolysis of the Cu(I) ions in 2^{2+} does not therefore occur in this solvent. No decoalescence was observed for $2[\text{BF}_4]_2$ at $T \geq 173$ K. The spectrum of $3[\text{BF}_4]_2$ exhibits one peak for the L^{tBu} alkyl protons at δ 1.11 at 293 K, which decoalesces into 2 singlets of equal integral at δ 1.04 and 1.06 at $T_c = 198(2)$ K (400 MHz); partial decoalescence of the aromatic region of the spectrum was also observed near this temperature. Therefore, the $\mu\text{-}\kappa^1, \kappa^2$ -co-ordination mode for L^{tBu} observed in the solid state also occurs in solution. An activation barrier $\Delta G^\ddagger(T_c) = 43.5(5)$ kJ mol⁻¹ can be calculated for the migration of the pyridyl groups between the Cu ions in 3^{2+} .¹⁰

The differing connectivities shown by 1^{2+} – 3^{2+} in the solid state are reminiscent of the structural chemistry of $[\{\text{Cu}(\mu\text{-Tp}^{\text{R}})\}_2]$ ($\text{Tp}^{\text{R}} = \text{tris}[3\text{-substituted pyrazol-1-yl]borate}^{11}$), which exhibit non-helical dinuclear structures in the crystal with connectivities which vary as a function of R.¹² Many of these latter compounds undergo extensive dissociation in solution,¹² so that the structural differences between these complexes in the solid may arise predominantly from crystal packing considerations. The observation of identical molecular structures in different crystal forms of 2^{2+} and 3^{2+} ,[§] together with the NMR data for 3^{2+} , imply that the solution chemistry of these complexes is probably dominated by the species present in the crystal structures. Hence, the unusual connectivity exhibited by 3^{2+} in the crystal appears to be retained in solution, and is therefore a

genuine consequence of the steric properties of the tridentate ligand employed. Further investigations of the effects of steric bulk on the structural, spectroscopic and redox properties of L^{R} complexes of Cu(I) and other transition ions are in progress, and will be reported in due course.

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Notes and references

† Analytical data for the complexes. $1[\text{PF}_6]_2$: Found: C, 31.2; H, 2.2; N, 16.4. Calc. for $\text{C}_{22}\text{H}_{18}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2$: C, 31.5; H, 2.2; N, 16.7%. $2[\text{BF}_4]_2$: Found: C, 57.1; H, 4.8; N, 11.3. Calc. for $\text{C}_{58}\text{H}_{58}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}\cdot\text{H}_2\text{O}$: C, 57.4; H, 5.0; N, 11.5%. $3[\text{BF}_4]_2$: Found: C, 47.7; H, 5.2; N, 14.5. Calc. for $\text{C}_{38}\text{H}_{50}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}$: C, 48.2; H, 5.3; N, 14.8%. $3[\text{PF}_6]_2$: Found: C, 42.6; H, 4.7; N, 12.9. Calc. for $\text{C}_{38}\text{H}_{50}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2$: C, 43.0; H, 4.8; N, 13.2%.

‡ Crystal data for $[\{\text{Cu}(\text{L}^{\text{H}})\}_2][\text{PF}_6]_2$ $1[\text{PF}_6]_2$: $\text{C}_{22}\text{H}_{18}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2$, $M = 839.48$, orthorhombic, $Pbcn$, $a = 11.670(4)$, $b = 22.314(4)$, $c = 22.809(4)$ Å, $V = 5940(3)$ Å³, $Z = 8$, $T = 223(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.651$ mm⁻¹; Siemens P4 diffractometer, 3814 measured reflections, 2981 independent, $R_{\text{int}} = 0.109$; $R(F) = 0.150$, $wR(F^2) = 0.385$, $S = 0.982$. The asymmetric unit contains two half-molecules, each of which lies on a crystallographic C_2 axis. While molecule 1 is well-defined, molecule 2 is badly disordered across this symmetry axis, which is suggestive of a twinning problem. A full refinement was not therefore possible.

Crystal data for $[\{\text{Cu}(\text{L}^{\text{Mes}})\}_2][\text{BF}_4]_2\cdot 2(\text{CH}_3)_2\text{CO}$ $2[\text{BF}_4]_2\cdot 2(\text{CH}_3)_2\text{CO}$: $\text{C}_{64}\text{H}_{70}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}\text{O}_2$, $M = 1312.00$, monoclinic, $C2/c$, $a = 20.430(3)$, $b = 21.288(3)$, $c = 14.450(2)$ Å, $\beta = 92.371(12)^\circ$, $V = 6279(2)$ Å³, $Z = 4$, $T = 223(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.753$ mm⁻¹; Siemens P4 diffractometer, 3914 measured reflections, 3371 independent, $R_{\text{int}} = 0.044$; $R(F) = 0.061$, $wR(F^2) = 0.192$, $S = 0.970$. The two Cu ions lie on a crystallographic C_2 axis, which relates the two ligands in the molecule. Disorder in the BF_4^- anion was modelled using partially occupied F atoms, such that the total number of F atoms equalled 4. All wholly occupied non-H atoms were refined anisotropically.

Crystal data for $[\{\text{Cu}(\text{L}^{\text{tBu}})\}_2][\text{PF}_6]_2$ $3[\text{PF}_6]_2$: $\text{C}_{38}\text{H}_{50}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2$, $M = 1063.90$, monoclinic, $C2$, $a = 20.732(5)$, $b = 12.235(2)$, $c = 9.238(5)$ Å, $\beta = 92.35(2)^\circ$, $V = 2333(1)$ Å³, $Z = 2$, $T = 223(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.068$ mm⁻¹; Siemens P4 diffractometer, 2580 measured reflections, 2373 independent, $R_{\text{int}} = 0.041$; $R(F) = 0.050$, $wR(F^2) = 0.132$, $S = 1.055$, Flack parameter = 0.01(3). There is a crystallographic C_2 axis perpendicular to the Cu⋯Cu vector, so that the asymmetric unit contains half a molecule. Relatively high thermal parameters indicated some rotational disorder of the 'Bu groups; this could not be resolved, however. All non-H atoms were refined anisotropically. CCDC reference number 186/1299 (full crystallographic supplementary data for $2[\text{BF}_4]_2\cdot 2(\text{CH}_3)_2\text{CO}$ and $3[\text{PF}_6]_2$). See <http://www.rsc.org/suppdata/dt/1999/521> for crystallographic files in .cif format.

§ Lower quality refinements from poorly diffracting crystals of stoichiometry $2[\text{BF}_4]_2\cdot 2.5\text{CH}_3\text{OH}$ and $3[\text{BF}_4]_2$ were also obtained. The connectivity of the complex molecules in these crystals is identical to those in the equivalent full structure determinations.‡

Crystal data for $[\{\text{Cu}(\text{L}^{\text{Mes}})\}_2][\text{BF}_4]_2\cdot 2.5\text{CH}_3\text{OH}$ $2[\text{BF}_4]_2\cdot 2.5\text{CH}_3\text{OH}$: $\text{C}_{60.5}\text{H}_{68}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}\text{O}_{2.5}$, $M = 1275.97$, monoclinic, $P2_1$, $a = 21.978(1)$, $b = 12.394(1)$, $c = 22.908(1)$ Å, $\beta = 98.08(1)^\circ$, $V = 6178.1(6)$ Å³, $Z = 4$, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.763$ mm⁻¹; Rigaku R-AxisIIC diffractometer, 27645 measured reflections, 17136 independent, $R_{\text{int}} = 0.096$; $R(F) = 0.081$, $wR(F^2) = 0.205$, $S = 0.949$, Flack parameter = 0.04(2).

Crystal data for $[\{\text{Cu}(\text{L}^{\text{tBu}})\}_2][\text{BF}_4]_2$ $3[\text{BF}_4]_2$: $\text{C}_{38}\text{H}_{50}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}$, $M = 947.58$, monoclinic, $C2$, $a = 20.599(4)$, $b = 11.705(2)$, $c = 9.194(2)$ Å, $\beta = 97.27(3)^\circ$, $V = 2199.0(7)$ Å³, $Z = 2$, $T = 223(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.041$ mm⁻¹; Rigaku AFC7-R diffractometer, 3032 measured reflections, 2477 independent, $R_{\text{int}} = 0.124$; $R(F) = 0.091$, $wR(F^2) = 0.204$, $S = 1.032$, Flack parameter = $-0.01(7)$.

¶ Although $2[\text{BF}_4]_2\cdot 2.5\text{CH}_3\text{OH}$, $3[\text{BF}_4]_2$ and $3[\text{PF}_6]_2$ crystallise in chiral space groups, there is no evidence for resolution of the bulk samples of these compounds.

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