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Structural variations in dicopper(I) double helicate complexes

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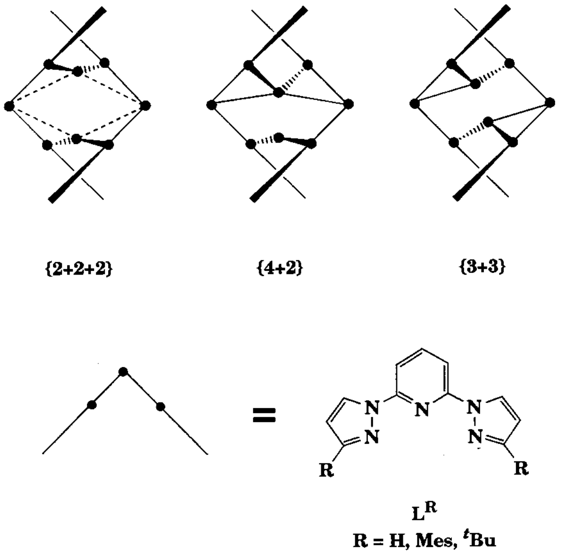
The helical dimers [{Cu(μ-L^R)}$_2$]$^{2+}$ exhibit three different solid state structures when R = H, Mes or ^{t}Bu; the latter complex, which is a unique example of a {3+3} double helicate, retains this structure in solution.

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 [{Cu(μ-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} connectivity[2] 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 [{Cu(μ-L^R)}$_2$]$^{2+}$ [R = H, Mes (mesityl), ^{t}Bu], 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 [Cu(NCMe)$_4$]X (X$^-$ = BF$_4^-$, PF$_6^-$) with 1 molar equivalent of L^R (R = H, Mes, ^{t}Bu)[7,8] in MeOH under N$_2$ yields moderately air-sensitive yellow-orange solutions, from which yellow crystalline products analysing as [{CuL^R}$_n$]X$_n$ (R = H, **1**X$_n$; R = Mes, **2**X$_n$; R = ^{t}Bu, **3**X$_n$) can be isolated in moderate yields upon concentration and addition of Et$_2$O.† 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 [{^{63}CuL^R}$_2$]$^+$ (**1**X$_n$, m/z = 485; **2**X$_n$, m/z = 1022; **3**X$_n$, m/z = 773). The resultant formulation of **1**X$_n$–**3**X$_n$ as dimeric complexes (*i.e.* n = 2) was confirmed by the structure determinations described below.

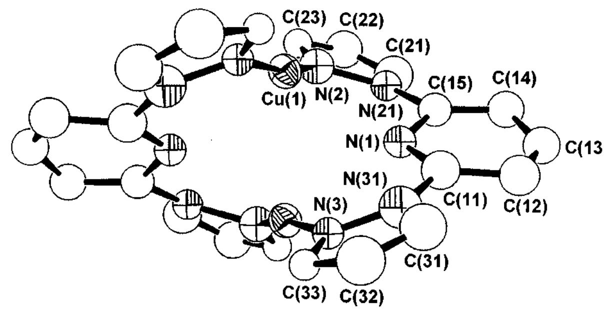


Fig. 1 View of the [{Cu(μ-L^H)}$_2$]$^{2+}$ dication in the crystal structure of **1**[PF$_6$]$_2$. For clarity, all H atoms have been omitted.

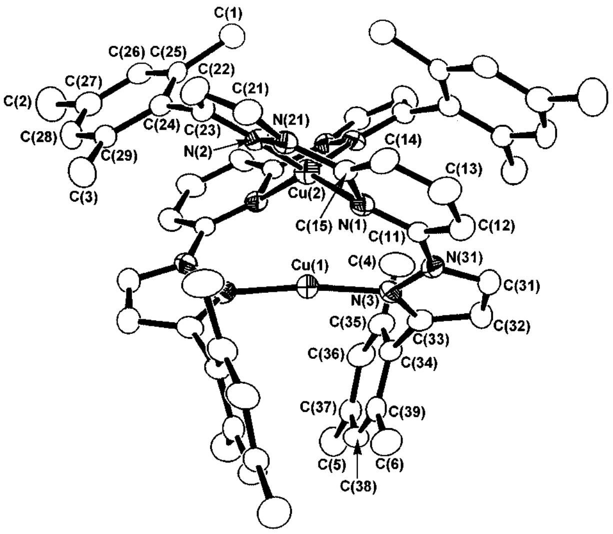


Fig. 2 View of the [{Cu(μ-L^{Mes})}$_2$]$^{2+}$ dication in the crystal structure of **2**[BF$_4$]$_2$·2(CH$_3$)$_2$CO. For clarity, all H atoms have been omitted. Selected bond distances (Å) and angles (°): Cu(1)–N(3) 1.863(6), Cu(2)–N(1) 2.221(6), Cu(2)–N(2) 1.956(6); N(3)–Cu(1)–N(3′) 172.1(4), N(1)–Cu(2)–N(1′) 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).

Crystals of **1**[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**[BF$_4$]$_2$·2(CH$_3$)$_2$CO and **3**[PF$_6$]$_2$.‡§¶ While the **2**$^{2+}$ dication exhibits a {4+2} helical structure (Chart 1, Fig. 2), **3**$^{2+}$ adopts a unique[1] {3+3} structure in the crystal (Chart 1, Fig. 3). The structure of **2**$^{2+}$ con-

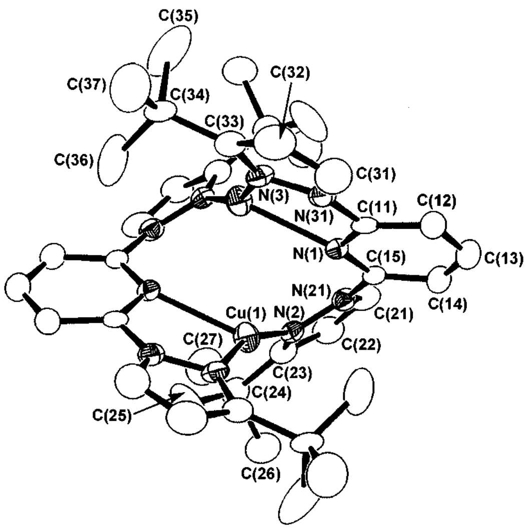


Fig. 3 View of the $[\{Cu(\mu\text{-}L^{t\mathrm{Bu}})\}_2]^{2+}$ dication in the crystal structure of **3[PF$_6$]$_2$**. For clarity, all H atoms have been omitted. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 2.293(4), Cu(1)–N(2) 1.929(6), Cu(1)–N(3′) 1.902(6); N(1)–Cu(1)–N(2) 79.1(2), N(1)–Cu(1)–N(3′) 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)° (*cf.* 90° for an ‘ideal’ tetrahedron[9]). 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 $L^{t\mathrm{Bu}}$ 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 ^{1}H NMR spectra of **1**[BF$_4$]$_2$–**3**[BF$_4$]$_2$ in $(CD_3)_2CO$ 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 $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ and demonstrates the fluxional nature of the compounds in solution.[2,5] In contrast to uncomplexed L^{Mes},[7] **2**[BF$_4$]$_2$ displays 3 distinct methyl resonances, reflecting hindered rotation of the mesityl substituents. Solvolysis of the Cu(I) ions in $\mathbf{2}^{2+}$ does not therefore occur in this solvent. No decoalescence was observed for **2**[BF$_4$]$_2$ at $T \geq 173$ K. The spectrum of **3**[BF$_4$]$_2$ exhibits one peak for the $L^{t\mathrm{Bu}}$ 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 μ-κ^1,κ^2-co-ordination mode for $L^{t\mathrm{Bu}}$ observed in the solid state also occurs in solution. An activation barrier $\Delta G^{\dagger}$ $(T_c) = 43.5(5)$ kJ mol^{-1} can be calculated for the migration of the pyridyl groups between the Cu ions in $\mathbf{3}^{2+}$.[10]

The differing connectivities shown by $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ in the solid state are reminiscent of the structural chemistry of $[\{Cu(\mu\text{-}Tp^R)\}_2]$ (Tp^R = tris[3-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 $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$,§ together with the NMR data for $\mathbf{3}^{2+}$, 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 $\mathbf{3}^{2+}$ 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**[PF$_6$]$_2$: Found: C, 31.2; H, 2.2; N, 16.4. Calc. for $C_{22}H_{18}Cu_2F_{12}N_{10}P_2$: C, 31.5; H, 2.2; N, 16.7%. **2**[BF$_4$]$_2$: Found: C, 57.1; H, 4.8; N, 11.3. Calc. for $C_{58}H_{58}B_2Cu_2F_8N_{10}\cdot H_2O$: C, 57.4; H, 5.0; N, 11.5%. **3**[BF$_4$]$_2$: Found: C, 47.7; H, 5.2; N, 14.5. Calc. for $C_{38}H_{50}B_2Cu_2F_8N_{10}$: C, 48.2; H, 5.3; N, 14.8%. **3**[PF$_6$]$_2$: Found: C, 42.6; H, 4.7; N, 12.9. Calc. for $C_{38}H_{50}Cu_2F_{12}N_{10}P_2$: C, 43.0; H, 4.8; N, 13.2%.

‡ Crystal data for $[\{Cu(L^H)\}_2][PF_6]_2$ **1**[PF$_6$]$_2$: $C_{22}H_{18}Cu_2F_{12}N_{10}P_2$, M = 839.48, orthorhombic, *Pbcn*, $a = 11.670(4)$, $b = 22.314(4)$, $c = 22.809(4)$ Å, $V = 5940(3)$ Å^3, $Z = 8$, $T = 223(2)$ K, μ(Mo-Kα) = 1.651 mm^{-1}; Siemens P4 diffractometer, 3814 measured reflections, 2981 independent, $R_{\mathrm{int}} = 0.109$; $R(F) = 0.150$, w$R(F^2) = 0.385$, $S = 0.982$. 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 $[\{Cu(L^{\mathrm{Mes}})\}_2][BF_4]_2\cdot 2(CH_3)_2CO$ **2**[BF$_4$]$_2$·2(CH$_3$)$_2$CO: $C_{64}H_{70}B_2Cu_2F_8N_{10}O_2$, $M = 1312.00$, monoclinic, *C*2/*c*, $a = 20.430(3)$, $b = 21.288(3)$, $c = 14.450(2)$ Å, $\beta = 92.371(12)°$, $V = 6279(2)$ Å^3, $Z = 4$, $T = 223(2)$ K, μ(Mo-Kα) = 0.753 mm^{-1}; Siemens P4 diffractometer, 3914 measured reflections, 3371 independent, $R_{\mathrm{int}} = 0.044$; $R(F) = 0.061$, w$R(F^2) = 0.192$, $S = 0.970$. 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 $[\{Cu(L^{t\mathrm{Bu}})\}_2][PF_6]_2$ **3**[PF$_6$]$_2$: $C_{38}H_{50}Cu_2F_{12}N_{10}P_2$, $M = 1063.90$, monoclinic, *C*2, $a = 20.732(5)$, $b = 12.235(2)$, $c = 9.238(5)$ Å, $\beta = 92.35(2)°$, $V = 2333(1)$ Å^3, $Z = 2$, $T = 223(2)$ K, μ(Mo-Kα) = 1.068 mm^{-1}; Siemens P4 diffractometer, 2580 measured reflections, 2373 independent, $R_{\mathrm{int}} = 0.041$; $R(F) = 0.050$, w$R(F^2) = 0.132$, 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 ^{t}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**[BF$_4$]$_2$·2(CH$_3$)$_2$CO and **3**[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**[BF$_4$]$_2$·2.5CH$_3$OH and **3**[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 $[\{Cu(L^{\mathrm{Mes}})\}_2][BF_4]_2\cdot 2.5CH_3OH$ **2**[BF$_4$]$_2$·2.5CH$_3$OH: $C_{60.5}H_{68}B_2Cu_2F_8N_{10}O_{2.5}$, $M = 1275.97$, monoclinic, $P2_1$, $a = 21.978(1)$, $b = 12.394(1)$, $c = 22.908(1)$ Å, $\beta = 98.08(1)°$, $V = 6178.1(6)$ Å^3, $Z = 4$, $T = 180(2)$ K, μ(Mo-Kα) = 0.763 mm^{-1}; Rigaku R-AXISIIc diffractometer, 27645 measured reflections, 17136 independent, $R_{\mathrm{int}} = 0.096$; $R(F) = 0.081$, w$R(F^2) = 0.205$, $S = 0.949$, Flack parameter = 0.04(2).

Crystal data for $[\{Cu(L^{t\mathrm{Bu}})\}_2][BF_4]_2$ **3**[BF$_4$]$_2$: $C_{38}H_{50}B_2Cu_2F_8N_{10}$, $M = 947.58$, monoclinic, *C*2, $a = 20.599(4)$, $b = 11.705(2)$, $c = 9.194(2)$ Å, $\beta = 97.27(3)°$, $V = 2199.0(7)$ Å^3, $Z = 2$, $T = 223(2)$ K, μ(Mo-Kα) = 1.041 mm^{-1}; Rigaku AFC7-R diffractometer, 3032 measured reflections, 2477 independent, $R_{\mathrm{int}} = 0.124$; $R(F) = 0.091$, w$R(F^2) = 0.204$, $S = 1.032$, Flack parameter = −0.01(7).

¶ Although **2**[BF$_4$]$_2$·2.5CH$_3$OH, **3**[BF$_4$]$_2$ and **3**[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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