Self-assembly of a helical dicopper(I) metallophane

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X-Ray crystallographic and ¹H NMR spectroscopic studies show that, in the presence of copper(1), 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^{1*a,c-e*} and cyclophane-like structures² is well documented. Either linear^{1*c-e*} or knotted ^{1*a*} 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 interactions³ (*cf.* [2.2]paracyclophane⁴). In several of the latter cases, the spacer directly participates in metal binding.^{2*a,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 preparation⁷ 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.

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 $\{[Cu2][BF_4]\}_n$ ‡ and in its FABMS spectrum (noba matrix) prominent signals centered at m/z = 750 and 837 were observed, corresponding to $[Cu2]_2^+$ and $[Cu2]_2[BF_4]^+$, respectively, and thus we assume a dimeric structure $[Cu2]_2^ [BF_4]_2$. In its electronic spectrum in acetonitrile, metal–ligand charge-transfer bands centered around 460 (1400) and 570 nm (700 dm³ mol⁻¹ cm⁻¹) were visible, and suggest an N₄-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 noninteractive Cu^I centers.

We were, however uncertain of its exact structure, as both *meso*- Λ , Δ and Λ , Λ/Δ , Δ -configured diasterometric pairs were reasonable structures. The ¹H NMR spectrum of [Cu2]₂[BF₄]₂ (400 MHz, CD₃CN), 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-N₄ 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 ¹³C 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 ¹H 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–H₂O, reflux, 2 h; ii, 1 equiv. I₂, CH₂Cl₂, 25 °C, 15 h; iii, 1 equiv. 1,2-diaminoethane, EtOH, reflux, 2 h; iv, 1 equiv. chloranil, xylenes, reflux, 16 h.

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Fig. 1 ¹H NMR spectra of $[Cu2]_2[BF_4]_2$ at (a) 21 and (b) -40 °C

¹H NMR spectroscopy can distinguish equilibrating mixtures of diastereomeric metallophanes^{2g} it is evident that $[Cu2]_2[BF_4]_2$ undergoes no such phenomenon.

In order to determine the stereochemistry of the dinuclear complex, its crystal structure was determined.§ Complex $[Cu2]_2[BF_4]_2$ 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 Cu2 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 $\Lambda,\Lambda/\Delta,\Delta$ -and *meso*- Λ,Δ -disastereomers, which indicate more efficient overlap for the former compound.

(1)

Fig. 2 Crystal structure of the [Cu2]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 $[Cu2]_2[BF_4]_2$: ¹H NMR (400 MHz, CD₃CN, -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''), 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'''); ¹³C NMR (100 MHz, CD₃CN -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 C₃₈H₂₆B₂Cu₂F₈N₁₀: C, 48.8; H, 2.97; N, 15.3. Found: C, 49.4; H, 2.84; N, 15.2%.

§ Crystallographic data for $[Cu2]_2[BF_4]_2$, $C_{38}H_{26}B_2Cu_2F_8N_{10}$, $M_r =$ 923.39, dark red blocks, $0.43 \times 0.28 \times 0.25$ mm, monoclinic, space group C2/c, a = 13.271(2), b = 11.368(2), c = 24.200(4) Å, $\beta = 95.72(2)^{\circ}$, U = 10.200(4) Å 3632.7(10) Å³, Z = 4, D_c = 1.688 Mg m⁻³, μ = 1.259 mm⁻¹, F(000) = 1856, graphite monochromated radiation with λ (Mo-K α) = 0.71073 Å, T = 100(2) K, 17 678 reflections measured (1.69 < θ < 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 SA-DABS11 (min., max. transmission factors: 0,572, 0.832) and structure solution and refinement on F2 using Siemens ShelXTL-V5. All nonhydrogen 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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