Mixed ligand helicates and mesocates

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A 1 : 1 mixture of the homoleptic double helicates [$M^{II}(L^1)_2$] and [$M^{II}(L^2)_2$] [M = Cu, Zn; $(L^1)^{2-}$ and $(L^2)^{2-}$ are bis-bidentate ligands containing two pyrazolyl-phenolate termini but with different spacers separating them] affords the mixed ligand complexes [$M(L^1)(L^2)$] in high yield, indicative of a favourable inter-ligand interaction in the mixed-ligand complexes. Whereas [$Cu(L^1)(L^2)$] is a double helicate, [$Zn(L^1)(L^2)$] is a mesocate with a 'face to face' arrangement of the two ligands.

Helicate complexes have become relatively common in the field of coordination chemistry and arise when a long, flexible bridging ligand is partitioned into distinct binding domains in a way such that two (or three) ligand strands can wrap around a spine of central metal ions whose stereoelectronic preference for a particular geometry matches the binding pockets provided by the ligand array. They have been of interest for the study of the metal–ligand assembly and recognition processes which lead to their formation as much as for their appealing architecture which has obvious biological echoes.[1] Related achiral assemblies in which the two ligands are 'side by side' rather than twisted around one another have been termed 'meso-helicates' or 'mesocates'.[2]

In all but a very few cases helicate complexes are homoleptic with all ligands being the same. Notable exceptions arise for a few quite distinct reasons. Lehn and co-workers showed that Cu(II) ions reacted with a mixture of ligands based on bipyridyl or terpyridyl binding sites to give the heteroleptic complex in which each Cu(II) is in a five-coordinate bipy + terpy environment, because of the unusual preference of Cu(II) for this coordination number (compared to the alternative geometries of tetrahedral and octahedral).[3] Rice and co-workers likewise showed how a mixed-ligand helicate could be favoured or disfavoured compared to the mixture of homoleptic helicates according to the stereoelectronic preferences of the metal ion concerned.[4] In both of these cases, therefore, the recognition of different ligands for one another in the assembly is driven by the metal ions, rather than by a favourable ligand–ligand interaction which is absent in the homoleptic complexes. Both Constable and co-workers[5] and Cohen and co-workers[6] detected mixed-ligand double helicates in solution which arose from redistribution reactions between the ligands of two different homoleptic helical complexes. The converse of this behaviour is shown in helicates where ligand–ligand self-recognition occurs, such that heteroleptic assemblies are actively disfavoured.[7]

We describe here unusual examples of mixed-ligand helicate/mesocate complexes based on bridging ligands H_2L^1 and H_2L^2 which both have bidentate N,O-donor pyrazolylphenol termini. These ligands both form conventional 2 : 2 double helicates with Co(II), Cu(II) and Zn(II) in which the metal ions are four coordinate.[8] A 1 : 1 mixture of H_2L^1 and H_2L^2 in dichloromethane, with a stoichiometric amount of triethylamine present to deprotonate the phenol donors, was treated with an appropriate metal salt [$Co(BF_4)_2 \cdot 6H_2O$, $Cu(OAc)_2.H_2O$ or $Zn(BF_4)_2 \cdot H_2O$] in methanol. The resulting mixture was stirred for 4 h, and the product filtered off and analysed by mass spectrometry to determine the distribution of the three possible products.

For Co(II) and Cu(II) the FAB mass spectrum of the product mixture showed a predominance of the mixed ligand system [$M_2(L^1)(L^2)$] (M = Co, Cu). For the Cu(II) system we observed

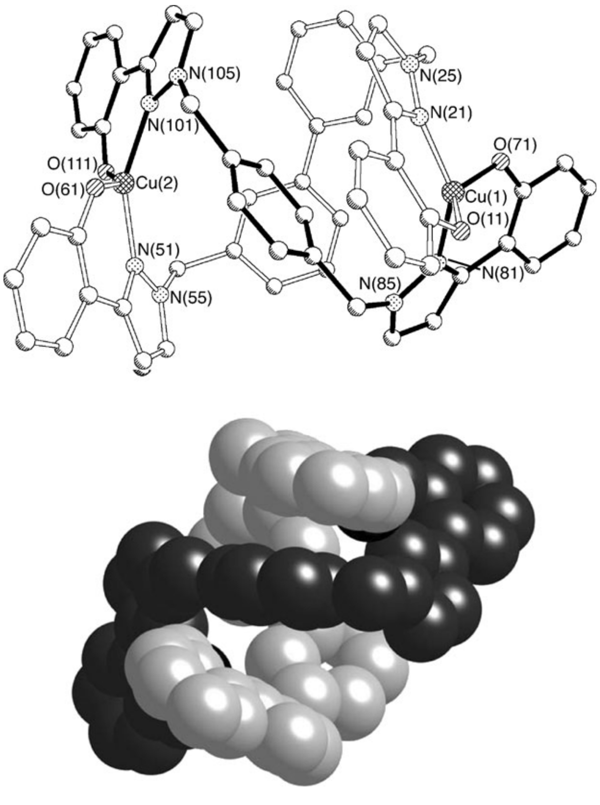

Fig. 1 (a) Molecular structure of [$Cu_2(L^1)(L^2)$]; (b) a space-filling picture (L^1 is coloured dark and L^2 is light).

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a 1 : 5 : 1 ratio of signal intensities at *m*/*z* 968, 1044 and 1120, corresponding to the species $[Cu_2(L^1)_2]$, $[Cu_2(L^1)(L^2)]$ and $[Cu_2(L^2)_2]$, respectively. A similar distribution was obtained with electrospray mass spectra; the good agreement between the product distributions shown by FAB and electrospray mass suggests that both techniques provide a reliable picture of the product distribution. With Zn(II) the preference for the mixed ligand complex was even higher with very little of the two homoleptic complexes formed (ratio ≈ 1 : 10 : 1 of the three species in the mass spectra, at *m*/*z* 972, 1047, 1123). In order to determine the speed with which the system comes to equilibrium an equal amount of $[Cu_2(L^1)_2]$ and $[Cu_2(L^2)_2]$ were mixed together in dichloromethane, and the solution was examined by FAB mass spectrometry. Formation of the mixed ligand complex $[Cu_2(L^1)(L^2)]$ was observed in the time it took to take a sample and record the mass spectrum, which was similar in appearance to that obtained from direct mixing of the ligands with $Cu(OAc)_2 \cdot H_2O$, *i.e.* the system had reached equilibrium in about 2 min or less. No further change in the mass spectrum was observed over two days.

The predominance of the mixed ligand complexes $[M_2(L^1)(L^2)]$ suggested that crystallisation may be possible. Crystals of $[Cu_2(L^1)(L^2)]$ were obtained from diisopropyl ether diffusion into a dichloromethane solution of the mixture of complexes; the structure is in Fig. 1 and reveals a double helicate.† The average Cu–O bond length of 1.88 Å and the average Cu–N bond length of 1.97 Å are similar to those observed for the homoleptic complexes characterised earlier.[8] The Cu(II) centres are in irregular four-coordinate environments with angles of 51.9 and 41.2° between the two coordinating units (as defined by the two CuNO planes at each metal). Angles of 0° and 90° would be expected for planar and tetrahedral geometries, respectively. The Cu···Cu distance of 7.72 Å is significantly shorter than in $[Cu_2(L^2)_2]$ (10.7 Å) and slightly longer than in $[Cu_2(L^1)_2]$ (7.2 Å). The biphenyl unit is not coplanar, with a twist angle of 42° between the two phenyl rings. The biphenyl-spaced ligand $(L^2)^{2-}$ twists around the two copper(II) ions such that a cavity is formed between the two pyrazolylphenolate termini, which are approximately coplanar, and the phenyl spacer of $(L^1)^{2-}$ sits inside this cavity and is sandwiched between, and undergoing π–π stacking with, both phenyl-pyrazole units of $(L^2)^{2-}$. Significantly, no such stacking was observed in the structures of either $[Cu_2(L^1)_2]$ or $[Cu_2(L^2)_2]$. Fig. 1(b) shows a space-filling view which illustrates the complementarity between the two ligands in this structure, and we suggest that this favourable ligand–ligand stacking interaction, which is present in neither of the homoleptic Cu(II) complexes, favours formation of the mixed-ligand complex.

Crystals of $[Zn_2(L^1)(L^2)] \cdot 4MeOH$ were obtained by slow evaporation of the solution arising from reaction of $Zn(BF_4)_2 \cdot H_2O$ with a mixture of H_2L^1 and H_2L^2.† X-ray crystallography (Fig. 2) showed the structure to be an achiral mesocate with a 'face to face' arrangement of the two ligands, in contrast to the helical structures observed for $[Cu_2(L^1)(L^2)]$ and for both the Cu(II) and Zn(II) complexes of L^1 and L^2. The average Zn–O bond length of 1.90 Å and the average Zn–N bond length of 1.99 Å are similar to those observed for the homoleptic helicate complexes.[8] The Zn(II) centres are in distorted four-coordinate geometries with angles of of 57.1 and 69.6° between the two ZnNO planes at Zn(1) and Zn(2). While this distortion from ideal tetrahedral geometry is less

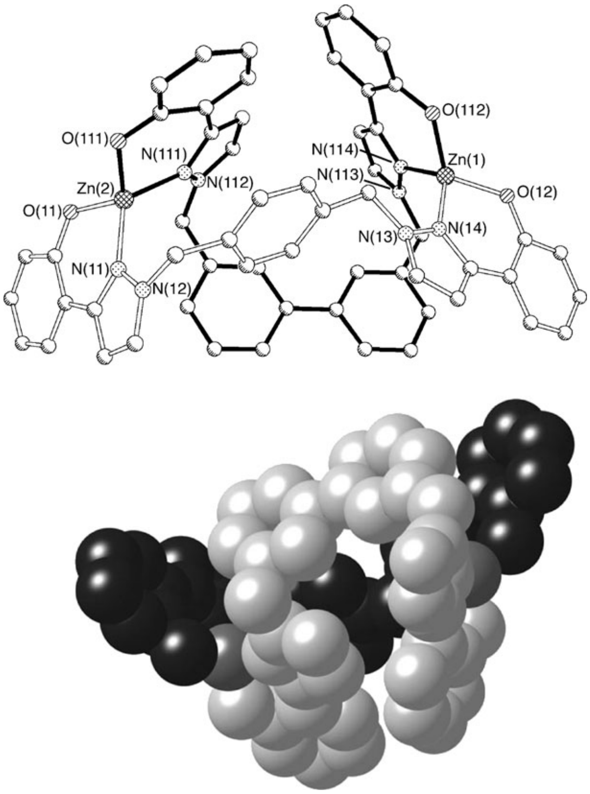

Fig. 2 (a) Molecular structure of $[Zn^2(L^1)(L^2)] \cdot 4MeOH$, with solvent molecules omitted; (b) a space-filling picture (L^1 is coloured dark and L^2 is light).

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† Crystal data for $[Cu_2(L^1)(L^2)]$: $C_{58}H_{44}Cu_2N_8O_4$, $M_r = 1044.09$, orthorhombic, space group *Pcba*, $a = 11.4252(7)$ Å, $b = 25.7105(16)$ Å, $c = 31.2552(19)$ Å, $V = 9181.1(10)$ Å^3, $Z = 8$, $\rho_{calc} = 1.511$ Mg m^{-3}, $F(000) = 4304$. A total of 47835 reflections was measured at $T = 100$ K in the range $5.6° \leq 2\theta \leq 100.2°$ giving 4713 unique reflections ($R_{int} = 0.3191$). The structure was solved by Patterson methods (SHELXS) and refined against all F^2 data to w$R2 = 0.0844$ (all data), $R1 = 0.0471$ [selected data with $I > 2\sigma(I)$]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Data were measured on a Bruker PROTEUM CCD area-detector diffractometer with Cu Kα radiation ($\lambda = 1.54187$ Å). Crystal data for $[Zn_2(L^1)(L^2)] \cdot 4MeOH$: $C_{62}H_{60}Zn_2N_8O_8$, $M_r = 1175.92$, orthorhombic, space group *Pbca*, $a = 14.0294(14)$ Å, $b = 28.052(3)$ Å, $c = 28.125(3)$ Å, $V = 11068.8(19)$ Å^3, $Z = 8$, $\rho_{calc} = 1.411$ Mg m^{-3}, $F(000) = 4896$. A total of 70930 reflections was measured at $T = 150$ K in the range $2.90° \leq 2\theta \leq 48.0°$, giving 8680 unique reflections ($R_{int} = 0.1822$). The structure was solved by Patterson methods (SHELXS) and refined against all F^2 data to w$R2 = 0.233$ (all data), $R1 = 0.0721$ [selected data with $I > 2\sigma(I)$]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except for a disordered methanol molecule which was refined isotropically. Restraints were applied to the disordered methanol molecule to ensure stable refinement. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Data were measured on a Bruker-SMART diffractometer with Mo Kα radiation, $\lambda = 0.710\ 73$ Å). CCDC reference numbers 289194 and 289195. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515154f

than that of the copper(II) complex, it is significantly greater than that of the homoleptic complexes $[Zn_2(L^1)_2]$ and $[Zn_2(L^2)_2]$. The Zn···Zn distance of 9.05 Å is significantly shorter than in $[Zn_2(L^2)_2]$ (10.53 Å) but similar to $[Zn_2(L^1)_2]$ (9.05 Å). In contrast to $[Cu_2(L^1)(L^2)]$, the biphenyl spacer of $(L^2)^{2-}$ is almost coplanar with a twist angle of 5°. Aromatic π–π stacking between the ligands is again observed, in two places: the central phenyl group of L^1 stacks with a pyrazolylphenolate group of L^2, and one of the phenyl rings from the biphenyl spacer of L2 [C(127)–C(132)] is stacked with one of the pyrazolyl groups of L1 [N(13), N(14), C(28)–C(30)]. In this case however stacking between the central phenyl or biphenyl units of the ligands in the homoleptic complexes $[Zn_2(L^1)_2]$ and $[Zn_2(L^2)_2]$ was also in evidence in the crystal structures.

The reason for the preference for the mixed-ligand complex with both Cu(II) and Zn(II) is not clear, especially in view of the fact that the structures are quite different. For the equilibrium in eqn (1), a 1 : 2 : 1 distribution of $[M_2(L^1)_2]$, $[M_2(L^1)(L^2)]$ and $[M_2(L^2)_2]$ is only expected when two conditions are met: (i) the two homoleptic complexes $[M_2(L^1)_2]$ and $[M_2(L^2)_2]$ have the same energy, and (ii) there is no favourable cooperative interaction between the two ligands in the mixed-ligand complex that is absent for the two homoleptic complexes. The homoleptic complexes $[M_2(L^1)_2]$ and $[M_2(L^2)_2]$ may be different in energy to start with, because of *e.g.* different metal–metal separations leading to different electrostatic contributions to the overall energy; different metal coordination geometries leading to different extents of ligand-field stabilisation energy (an issue for Cu^{2+}, but not of course for Zn^{2+}); or differing inter-ligand stacking interactions. If this is the case than there is no reason to expect a 1 : 2 : 1 product distribution, but one of the homoleptic complexes will be more abundant than the other. If there is some feature of the mixed-ligand complex which favours it over either of the homoleptic complexes, then it will dominate the equilibrium, as we see here.

$$[M_2(L^1)_2] + [M_2(L^2)_2] \rightleftharpoons [M_2(L^1)(L^2)] \qquad (1)$$

$[Cu_2(L^1)(L^2)]$ clearly shows inter-ligand aromatic stacking interactions which are absent for the homoleptic complexes, and this may be a significant factor. For the Zn(II) complexes all three complexes (two homoleptic, one heteroleptic) show evidence of some inter-ligand stacking, and the factors favouring its formation are less obvious; it is interesting however that this complex is a mesocate whereas the two homoleptic complexes are helicates. The central phenyl ring of L^1 is involved in face-to-face stacking with one of the pyrazolylphenol units of L^2, and two of the H atoms of this phenyl ring are directed towards the π-electron cloud of ring C(111)–C(116) (from L^2) in an 'edge-to-face' arrangement. Solution ^{1}H NMR studies to examine these interactions in more detail are unfortunately precluded by the poor solubility of the complexes. However the product distributions in both cases indicate that the heteroleptic complexes are significantly stabilized compared to the homoleptic ones to an extent which allows them to be isolated by simple crystallization. The observation of these product distributions in solution by ESMS indicates that stabilization of the heteroleptic complexes is related to some favourable feature of the individual complex molecules, and not to *e.g.* 'crystal packing effects'.

Polynuclear complexes based on labile metal ions, in which a mixture of ligands is selected, remain very rare compared to the huge numbers of homoleptic complexes of varying architectures, principally for the simple reason that mixtures of ligands have scarcely been investigated in self-assembly processes.[3–5,9] Mixed-ligand complexes can however form easily in favourable circumstances and offer access to a new range of self-assembled structures.

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