

Guest-induced formation of an icosahedral coordination cage†

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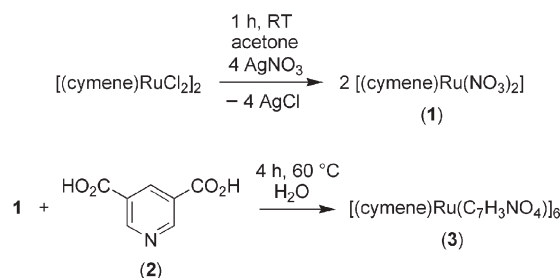
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A coordination cage with an elusive icosahedral geometry was obtained by K^+ -induced rearrangement of a hexanuclear [(cymene)Ru(pyridine-3,5-dicarboxylate)]₆ complex.

Transition metal-based self-assembly processes have extensively been used to construct discrete coordination cages.¹ The investigation of such complexes is of interest from a fundamental point of view because it contributes to our understanding of how to access structurally defined assemblies of nanometer dimensions. Furthermore, coordination cages can display a fascinating host-guest chemistry.¹ An octahedral Pd-based cage, for example, has been shown to act as a specific receptor for the sequence selective recognition of peptides in water² and a tetrahedral Ga₄L₆ cage was found to act as a nanoscale reaction vessel for aza-Cope rearrangements.³ For these two examples, as well as in most other cases, the interaction with the guest takes place in the cavity of the cage. In the following we describe the synthesis and the structure of a hexanuclear organometallic cage, which acts as an *exo*-receptor⁴ for alkali metal ions. The metal ions are able to induce a structural rearrangement into a dodecanuclear cage with an elusive icosahedral geometry.

Over the last few years, we have shown that the combination of (arene)Ru²⁺ fragments with dianionic N,O,O-ligands can be used to construct neutral metallamacrocycles.⁵ In these complexes, the two O-donor atoms coordinate to one (arene)Ru²⁺ fragment and the N-donor atom to an adjacent one thereby forming a cyclic compound. We reasoned that the same type of reaction can be used to construct three-dimensional cage complexes, given that the three donor atoms of the ligand are not able to coordinate to the same (arene)Ru²⁺ fragment.⁶ To test this hypothesis, we have investigated the reaction of [(cymene)Ru(NO₃)₂] (1) with 3,5-pyridinedicarboxylic acid (2). Complex 1 was prepared *in situ* by reaction of [(cymene)RuCl₂]₂ with four equivalents of AgNO₃ followed by separation of AgCl (Scheme 1).⁷ Subsequent reaction with ligand 2 in water gave an orange precipitate (3), which was isolated and washed with H₂O (yield: 48%).

A ¹H NMR spectroscopic analysis of the product 3 in CD₃OD showed that a highly symmetric complex with a (cymene)Ru to ligand ratio of 1 : 1 had formed (see ESI†). Only one doublet was observed for the CH₃ protons of the *i*-Pr group indicating that all cymene ligands of assembly 3 are identical and that the complex is achiral. Attempts to characterize the complex by ESI-MS were only partially successful: a weak signal, which can be attributed to



Scheme 1 Synthesis of the hexanuclear cage 3 by reaction of complex 1 with ligand 2.

a hexamer, was observed but neither the intensity nor the quality of the signal was sufficient to draw definite conclusions.

Decisive information about the structure of complex 3 was obtained by a single crystal X-ray analysis.† The assembly is indeed composed of six (cymene)Ru fragments, which are connected by six 3,5-pyridinedicarboxylate ligands (Fig. 1). Each ligand is coordinated to three different metal atoms *via* the carboxylate O-atoms (Ru–O = 2.10 ± 0.01 Å) and the pyridine N-atom (Ru–N = 2.12 ± 0.01 Å). The Ru atoms are positioned in the corner of a trigonal antiprism with two distinct distances for adjacent Ru-atoms of 8.00 ± 0.01 Å (e.g. Ru1'···Ru3; Ru1···Ru2; Ru2···Ru3) and 8.61 ± 0.02 Å (e.g. Ru1···Ru2'; Ru2···Ru3'; Ru1···Ru3), respectively. The cage displays a crystallographic inversion center in agreement with the lack of diastereotopic signals in the ¹H NMR spectrum. A disordered methanol molecule is found in the cavity of the complex.

Half of the carbonyl O-atoms of the ligand are positioned in close proximity to each other: the atoms O1', O8, and O9' are on average 4.25 ± 0.03 Å apart from each other and the symmetry related atoms O1, O8' and O9 as well. Given the negative polarization of these atoms, it appeared likely that the two clusters of oxygen atoms represent binding sites for metal cations (Fig. 2).

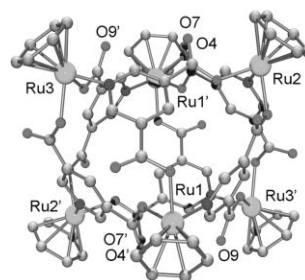


Fig. 1 Ball and stick representation of the molecular structure of complex 3 in the crystal. The side chains of the π -ligand, the hydrogen atoms and the solvent molecules (8 MeOH) have been omitted for clarity. Atoms marked with a prime (') are at equivalent positions ($-x, -y, -z$).

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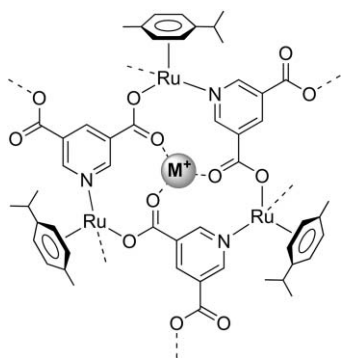


Fig. 2 Three carbonyl O-atoms of the bridging 3,5-pyridinedicarboxylate ligand constitute a binding site for metal ions. Only part of the cage is shown for clarity.

To test this, we have investigated the interaction of complex **3** with alkali metal ions by NMR spectroscopy. Upon addition of 10 equivalents of NaOAc, KOAc, or CsOAc to a solution of complex **3** (12.5 mM, CD₃OD), pronounced differences were observed for the chemical shifts of several ¹H and ¹³C NMR signals. The nature of the anion did not affect the chemical shift to a significant extent. This was confirmed in control experiments with KCl instead of KOAc. The addition of KOAc or CsOAc generally resulted in larger differences of the chemical shifts than the addition of NaOAc (see ESI†). For the H-atom in the 4-position of the pyridine ligand, for example, the following values were obtained: $\Delta\delta = 0.015$ ppm (Na⁺), 0.045 ppm (K⁺) and 0.047 ppm (Cs⁺). Attempts to obtain quantitative data for the complexation constants by fitting of the binding isotherms were not made because a detailed inspection of the ¹³C NMR spectra revealed the presence of a second (cymene)Ru complex, the concentration of which increased upon addition of increasing amounts of the alkali metal salts.

Parts of the ¹³C NMR spectra obtained for an NMR titration of complex **3** with KOAc (0, 5, 10, and 20 equiv.) are shown in Fig. 3. The signals correspond to two of the aromatic C-atoms of the cymene π -ligand. From the spectra it is evident that the addition of K⁺ not only affects the chemical shifts of the signals but also results in the differentiation of a second set of signals, the intensity of which goes with increasing KOAc concentration. Upon addition of 20 equiv. of K⁺, the two signals have approximately the same intensity. A splitting of this kind is also

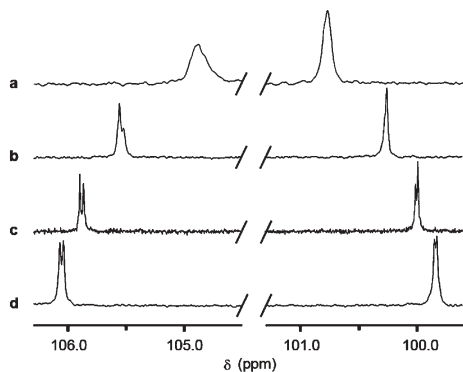


Fig. 3 Part of the ¹³C NMR spectrum of a solution of complex **3** (12.5 mM, CD₃OD) containing different amounts of KOAc: (a) 0 mM, (b) 62.5 mM, (c) 125 mM, (d) 250 mM.

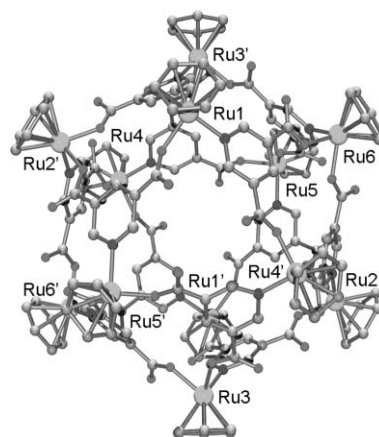


Fig. 4 Ball and stick representation of the molecular structure of complex **4** in the crystal. The side chains of the π -ligand, the hydrogen atoms, the potassium salts and the solvent molecules have been omitted for clarity. Atoms marked with a prime (') are at equivalent positions ($-x, -y, -z$).

evident for some other ¹³C NMR signals but not for all, indicating that the new species is structurally very similar to complex **3**. The addition of NaOAc or CsOAc resulted in the formation of a second set of signals as well but in comparison to KOAc, slightly higher concentrations were needed to observe comparable amounts of the new species.

To obtain more information about this species, we have tried to co-crystallize complex **3** with MOAc (M = Na, K, Cs). For KOAc (**4**) and CsOAc (**5**) we were able to obtain single crystals, which were analyzed by X-ray crystallography. Both complexes show a similar overall structure but due to the very low quality of the data obtained for **5**, we restrict the discussion to complex **4**.[‡] Complex **4** is composed of a dodecanuclear coordination cage (Fig. 4), which is coordinated to eight K⁺ ions (Fig. 5). The connectivity is similar to what was found for **3**: each (cymene)Ru fragment is coordinated to two carboxylate O-atoms and one pyridine N-atom of three different ligands. The Ru-atoms are positioned on the vertices of an icosahedron with adjacent Ru-atoms being 8.41 ± 0.24 Å apart from each other and with Ru–Ru–Ru angles of $60.0 \pm 2.5^\circ$. It should be noted that although dodecanuclear coordination cages have been described,⁸ a complex with an icosahedral geometry has—to best of our knowledge—not been reported so far. In nature, on the other hand, self-assembled icosahedral capsules are ubiquitous, because most spherical viruses possess icosahedral symmetry.⁹

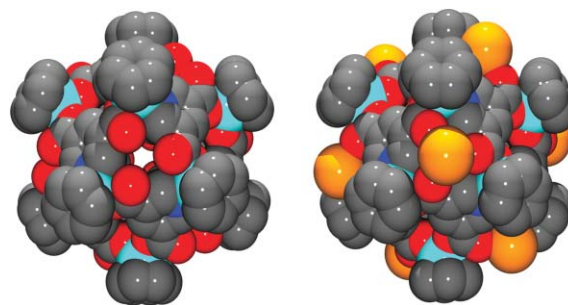


Fig. 5 CPK representation of the molecular structure of complex **4** in the crystal with (right) and without (left) the K⁺ ions coordinated to the eight binding sites. The side chains of the π -ligand, the hydrogen atoms, the anions and the solvent molecules have been omitted for clarity.

The symmetry related Ru-atoms of complex **4** are $15.98 \pm 0.07 \text{ \AA}$ apart from each other and the symmetry-related N-atoms have a distance of $13.83 \pm 0.06 \text{ \AA}$. The internal volume of the cavity is approximately 1100 \AA^3 and is filled with 18 disordered water molecules.¶ The outside diameter of the dodecamer is 23.8 \AA . 12 out of the 20 faces of the icosahedra are occupied by the bridging 3,5-pyridinecarboxylate ligands. The remaining 8 faces have a small opening, which is surrounded by three carbonyl groups. The O-atoms constitute a metal binding site, very similar to what was observed for complex **3**. In the crystal, all eight sites are occupied by K^+ ions (Fig. 5). The latter are coordinated to disordered acetate and methanolate anions, which connect the icosahedra in the crystal.

The rearrangement of a hexanuclear complex into a dodecanuclear one is entropically disfavoured. In our case, two factors are likely to contribute to the compensation of this 'entropic penalty'. First of all, in complex **4** all carbonyl O-atoms are part of a potential binding site. In complex **3**, on the other hand, only 6 out of the 12 carbonyl O-atoms are predisposed to bind to a metal ion. An excess of K^+ ions will thus favour the formation of complex **4** because the $\text{K}^+\text{-O}$ interactions can be maximized. Secondly, the geometry of the binding sites of complex **4** is more suited for the complexation of alkali metal ions. The O-atoms in the hexanuclear complex **3** are $4.25 \pm 0.03 \text{ \AA}$ apart from each other. This is rather long, even for the large K^+ and Cs^+ ions.¹⁰ In the dodecanuclear complex **4**, on the other hand, the carbonyl groups are closer together ($\text{O}\cdots\text{O} = 3.81 \pm 0.04 \text{ \AA}$) because of the reduced surface curvature of the cage.

In summary, we have described the synthesis and the structure of a hexanuclear coordination cage (**3**), which can be obtained by reaction of [(cymene)Ru(NO₃)₂] (**1**) with 3,5-pyridinedicarboxylic acid (**2**). The cage is neutral and acts as an *exo*-receptor for alkali metal ions. This is in contrast to what is found for other coordination cages, which are typically highly charged species with potential guests being bound in the interior of the complex.¹ Addition of an excess of M^+ ions leads to a rearrangement¹¹ of complex **3** into the dodecanuclear coordination cage **4** with an elusive icosahedral geometry.

Notes and references

‡ Crystal data for complex **3**: $\text{C}_{110}\text{H}_{134}\text{N}_6\text{O}_{32}\text{Ru}_6$, $M_r = 2658.65$, triclinic, space group $P\bar{1}$, $a = 15.1057(12)$, $b = 15.1722(18)$, $c = 15.3876(8) \text{ \AA}$, $\alpha = 84.003(7)$, $\beta = 63.988(6)$, $\gamma = 63.110(8)^\circ$, $V = 2807.3(4) \text{ \AA}^3$, $Z = 1$, $\mu = 0.867 \text{ mm}^{-1}$, 45425 reflections collected, 9885 independent reflections, $R_{\text{int}} = 0.0626$, $R_1 [I > 2\sigma(I)] = 0.0598$, wR_2 (all data) = 0.1523. Crystal data for complex **4**: $\text{C}_{222}\text{H}_{300}\text{K}_8\text{N}_{12}\text{O}_{106}\text{Rh}_{12}$, $M_r = 6358.38$, monoclinic, space group $C2/c$, $a = 34.133(3)$, $b = 32.347(3)$, $c = 26.317(3) \text{ \AA}$, $\beta = 93.534(8)^\circ$, $V = 29001(5) \text{ \AA}^3$, $Z = 4$, $\mu = 0.807 \text{ mm}^{-1}$, 85260 reflections collected, 23153 independent reflections, $R_{\text{int}} = 0.1566$, $R_1 [I > 2\sigma(I)] = 0.1086$, wR_2 (all data) = 0.3121. CCDC 606774 and 606775. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607512f

§ The dodecanuclear complex **4** has the shape of an icosahedron but not icosahedral I symmetry. The cage has a crystallographic inversion center and an idealized T_h symmetry.

¶ The internal volume of the cage was calculated with the program MCAVITY (L. J. Barbour, 2003, <http://x-seed.net/cavity.html>) using the crystallographic coordinates of the cage after removal of the guest molecules.

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