Solid state characterization of oligopyridine dicarboxamide helicates

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A heptameric amide of 2,6-diaminopyridine and 2,6-pyridinedicarboxylic acid coordinates to Cu(II) to assemble into a double helical complex with a string of six shortly spaced Cu ions.

Controlling the conformation of large molecular structures and triggering structural changes of large amplitude—molecular motions—are keys to the development of mechanical molecular devices.[1] Toward this end, aromatic oligoamides derived from 2,6-diaminopyridine and 2,6-pyridinedicarboxylic acid (AOA's) may represent a highly versatile tool. AOA's fold into stable single helical conformations in a variety of solvents.[2] A remarkable feature of these helices is their ability to entwine and to form double helical dimers.[3] The double helices are stabilized by direct interactions between the two strands, in contrast with helicates which consist of molecular strands held in a helical arrangement through metal ion coordination.[4] The conformation of AOA's can be tuned upon selective protonation of the diaminopyridine units and the pyridinedicarbonyl units, leading to the unfolding of the helix into a linear strand and its refolding into a different helix.[5] Here, we report our initial studies of the conformational changes induced in AOA's upon metal coordination.

The ability of 2,6-bis(carbonylamino)pyridine to chelate transition metal ions (e.g. Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}) has been reported before.[6] It involves a 180° rotation about each pyridine–amide linkage, similar to what occurs upon protonation,[5,7] that allows each amide carbonyl to be involved in the chelation (Fig. 1b). On the other hand, 2,6-pyridinedicarboxamides are excellent tridentate ligands for transition metals (e.g. Cu^{2+}, Ni^{2+}) after deprotonation of the amide nitrogens.[8] In this case, complexation does not induce a conformational change of the ligand (Fig. 1c). We wondered how the coordination modes of 2,6-bis(carbonylamino)pyridine and of 2,6-pyridinedicarboxamide would combine when these units are arranged alternately within an oligomer, and explored the complexation of Cu(II) by trimeric 1 and heptameric 2.

Thus, 1 was deprotonated with 2 equiv. of NaH in DMF, and 1 equiv. of $Cu(OAc)_2$ was added. The solution immediately turned dark green. It was then diluted with DMSO/acetonitrile (1 : 1 vol/vol) and layered with Et_2O for liquid–liquid diffusion in a crystallization tube, which produced large dark green prisms. X-ray diffraction analysis of the crystals showed that a neutral, C_2 symmetrical, head to tail heterotopic double helical dimer $(1\cdot Cu)_2$ had formed (Fig. 2).† Only two pyridine rings per strand are involved in metal coordination. The two central amide groups of each strand have been selectively deprotonated and coordinate to Cu^{2+} in the conformation expected from previous studies (Fig. 1c).[8] The two peripheral amide groups remain protonated. The metal has a pseudo-square planar geometry. It sits in the middle of a square comprising the three coordinating nitrogens of a pyridinedicarboxamide unit from one strand (Cu–N_{pyr} = 1.92 Å; Cu–N_{amide} = 2.04, 2.08 Å), and the endocyclic nitrogen of a diaminopyridine unit of the other strand (Cu–N_{pyr} = 1.99 Å). These two pyridine rings are almost perpendicular, which allows the oxygen of the acetyl moiety to provide axial coordination as well (Cu–O = 2.29 Å). Another oxygen from a benzyloxy group is also found in an axial position. But it is as far as 7.79 Å from the metal and does not participate in the coordination. The torsion angle at some pyridine–amide nitrogen linkages is, as expected from other complexes,[6] close to 180° from its position in the free ligand (Fig. 1b). However, when the amide nitrogen is itself involved in the coordination, the torsion angle at the pyridine–amide nitrogen linkages is then close to 90°. The Cu–Cu distance (3.74 Å) is shorter than in most helicate or grid complexes described up to now.[4,9] The double stranded helicate is essentially stabilized through metal-mediated interstrand contacts. Additional stabilization is brought about by two interstrand hydrogen bonds (N–O = 2.83 Å) between terminal acetamide protons and amide carbonyl oxygens (Fig. 2).

In order to see whether the double helical motif of $(1\cdot Cu)_2$ can be extended over a longer sequence, a similar complexation experiment was performed with heptameric strand 2.‡ Using 4 equiv. of NaH, and 2 equiv. of $Cu(OAc)_2$, dark green prisms grew, along
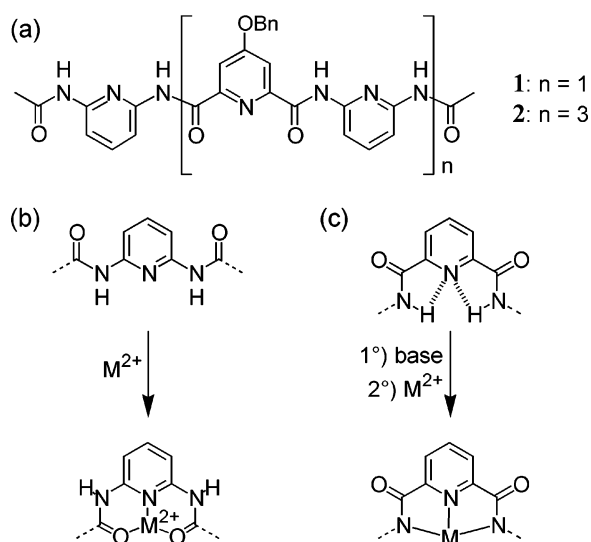

Fig. 1 (a) Structure of oligomeric strands 1 and 2; (b) and (c) expected transition metal coordination modes of 2,6-bis(carbonylamino)pyridines and 2,6-pyridinedicarboxamides, respectively.
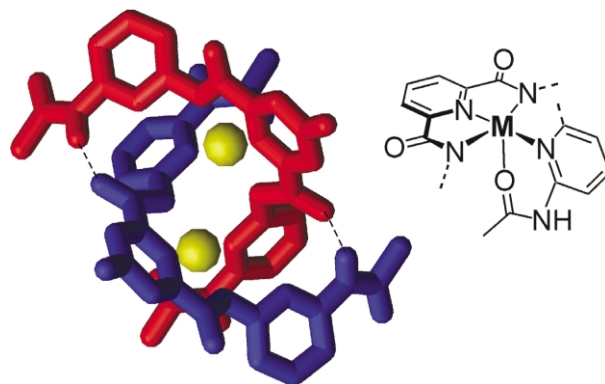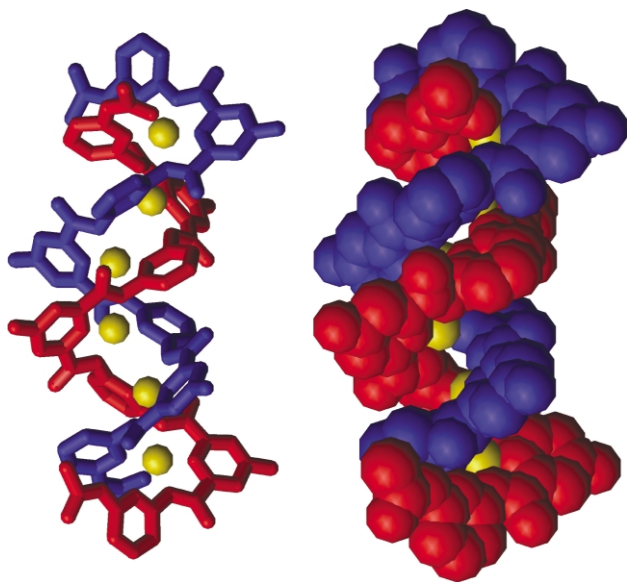

Fig. 2 Structure of the complex $(1\cdot Cu)_2$ in the crystal and schematic representation of the organization of the ligand around each metal. Included solvent molecules, benzyl groups, and hydrogens except amide hydrogens have been omitted for clarity.

with colourless crystals of the free ligand **2**. X-ray diffraction analysis of the green crystals again showed a neutral, C_2 symmetrical, head to tail heterotopic double helical structure (Fig. 3).† Its composition, $(2 \cdot Cu_3)_2$, differs from the initial stoichiometry of ligand, base, and metal. Indeed, six amide groups of each ligand have been deprotonated (all but the two terminal acetamides) to coordinate three Cu(II) ions. It is unlikely that the deprotonation step with NaH occurs selectively. Therefore, the difference between the initial stoichiometry and the composition of the complex, and the subsequent excess of free ligand suggest that the crystallized double helix is thermodynamically stabilised.

The structure of $(2 \cdot Cu_3)_2$ strongly relates to that of $(1 \cdot Cu)_2$. Six of the seven pyridine rings of each strand are involved in the coordination and a similar complex would probably form from a strand shorter by one unit. Nevertheless, as for $(1 \cdot Cu)_2$, the pyridine rings not involved in metal coordination participate in the duplex stabilization through hydrogen bonds between the terminal acetamide proton and carbonyl groups of the other strand. The complex comprises six metal ions which, to the best of our knowledge, is the highest number reported up to now for a helicate.[4] The Cu–Cu distances are even shorter than in $(1 \cdot Cu)_2$: 3.61, 3.58 and 3.59 Å from peripheral to central positions, respectively. The string of metals describes a single helix around the axis of the helicate. The crystallographic C_2 axis is perpendicular to the helical axis. The two strands are not axially in register, which defines a large groove and a narrow groove in the duplex. One helical turn is spanned by approximately four pyridine units, which is slightly lower than the 4.5 units per turn found in the helical structure of the free ligand.‡ The double helical pitch is 13.1 Å, to be compared with 3.45 Å in the free ligand and 6.9 Å in its double helix.[2,3] Thus, metal coordination in **2** causes a large spring-like extension of the helix.

All six metals in the duplex have a pseudo-square planar geometry. The two peripheral Cu have the same coordination sphere as the metals in $(1 \cdot Cu)_2$: a square of four nitrogens, three of them from a planar tridentate chelate of a pyridine dicarboxamide and one from the endocyclic nitrogen of a diaminopyridine unit of the other strand, as well as a more remote amide oxygen in an axial position. The four central Cu have a similar environment but apparently completely lack axial coordination (Cu–X distances < 2.8 Å).

Fig. 3 Stick and CPK representations of the structure of the complex $(2 \cdot Cu_3)_2$ in the crystal. Included solvent molecules, benzyl groups, and hydrogens have been omitted for clarity.

The structures of $(1 \cdot Cu)_2$ and $(2 \cdot Cu_3)_2$ demonstrate that the geometrical requirements of the coordination of pyridine dicarboxamides (Fig. 1c) dominate over those of bis(carbonylamino)pyridines (Fig. 1b) when these two units are combined in the same molecular strands. The carbonyl oxygens of bis(carbonylamino)pyridines are weaker Lewis bases than the nitrogens of tridentate pyridine dicarboxamides. The oxygens come into play only when the geometry of the complex allows it, as for the terminal units of the helicates.

AOA's significantly longer than **2** have already been prepared,[2,5] and open the way to long helicates comprising an even larger number of metals. Solution studies on these new helicates using, for example, coordination of diamagnetic Ni(II) will be undertaken to assess their stability in solution. Another interesting aspect is the potential magnetic coupling of the shortly spaced Cu(II) centres in the complexes.[9]

Notes and references

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