Self-assembly of a helical dicopper(I) metallophane

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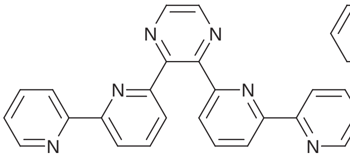
X-Ray crystallographic and ^{1}H NMR spectroscopic studies show that, in the presence of copper(I), an oligopyridyl pyrazine derivative spontaneously forms a single chiral, cyclophane-like dimeric complex and that this is the sole species present in solution and the solid state.

The self-assembly[1,2] of appropriate ligands and labile metal centers to result in double-stranded helicates[1a,c–e] and cyclophane-like structures[2] is well documented. Either linear[1c–e] or knotted [1a] shapes are typical for the former, and a distinguishing characteristic of the latter is frequently the coplanar orientation of aromatic spacer units. In some of these 'metallophanes', this results in a cavity, whilst in others, the non-bonding distances between the spacers are within those values considered to be crucial for π-stacking interactions[3] (*cf.* [2.2]paracyclophane[4]). In several of the latter cases, the spacer directly participates in metal binding.[2a,b]

While helicates are, by definition chiral,[5] this is not so for metallophanes. The majority of such complexes are achiral (*meso*)[2a–d,f] although studies describing a chiral, dizinc(II) metallophane which is stable in dilute solution have also recently appeared.[2e] Chiral metallophanes,whose formation is templated by the inclusion of an aromatic guest molecule, have also been recently described,[2d,e] as have equilibrating mixtures of similar chiral and *meso* complexes.[2d,g,6]

We are interested in the preparation[7] and supramolecular complexation chemistry[2a] of 2,3-bis(2,2′-oligopyridyl)pyrazines. We anticipate that the influences of internitrogen pyrazine base strength within the plane of that ring[8a] and stacking effects perpendicular to it[8b] should together determine the behaviour of this ligand class. Simpler pyrazine-containing ligand systems are known to form cyclic trimeric or tetrameric supramolecular complexes.[8a,9]

Along these lines, we have already shown that the symmetrical 2,3-bis(2,2′-bipyridyl)pyrazine **1** and Co^{II} self-assemble to give a dimetallic *meso*-metallophane in which two roughly orthogonal binding domains having different dendicity are generated to geometrically satisfy the metal coordination requirements.[2a] We wished to further test these premises on a 2,3-bis(2,2′-oligopyridyl)pyrazine derivative possessing oligopyridyl groups of explicitly unlike dendicity. The simplest such ligand is the previously unknown 2-(2,2′-bipyridyl)-3-(2-pyridyl)pyrazine **2**. Either tridentate/monodentate or bidentate/bidentate binding modes are conceivable for **2**, and thus we anticipated that it should bind cooperatively with tetrahedral Cu^I.



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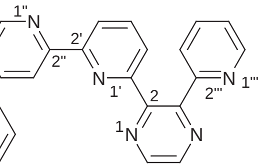

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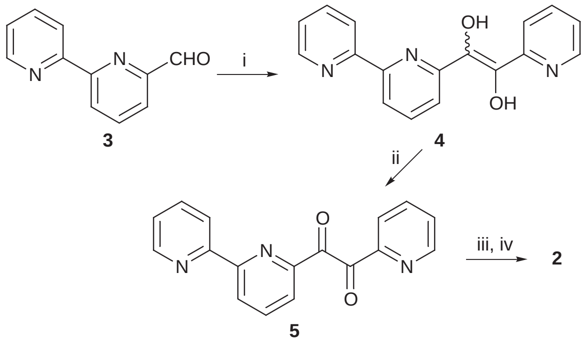
A crude, but reasonable synthesis of **2** is described in Scheme 1. Thus, condensation of 2,2′-bipyridine-6-carbaldehyde **3**[7] with an excess of pyridine-2-carbaldehyde in the presence of potassium cyanide afforded a mixture of the enediol **4** and 1,2-bis(2′-pyridyl)-1,2-dihydroxyethene. This mixture was directly oxidized with iodine to the corresponding α-diketones, from which the desired product **5** was purified in 14% overall yield. Condensation of **5** with 1,2-diaminoethane, then chloranil-oxidation, afforded **2** in 64% yield.‡

Treatment of **2** with 1 equiv. of [Cu(MeCN)$_4$][BF$_4$] in methanol under reflux and addition of an excess of [NH$_4$][BF$_4$] resulted in the precipitation of a dark red complex which could be recrystallized from nitromethane–diethyl ether. This substance analysed as $\{[\mathrm{Cu}\mathbf{2}][\mathrm{BF}_4]\}_n$‡ and in its FABMS spectrum (noba matrix) prominent signals centered at m/z = 750 and 837 were observed, corresponding to $[\mathrm{Cu}\mathbf{2}]_2^+$ and $[\mathrm{Cu}\mathbf{2}]_2[\mathrm{BF}_4]^+$, respectively, and thus we assume a dimeric structure $[\mathrm{Cu}\mathbf{2}]_2[\mathrm{BF}_4]_2$. In its electronic spectrum in acetonitrile, metal–ligand charge-transfer bands centered around 460 (1400) and 570 nm (700 dm^3 mol^{-1} cm^{-1}) were visible, and suggest an N$_4$-environment for Cu^I.[10] The cyclovoltammogram in MeCN indicated a single, reversible Cu^I–Cu^{II} redox process at −0.16 V *vs.* Fc–Fc$^+$. In analogy to literature precedent,[2b,10] we ascribe this to a dimetallic complex containing two identical non-interactive Cu^I centers.

We were, however uncertain of its exact structure, as both *meso*-Λ,Δ and Λ, Λ/Δ,Δ-configured diasteromeric pairs were reasonable structures. The ^{1}H NMR spectrum of $[\mathrm{Cu}\mathbf{2}]_2[\mathrm{BF}_4]_2$ (400 MHz, CD$_3$CN), recorded at 21 °C, displayed a single set of broad resonances, integrating to 13 protons [Fig. 1(*a*)]. This suggested either the ready interconversion of the three diasteromers, like in other dimeric oligopyridine complexes[2d,f,g,6,11] or some type of exchange process with the coordinating solvent, as has been observed for other dicopper(I) bis-N$_4$ systems[2g,10] were occurring. Upon cooling to −40 °C [Fig. 1(*b*)], these absorption sharpened to result in the profile of a single compound, while at 40 °C, a broadening of the same shifts is apparent. As well, the ^{13}C NMR spectrum of the complex, recorded at −40 °C, exhibited 13 C–H correlated resonances displaying NOE enhancement. At no temperature could a decoalescence of signals in the ^{1}H NMR spectra be observed, and the chemical shifts were essentially temperature independent. Since others have already demonstrated that low-temperature



Scheme 1 Preparation of ligand **2**. *Reagents and conditions:* i, 15 equiv. pyridine-2-carbaldehyde, KCN, EtOH–H$_2$O, reflux, 2 h; ii, 1 equiv. I$_2$, CH$_2$Cl$_2$, 25 °C, 15 h; iii, 1 equiv. 1,2-diaminoethane, EtOH, reflux, 2 h; iv, 1 equiv. chloranil, xylenes, reflux, 16 h.

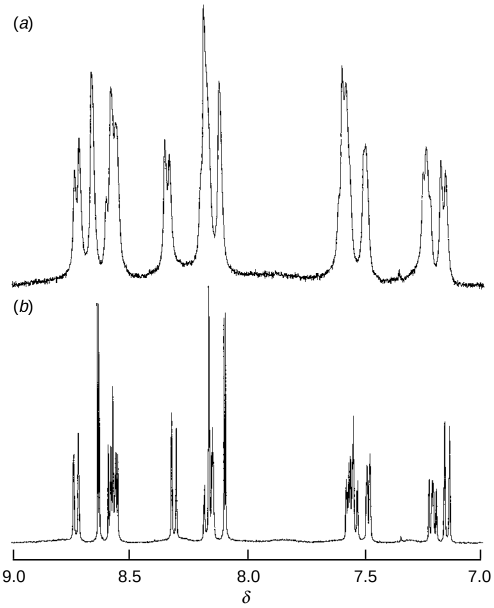


Fig. 1 ^{1}H NMR spectra of $[Cu\mathbf{2}]_2[BF_4]_2$ at (*a*) 21 and (*b*) −40 °C

^{1}H NMR spectroscopy can distinguish equilibrating mixtures of diastereomeric metallophanes[2g] it is evident that $[Cu\mathbf{2}]_2[BF_4]_2$ undergoes no such phenomenon.

In order to determine the stereochemistry of the dinuclear complex, its crystal structure was determined.§ Complex $[Cu\mathbf{2}]_2[BF_4]_2$ crystallizes in a centrosymmetric space group. Consequently, the dication occurs as a racemic mixture of Λ,Λ- and Δ,Δ-configured enantiomers, whereby the equivalent Cu**2** fragments are inter-related by the C_2 axis which runs parallel to the pyridyl pyrazine surfaces and between the bipyridyl flanks.¶ The *P*-helical enantiomer is displayed in Fig. 2. The pyridyl pyrazine copper(I) 'decks' of the metallophane are arranged in a head-to-head fashion. Interdeck non-bonding distances between closest pairs of atoms are 3.47–3.57 Å for the pyrazine rings and 3.42–3.62 Å for the monosubstituted pyridine rings; the pairs of pyrazine and pyridine rings are parallel to within 2.10 and 2.03°, respectively. The bipyridyl and pyridylpyrazine binding domains are twisted by 72.3° with respect to one another, giving the observed rectangular molecular geometry. The intermetallic distance is 5.08 Å. All metal–ligand bonding parameters are within expected values.

Ligand **2** diastereoselectively self-assembles to form a chiral metallophane, which is also stable in solution. That this phenomenon is influenced by stacking of metal-binding pyridyl pyrazine fragments is suggested by molecular models of the Λ,Λ/Δ,Δ-and *meso*-Λ,Δ-disastereomers, which indicate more efficient overlap for the former compound.

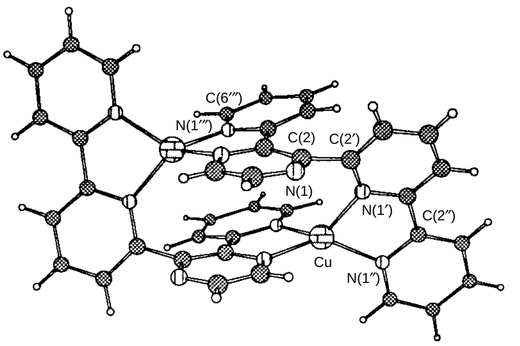


Fig. 2 Crystal structure of the $[Cu\mathbf{2}]_2$-dication. Selected bond angles (°) and lengths (Å): N(4)–Cu–N(1″) 138.46(7), N(1″)–Cu–N(1′) 82.17(7), N(1″)–Cu–N(1‴) 114.39, N(4)–Cu–N(1′) 120.80(7), N(4)–Cu–N(1‴) 80.91(7), N(1′)–Cu–N(1‴) 126.72(7); Cu–N(4) 1.991(2), Cu–N(1′) 2.033(2), Cu–N(1″) 2.005(2), Cu–N(1‴) 2.038(2).

We are currently investigating the extent which stacking interactions control self-assembly in related substances.

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Notes and References

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‡ Correct spectral and analytical data (C, H, N) were obtained for **2** and **5**. Spectral data for $[Cu\mathbf{2}]_2[BF_4]_2$: ^{1}H NMR (400 MHz, CD_3CN, −40 °C), δ 8.72 (dd, *J* 1.0, 8.2 Hz, 1 H, H-3′/5′), 8.63 (d, *J* 2.7 Hz, 1 H, H-5/6), 8.57 (t, *J* 7.8 Hz, 1 H, H-4′), 8.56 (d, *J* 8.2 Hz, 1 H, H-3″), 8.31 (dd, *J* 0.7, 7.6 Hz, 1 H,H-5′/3′), 8.14–8.19 (m, 2 H, H-4″, H-5″/6″), 8.09 (d, *J* 2.4 Hz, 1 H, H-6/5), 7.53–7.58 (m, 3 H, H-6″/5″, H-4‴,), 7.48 (dt, *J* 1.2, 4.8 Hz, 1 H, H-6‴), 7.21 (ddd, *J* 1.0, 5.3, 8.2 Hz, 1 H, H-5‴), 7.15 (d, *J* 8.2 Hz, 1 H, H-3‴); ^{13}C NMR (100 MHz, CD_3CN −40 °C), δ 149.35 (2C), 146.46, 141.96 (2C), 139.63, 137.79, 129.29, 127.68 (2C), 125.74, 124.18, 123.42. Anal. Calc. for $C_{38}H_{26}B_2Cu_2F_8N_{10}$: C, 48.8; H, 2.97; N, 15.3. Found: C, 49.4; H, 2.84; N, 15.2%.

§ *Crystallographic data* for $[Cu\mathbf{2}]_2[BF_4]_2$, $C_{38}H_{26}B_2Cu_2F_8N_{10}$, M_r = 923.39, dark red blocks, 0,43 × 0.28 × 0.25 mm, monoclinic, space group *C*2/*c*, a = 13.271(2), b = 11.368(2), c = 24.200(4) Å, β = 95.72(2)°, U = 3632.7(10) Å^3, Z = 4, D_c = 1.688 Mg m^{-3}, μ = 1.259 mm^{-1}, $F(000)$ = 1856, graphite monochromated radiation with λ(Mo-Kα) = 0.710 73 Å, T = 100(2) K, 17 678 reflections measured ($1.69 < \theta < 30.00°$) of which 5262 were independent (R_{int} = 0.0241), collected on a Siemens SMART diffractometer with CCD detector taking frames at 0.3° in ω. Data corrected for Lorentz and polarization effects, absorption correction using SADABS[11] (min., max. transmission factors: 0,572, 0.832) and structure solution and refinement on F^2 using Siemens ShelXTL-V5. All non-hydrogen atoms refined anisotropically, hydrogen atoms placed at calculated positions and refined isotropically. R_1 = 0.0426, wR_2 = 0.1041, goodness-of-fit: 1.049 for 4353 reflections with $I > 2\sigma(I)$ and 271 parameters. Residual positive, negative electron density: +1.34, −0.49 Å^{-3}. CCDC 182/883.

¶ The hypothetical *meso*-dicopper(I) metallophane is characterized by a 'head-to-tail' orientation of the pyridylpyrazine decks and an inversion axis (S_2) in roughly the same location as for the chiral form.

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