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A rigid cavity containing tetra-cobalt(III) [2 × 2] grid complex

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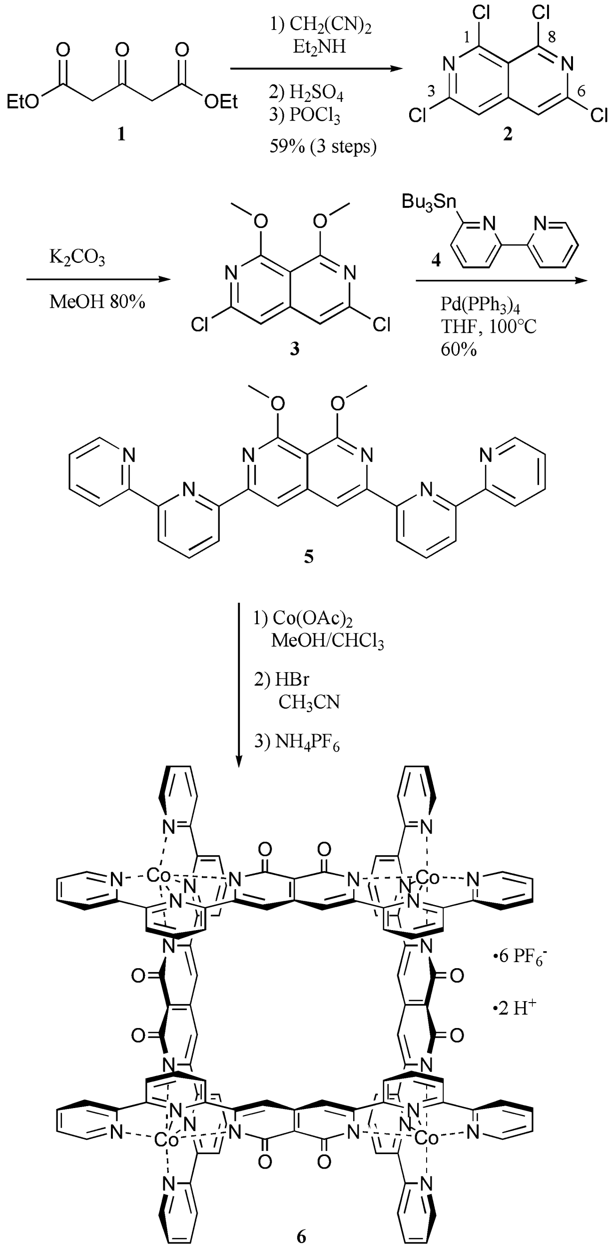
The synthesis and structure of a rigid, cavity containing tetra-cobalt(III) [2 × 2] grid complex using an unusual bis(bipyridine)dimethoxynaphthyridine ligand is described.

Modern methods in self assembly have been very useful in the construction of supramolecular structures based on hydrogen bonding, hydrophobic interactions and metal ion coordination.[1] These structures have potential utility in various aspects of nanoscience. We, in particular, have been interested in designing receptors for biologically relevant compounds. In this regard, metal coordination based self-assembly of receptors is very attractive as hydrogen bonding is disfavored under biological (*i.e.* aqueous) conditions and coordination complexes are often water soluble. Indeed, self-assembled cavity and cleft containing compounds have found utility as receptors.[2] As part of a program geared toward the preparation of molecular capsules, we have been interested in preparing tube shaped cavities using a novel class of expanded calixarenes based on a naphthalene core.[3] Such molecular tubes with sufficiently large dimensions may provide pores for shape selective ion and molecule recognition or transport. As a complement to the calixarene approach, an appropriately sized [2 × 2] grid complex appeared to be attractive for construction of such structures. The formation of several recent coordination based receptors are templated by the guest and indeed often collapse around the guest distorting the metal coordination geometry.[4] For many receptor applications, a stable, rigid complex is often deemed desirable. Lehn's bis-terpyridine [2 × 2] grid complexes are both rigid and substitutionally inert, though lacking a cavity of useful size.[4c,5] Thus, we have explored the use of an expanded bis-terpyridine ligand which might form a grid complex with an appropriate cavity size.

We chose to use a 2,7-naphthyridine unit for the expanded ligand as it is easily prepared[6] and has the appropriate regiochemistry for a terpyridine ligand. Thus, ligand **5** was prepared as shown in Scheme 1. Knovenagel condensation of **1** with malononitrile followed by acid promoted condensation and chlorination gave the tetrachloronaphthyridine **2**. Treatment of **2** with methoxide resulted in substitution of only the 1 and 8 chlorides giving the dichloride **3**.[6a] Coupling of the remaining chlorides to bipyridyl stannane **4**[7] *via* palladium catalysis produced the bistridentate metal ligand **5**. Reaction of **5** with $Co(OAc)_2$[8] in methanol/chloroform produced a Co_4L_4 complex as indicated by mass spectrometry. Interestingly, the observed mass suggested that each ligand had been demethylated to give a pyridone coordinated cobalt. Apparently, cobalt coordination activated the methoxypyridine units to dealkylation[9] by either acetate or a metal bound solvent.[10] The dealkylation was not complete, as ions for the Co_4L_4 complex with 1, 2, 3, and 4 remaining methyl groups were also observed in the mass spectrum. In order to achieve a uniform product, the mixture was heated with HBr or excess NaBr in acetonitrile to fully demethylate the complex with concomitant oxidation to Co(III). Anion metathesis gave the complex as the hexafluorophosphate salt.†

The NMR spectra of **6** were broad and undefined. X-Ray quality crystals of **6** were grown by slow diffusion of benzene into an acetone solution. Single crystal X-ray analysis of the complex confirmed the expected structure of the tetra-Co(III) grid (Fig. 1).‡ The complex crystallized with six counterions indicating that two of the ligands had been protonated.[11] The mass spectrum supports this assignment. The protons are most likely shared between two adjacent pyridone oxygen atoms, however, their positions in the X-ray structure are not clear. The four Co atoms line in a plane forming a nearly perfect square with angles of 89.2 and 90.8° and Co–Co distances of 8.48 and



Scheme 1 Synthesis of complex **6**.

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8.62 Å. Opposing naphthyridine rings are canted at a 30–31° angle due to the geometric constraints of the octahedral Co coordination. This 'convergence' angle has been described in detail for related rack complexes.[12] The convergence angle in **6** produces a cavity which is 11.5 Å deep and rectangular on each end. The atom-to-atom distance at each end of the cavity is 7.1 Å (C4a–C5a′) by 9.3 Å (O11a–O12a′). This rectangular cavity is well suited to an aromatic guest and indeed, two benzene molecules crystallized inside the complex, one at each end of the cavity. Thus, the contention that complexes such as **6** would serve as rigid receptors, at least in the solid state, is verified.

Thus, a square [2 × 2] grid has been produced from a dimethoxynaphthyridine based metal ligand. The complex has a rectangular internal cavity to the convergence angle of the ligands, yet traps guest in the solid state. The convergence angle can be controlled by varying the substitution pattern on the ligand.[12] Thus, it should be possible to substitute the tetrachloronaphthyridine **2** with alkoxides which are less prone to dealkylation in order to manipulate the cavity size and shape. These alkoxy substituents may also serve as a convenient handle for the placement of additional functional groups for specific molecular recognition. The recognition properties of this type of complex are currently being explored.

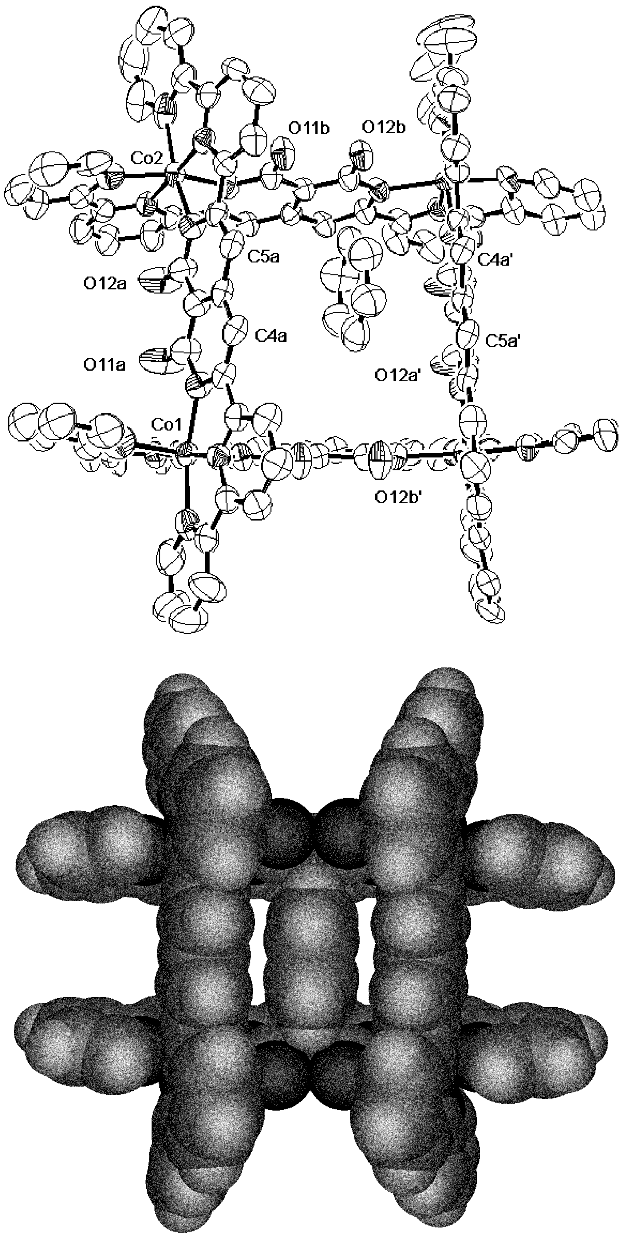

Fig. 1 ORTEP (50% probability) and CPK representations of complex **6**. The asymmetric unit is comprised of half of the complex. The symmetry transformations used to generate equivalent atoms (′): $-x + 1, y, -z + 1/2$.

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Notes and references

† Compound **5** (44.5 mg, 0.089 mmol) and $Co(OAc)_2{\cdot}4\,H_2O$ (22.1 mg, 0.088 mmol) were stirred at a reflux in 1 : 1 methanol : chloroform (16 ml) for 24 h. The solvent was removed under vacuum, the residue suspended in water, and an excess of NH_4PF_6 was added. The product was isolated as a yellow powder (64.6 mg 25%). The powder was dissolved in acetonitrile and HBr (1 ml, 47%) was added and the solution stirred at 60 °C for 2 hours. This mixture was diluted in H_2O (50 ml) and neutralized with aqueous KOH (pH = 8). NH_4PF_6 (excess) was added and the solution was cooled to 5° C. The solid product was isolated and washed with H_2O to yield a yellow powder (35.4 mg, 60%). λ_{max} (CH_3CN)/nm (ε) 402 (22 900), 418 (21 100), 473 (6 770); MS (ESI): 897 ($Co_4L_4 + 2\,H^+ + 4\,PF_6$, $z = 3$), 673 ($Co_4L_4 + 2\,H^+ + 4\,PF_6$, $z = 4$), 637 ($Co_4L_4 + 2\,H^+ + 3\,PF_6$, $z = 4$), 600 ($Co_4L_4 + 2\,H^+ + 2\,PF_6$, $z = 4$); Elemental analysis: found C 46.9, H 2.9, N 11.0; cald. for **6**·benzene·acetone C 46.6, H 2.5, N 10.8%.

‡ *Crystal Data:* for **6**·7.12 (C_3H_6O)·4.88 (C_6H_6): ($C_{112}H_{64}Co_4N_{24}O_8P_6F_{36}$)·7.12 ($C_3H_6O$)·4.88 ($C_6H_6$), M = 3772.76, Monoclinic, space group $C2/c$, $a = 39.027(4)$, $b = 13.9229(13)$, $c = 32.327(3)$ Å, $\alpha = 90°$, $\beta = 113.855(2)°$, $\gamma = 90°$, $V = 16065(3)$ Å^3, $T = 100$ K, $Z, Z' = 4, 0.5$, μ(Mo Kα, $\lambda = 0.71073$ Å) = 0.579 mm^{-1}, 44663 data measured, 14083 unique, $R_{int} = 0.0974$, all data used in refinement against F^2 values to give $wR = 0.3067$, $R = 0.0955$ {for 6667 data with $F > 4\sigma(F)$}. One solvent site (per unit cell) was found to be disordered as a mixture of acetone and benzene with occupancies of 0.556(9) for acetone and 0.444(9) for benzene. As a result, the terminal pyridine of one of the ligands was disordered and was refined in two orientations, only one of which is depicted in Fig. 1. CCDC 190379. See http://www.rsc.org/suppdata/cc/b2/b207039a/ for crystallographic files in CIF or other electronic format.

1 (*a*) M. Fujita, K. Umemoto, M. Oshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*b*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*c*) B. Holliday and C. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (*d*) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.

2 (*a*) M. Aoyagi, K. Biradha and M. Fujita, *J. Am. Chem. Soc.*, 1999, **121**, 7457; (*b*) M. Yoshizawa, T. Kusukawa, M. Fujita, S. Sakamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 2001, **123**, 10454; (*c*) L. R. ; MacGillivray, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676; (*d*) S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 4554.

3 (*a*) B. J. Shorthill and T. E. Glass, *Org. Lett.*, 2001, **3**, 577; (*b*) B. J. Shorthill, R. G. Granucci, D. R. Powell and T. E. Glass, *J. Org. Chem.*, 2002, **67**, 904.

4 (*a*) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel and D. Fenske, *Chem. Commun.*, 1997, 2231; (*b*) G. S. Hanan, D. Volkmer, U. S. Shubert, J.-M. Lehn, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1842; (*c*) J. Rojo, F. J. Romero-Salguero, J.-M. Lehn, G. Baum and D. Fenske, *Eur. J. Inorg. Chem.*, 1999, 1421; (*d*) S. Toyota, C. R. Woods, M. Benaglia, R. Haldimann, K. Wärnmark, K. Hardcastle and J. S. Siegel, *Angew. Chem., Int. Ed.*, 2001, **40**, 751.

5 See also: J. Rojo, J.-M. Lehn, G. Baum, D. Fenske, O. Waldmann and P. Müller, *Eur. J. Inorg. Chem.*, 1999, 517.

6 (*a*) B. M. Ferrier and N. Campbell, *J. Chem. Soc.*, 1960, 3515; (*b*) J. A. VanAllan, G. A. Reynolds, C. C. Petropoulos and D. P. Maier, *J. Heterocylic Chem.*, 1970, **7**, 495.

7 G. S. Hanan, U. S. Schubert, D. Volkmer, E. Rivière, J.-M. Lehn, N. Kyritsakas and J. Fischer, *Can. J. Chem.*, 1997, **75**, 169.

8 U. S. Schubert and C. Eschbaumer, *Org. Lett.*, 1999, **7**, 1027.

9 For a recent related study, see: T. R. Kelly, M. Caverao and Y. Zhao, *Org. Lett.*, 2001, **3**, 3895.

10 J. T. Groves and L. A. Baron, *J. Am. Chem. Soc.*, 1989, **111**, 5442.

11 Protonation of demethylated **5** has been observed in other simple dinuclear complexes: J. P. Plante and T. E. Glass, unpublished work.

12 G. S. Hanan, C. R. Arana, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1996, **2**, 1292.