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A metallosupramolecular tetrahedron with a huge internal cavity†

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A huge molecular tetrahedral complex forms quantitatively by self-assembly from four ligands L-H_6 and four titanium(IV) ions; in the solid state it encapsulates four $\{K(DMF)_3\}^+$ units in its interior.

Container-molecules[1] possess the potential to bind guests,[2] to stabilise reactive intermediates[3] or to promote chemical reactions in their interior.[4] Usually the preparation of the containers has to be performed in costly multistep syntheses.[5]

An easy way to obtain container-molecules is the self-assembly of molecular building blocks into highly sophisticated supramolecular aggregates, *e.g.* by hydrogen bonding interactions.[6] Metal coordination also represents an attractive way to obtain cage molecules by simple self-assembly processes from organic donor molecules and appropriate metal ions. Such metal containing container-molecules possess the advantages of good accessibility and relative high stability.[7,8]

A simple geometric body which forms an internal cavity is the tetrahedron.[9] Different approaches can be envisaged to form molecular tetrahedra in metal-directed self-assembly processes.[8] On the one hand, linear ligands with two metal binding sites can be located on the edges of the tetrahedron and a $M_4(ligand)_6$ complex is obtained. Starting with the pioneering work of Saalfrank,[10] many such complexes have been described,[11,12] the inclusion of guest species has been studied and reactive species could be stabilized inside of the cavity.[13]

On the other hand, ligands, which possess three metal-binding sites and an idealized C_3-axis, can connect the metal ions by spanning the faces (Fig. 1).[14] Three examples are already described in the literature, where tetrahedral coordination compounds $M_4(ligand)_4$ were obtained and structurally characterized.[15–18] It should be mentioned, that related ligands also can form $[M_6(ligand)_6]$ complexes.[11,18]

Due to the small size of the previously described ligands, no inclusion of guests could be observed in the interior of the tetrahedral complexes.[15–18] However, o,o′,o″-aminotrisbenzoic acid forms a related tetrahedral aggregate by hydrogen bonding and encapsulates one molecule of ethanol.[19]

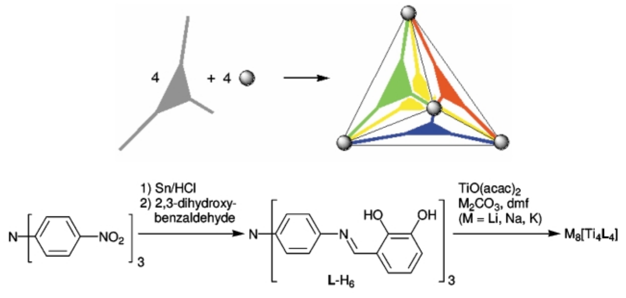

Fig. 1 Representation of the design principle to obtain a molecular tetrahedron from C_3-symmetric ligands and the preparation of **L**–H_6 and $M_8[Ti_4\mathbf{L}_4]$.

On the other hand, a series of organic ligands with three pyridine units, which possess a C_3-axis, are used to obtain huge metal complexes with big cavities and different geometries.[20–22] Hereby not only guests are encapsulated in the interior[23] but in addition highly reactive intermediates can be stabilized[24] or chemical reactions can be promoted.[25]

Our aim was to obtain a tetrahedral $M_4(ligand)_4$ complex, but to extend the size of the ligand compared to those, which are described in the literature,[15–18] so that a large cavity is formed which has the ability to bind either one big or several small guest molecules. Therefore we prepared ligand **L**–H_6 (Fig. 1) by reduction of the corresponding tri-nitro derivative[26] followed by condensation with 2,3-dihydroxybenzaldehyde.[27] Compound **L**–H_6 was thus obtained in 74% over two steps.

A coordination study of the derivative **L**–H_6 with $TiO(acac)_2$ and alkali metal carbonate (molar ratio: 1 : 1 : 1) was performed in DMF at 80 °C for 5 h, to guarantee the thermodynamically driven quantitative formation of the tetranuclear complexes $M_8[Ti_4\mathbf{L}_4]$ (M = Li, Na, K).

All three salts $M_8[Ti_4\mathbf{L}_4]$ show very similar simple NMR spectra in CD_3OD *e.g.* for the potassium salt we detected signals at $\delta = 9.08$ (s), 7.34 (d, $J = 7.9$ Hz), 7.28 (d, $J = 7.4$ Hz), 7.04 (d, $J = 7.9$ Hz), 6.57 (t, $J = 7.4$ Hz), and 6.50 (d, $J = 7.4$ Hz). The simplicity of the spectra shows the high symmetry of the obtained coordination compounds. The composition of the complexes to be $M_8[Ti_4\mathbf{L}_4]$ is deduced from FT-ICR MS (in methanol). Only peaks which can be assigned to the tetranuclear coordination compounds are found. For the representative potassium complex $K_8[Ti_4\mathbf{L}_4]$ signals are observed which all show the expected isotopic pattern. The peaks with only the major isotopes are observed at $m/z = 1444.5$ $\{K_3H_3[Ti_4\mathbf{L}_4]\}^{2-}$, 1425.5 $\{K_2H_4[Ti_4\mathbf{L}_4]\}^{2-}$, 1406.5 $\{KH_5[Ti_4\mathbf{L}_4]\}^{2-}$, 962.7 $\{K_3H_2[Ti_4\mathbf{L}_4]\}^{3-}$, 950.0 $\{K_2H_3[Ti_4\mathbf{L}_4]\}^{3-}$, 937.3 $\{KH_4[Ti_4\mathbf{L}_4]\}^{3-}$, 925.0 $\{H_5[Ti_4\mathbf{L}_4]\}^{3-}$, 722.0 $\{K_3H[Ti_4\mathbf{L}_4]\}^{4-}$, 712.2 $\{K_2H_2[Ti_4\mathbf{L}_4]\}^{4-}$, 702.8 $\{KH_3[Ti_4\mathbf{L}_4]\}^{4-}$, and 693.5 $\{H_4[Ti_4\mathbf{L}_4]\}^{4-}$.

Crystallization of the complex salts $M_8[Ti_4\mathbf{L}_4]$ from DMF/ether affords single crystals as needles with a length of up to one cm. Due to the high content of solvent molecules in the crystal and the connected instability, we were able to obtain only the X-ray structure of the potassium salt.‡

$K_8[Ti_4\mathbf{L}_4]\cdot 23DMF$ crystallizes in the monoclinic space group C_2/c. The solid state structure of the octaanion $[Ti_4\mathbf{L}_4]^{8-}$ is represented in Fig. 2a. Four titanium(IV) ions are located on the corners of a slightly distorted tetrahedron with all four complex units having the same configuration. The triangular faces are blocked by four of the ligands **L** which each coordinate to three of the metal centers. A huge internal cavity is formed. Four of the potassium counter cations are located in the interior of the cavity, each binding to the three internal oxygen atoms of the four titanium tris(catecholate) units.[28] Additionally each potassium cation binds three DMF molecules (Fig. 2b). In the center of $[\{(DMF)_3K\}_4\subset\{Ti_4\mathbf{L}_4\}]^{4-}$ is still some space left which is filled with solvent molecules. Those molecules are severely disordered and can not be resolved by X-ray crystallography. However, it can be estimated that about three DMF molecules can fit into the center of the cavity.

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† Dedicated to Professor Bernt Krebs on the occasion of his 65th birthday.

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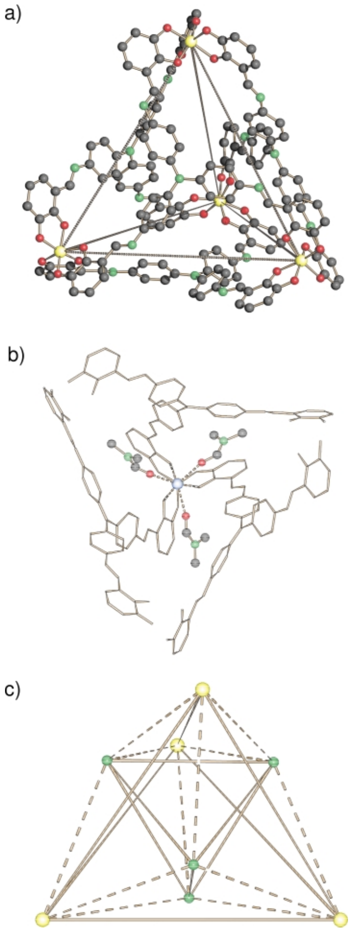

Fig. 2 Representations of the solid state structure of (a) the octaanion $[Ti_4\mathbf{L}_4]^{8-}$, (b) the coordination at an encapsulated $\{K(DMF)_3\}$-unit, and (c) the four central nitrogen atoms of ligands **L** and the four titanium(IV) ions. Those eight atoms define the cavity size of the supramolecular tetrahedron (yellow: titanium, blue: potassium, grey: carbon, green: nitrogen, red: oxygen; hydrogen atoms are omitted for clarity).

Fig. 2c represents the titanium atoms and the central nitrogen atoms of the ligand, which all together define the size of the cavity. Hereby the titanium(IV) ions (Ti⋯Ti = 16.7–17.1 Å) as well as nitrogen atoms (N⋯N = 9.7–10.0 Å) form two tetrahedra with the smaller one fitted into the bigger one. Titanium–nitrogen distances within the ligands are 10.0 to 10.2 Å, while the Ti–N distances through the cavity are in the region of 16.3 Å.

The concept to use ligands with C_3-symmetry to obtain tetranuclear $[M_4(\text{ligand})_4]$ complexes was already introduced by others.[15,17] However, we describe the first example of a tetrahedral tetranuclear coordination compound which binds guest species in its interior. The cavity of the complex possesses an extraordinary size and is able to encapsulate four $\{K(DMF)_3\}$-units and three additional DMF molecules. Therefore this huge coordination compound should be well suited for the investigation of guest encapsulation and guest exchange in solution. The big pores of the tetrahedron hereby should not be a problem as was shown by the work of Fujita.[20] Corresponding studies are momentarily going on in our laboratories.

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Notes and references

‡ Crystal data for $[K(C_3H_7NO)_3]_4[C_{156}H_{96}N_{16}O_{24}Ti_4]\cdot K_4(C_3H_7NO)_{10}(C_3H_7NO)_{2/2}$, $M = 4764.10$, monoclinic, space group $C2/c$ (No. 15), $a = 35.628(1)$, $b = 32.922(1)$, $c = 26.300(1)$ Å, $\beta = 123.79(1)°$, $V = 25637.6(14)$ Å^3, $D_c = 1.234$ g cm^{-3}, $\mu = 3.26$ cm^{-1}, $Z = 4$, $\lambda = 0.7103$ Å, $T = 198$ K, 44276 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 16324 independent ($R_{\text{int}} = 0.084$) and 9559 observed reflections $[I \geq 2\,\sigma(I)]$, 1291 refined parameters, $R = 0.129$, $wR^2 = 0.324$. CCDC 210953. See http://www.rsc.org/suppdata/cc/b3/b309495b/ for crystallographic data in .cif or other electronic format.

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