Self-assembly of supramolecular boxes

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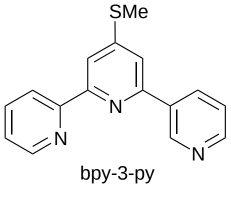
Supramolecular boxes are prepared from a dinucleating ligand and redox-active metal centres incorporated into the cavity framework without the need for ancillary ligands to block coordination sites on the metal; crystal structures of copper(I) and cadmium(II) cage structures of 4-thiomethyl-6-(3-pyridyl)-2,2′-bipyridine are reported.

There is much interest in the use of the supramolecular synthetic approach to assemble large molecular aggregates.[1] The metallosupramolecular approach has enjoyed particular success and nanoscale arrays containing up to 15 components have been assembled.[2] Following the elegant work of Fujita *et al.*[3] and others[4] we were drawn to the assembly of supramolecular species containing cavities as they represent readily prepared analogues of organic macrocycles. As described by Fujita *et al.*, a square-shaped cyclophane analogue results from mixing the pre-prepared complex [Pd(en)(NO_3)$_2$] with the bis-monodentate ligand 4,4′-bipyridine.[3] In this reaction the ethylenediamine ligand acts as a blocking ligand sealing up two coordination sites on the palladium centre. In the absence of blocking ligands polymeric arrays result.[8]

We reasoned that, with judicious design, it should be possible to assemble boxes from ligands incorporating chelating units. The incorporation of chelating units into the framework is desirable as it should (*a*) remove the need for ancillary blocking ligands and (*b*) permit the incorporation of a more varied selection of metal ions into the cage arrays. Using our design, cage structures might be assembled in a single self-assembly process involving simple mixing of metals and ligands rather than the stepwise approach, involving pre-preparation of the blocked metal complex, inherent in the previous work.[3,4] Such a design requires the preparation of ligands which contain two coordination sites, linked in such a fashion that they cannot both coordinate to the same metal ion. Moreover the position of the link must lead logically to the formation of a defined closed structure when metal ions coordinate to the ligand, and the closed structure that results must contain an aryl-linked cavity. The coordination sites used might be either two polydentate sites or one polydentate and one monodentate site. We have chosen to initiate our studies with the latter and wish to report our preliminary results in this area.

Following our design, we have prepared the substituted terpyridine ligand 4-thiomethyl-6-(3″-pyridyl)-2,2′-bipyridine (bpy-3-py). This ligand is constrained by its connectivity to act as a dinucleating ligand, presenting a didentate binding site to one metal ion and a monodentate to the other. The ligand was prepared in good yield (64%) in a one-pot Potts[5] reaction of 3,3-bis(methylthio)-1-(2′-pyridinyl)prop-2-en-1-one with the potassium enolate of 3-acetylpyridine, followed by ring closure with ammonium acetate.



bpy-3-py

Warming methanolic or acetonitrilic solutions of the ligand with 1 equiv. of copper(i) salts [Cu(MeCN)$_4$]X (X = PF_6, BF_4) leads to the rapid formation of red solutions from which red–brown salts of formula [Cu_2(bpy-3-py)$_2$(MeCN)$_2$]X_2 are isolated on cooling. Mass spectrometric analysis (FAB) shows the presence of dinuclear M_2L_2 and M_2L_2X peaks consistent with this formulation. Cyclic voltammetric analysis of acetonitrilic solutions of the complexes shows a single reversible oxidation at +0.13 V (*vs.* Fc–Fc$^+$) consistent with copper(i) in an N_4 coordination environment.[6] More importantly this implies that there are not two different types of copper(i) centre present in the molecule. The absorption spectra of acetonitrilic solutions of the complexes show charge-transfer bands centred at 537 (ε = 1300) and 426 nm (2300 M^{-1} cm^{-1}), which are also consistent with an N_4 coordination set containing polypyridyl units.[6] The ^{1}H NMR spectra of CD_3CN solutions of the salts show the expected number of resonances in the aromatic region and the presence of a single thiomethyl resonance. The spectra are slightly broadened at room temperature, most probably as a result of 'ring-wobbling' processes similar to those that we have previously observed[6,7] in other oligopyridine assemblies.

Recrystallisation of the hexafluorophosphate salt from acetonitrile solution by the slow diffusion of diethyl ether afforded deep red crystals, the structure of which has been determined† and which is shown in Fig. 1. As anticipated the bpy-3-py ligand bridges between two metal centres. Each copper(i) centre is bound to a bipyridyl unit from one ligand and a pyridyl from the other, resulting in the formation of a dimeric M_2L_2 species. The pseudo-tetrahedral coordination sphere of the metal centre is completed by an acetonitrile solvent molecule. The metal–ligand bond lengths and angles are unremarkable and the intermetallic Cu···Cu distance is 5.178(1) Å. The pyridyl and bipyridyl binding domains are twisted with respect to each other [dihedral angle 50.26(13)°] and a cavity between the pyridyl units of the two ligands results. This twisting is anticipated; indeed we have previously used it to generate double-helical complexes.[6] In this case the twisting results in the aromatic rings defining the desired aryl-lined cavity.

The cage structure furnishes each metal ion with only three donor atoms (one from the pyridyl unit of one ligand and two from the bipyridyl of the ligand). The box structure is

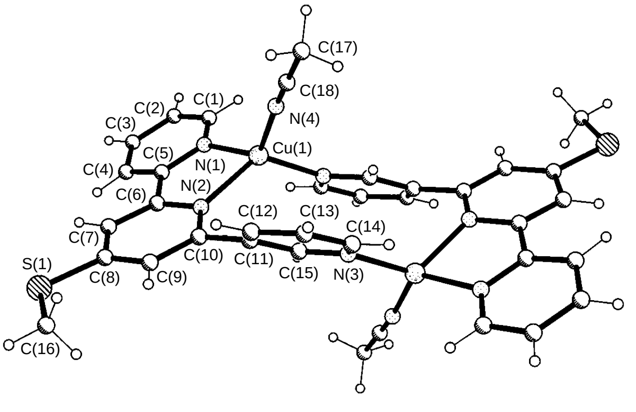


Fig. 1 Crystal and molecular structure of the cation [Cu_2(bpy-3-py)$_2$(MeCN)$_2$]$^{2+}$

nevertheless formed with the tetrahedral copper(I) ion. We have therefore investigated whether the structure might also be supported by metal ions with a higher coordination number requirement.

Reaction of a methanolic solution of the ligand with cadmium(II) acetate gives a pale green solution from which beautiful green blocks crystallise on the addition of methanolic ammonium hexafluorophosphate. On isolation the crystals rapidly lose solvent to give an apple-green solid. An X-ray crystallographic study has been undertaken on the crystalline material† and the structure is shown in Fig. 2. Once again a dimeric M_2L_2 cage structure is formed with the ligand bridging between the two metal centres and each cadmium(II) ion bound to a pyridyl group from one ligand and a bipyridyl unit from the other ligand. The twisting about the aryl–aryl bonds between the pyridyl and bipyridyl units [dihedral angle 55.40(13)°] again results in the desired aryl-lined cavity. In contrast to the pseudo-tetrahedral copper(I) cations the cadmium(II) dications occupy a pseudo-octahedral environment. The remaining coordination sites are completed by a didentate acetate ligand and a methanol solvent molecule. The two cadmium centres are separated by 5.6788(8) Å.

The structure may be contrasted with the polymeric species obtained from mixing cadmium(II) salts with 4,4′-bipyridine.[8] While the reaction of $[Pd(en)(NO_3)_2]$ with 4,4′-bipyridine gives rise to a molecular square, the reaction of the cadmium(II) metal salt, which does not contain a blocking ethylenediamine ligand, gives rise to a polymeric array of squares. As anticipated, the introduction of the chelating unit within our system does lead to the formation of the box structure, rather than a polymeric array.

We have thus established a novel ligand which allows us to form metallosupramolecular cage species with a variety of metal ions without the need for ancillary ligands which deliberately block coordination sites. We are also applying the principles learnt in this study to the development of polymeric arrays (‘crystal engineering’) and will address our studies in that area in a subsequent paper.

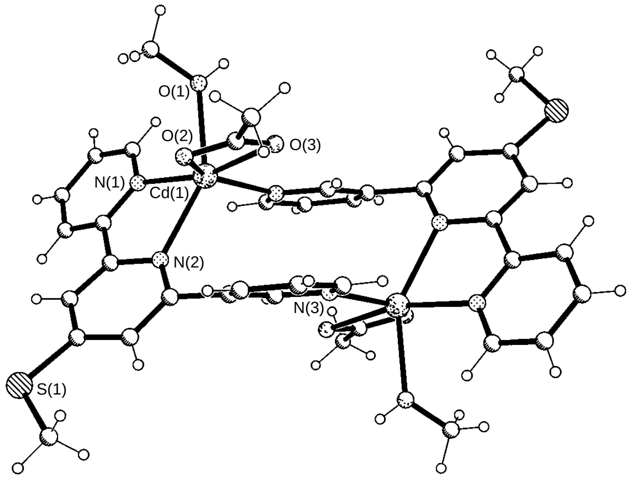


Fig. 2 Crystal and molecular structure of the cation $[Cd_2(bpy\text{-}3\text{-}py)_2(O_2CMe)_2(MeOH)_2]^{2+}$

We are grateful to the Royal Society for a grant enabling the purchase of an electrochemical workstation (M. J. H.), the EPSRC for a studentship (C. L. P.) and the EPSRC and Siemens for grants enabling the purchase of the diffractometer.

Footnote

† *Crystal data*: $[Cu_2(bpy\text{-}3\text{-}py)_2(MeCN)_2][PF_6]_2\cdot 2MeCN$; $C_{40}H_{38}Cu_2F_{12}N_{10}P_2S_2$, $M = 1139.94$, monoclinic, space group $P2_1/n$, $a = 7.4991(4)$, $b = 20.3814(4)$, $c = 15.6175(3)$ Å, $\beta = 101.837(3)°$, $U = 2336.25(14)$ Å^3, 200 K; final $R1$, $wR2$ and S are 0.046, 0.118 and 1.13 for 310 parameters.

$[Cd_2(bpy\text{-}3\text{-}py)_2(MeOH)_2(O_2CMe)_2][PF_6]_2\cdot 2MeOH$; $C_{40}H_{48}Cd_2F_{12}N_6O_8P_2S_2$, $M = 1319.70$, triclinic, space group $P\bar{1}$, $a = 7.99110(10)$, $b = 12.9262(3)$, $c = 13.5037(4)$ Å, $\alpha = 107.7130(10)$, $\beta = 95.8010(10)$, $\gamma = 107.1700(10)°$, $U = 1241.28(5)$ Å^3, 180 K; final $R1$, $wR2$ and S are 0.049, 0.110 and 0.968 for 358 parameters.

Data were collected using a Siemens SMART CCD area-detector diffractometer. Refinement was by full-matrix least squares on F^2 for all data using SHELXL-96.[9] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/342.

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