



Dinuclear arene ruthenium dichloro complexes designed for host–guest propensity

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ARTICLE INFO

Article history:

Received 9 February 2012

Received in revised form

14 March 2012

Accepted 15 March 2012

Keywords:

Wheel-and-axle

Half-sandwich

Ruthenium

Crystal engineering

Solvates

ABSTRACT

The synthesis and the crystal structures of several wheel-and-axle metal–organic (waamo) complexes are studied. The design of such systems is basically constituted by the binding between two Ru(II)(*p*-cymene)Cl₂ units (wheels) and an organic spacer (axle), bearing pyridinic and/or cyano functions. Particular attention is given to the solid-state organization of the waamo complexes and to their propensity to create acceptors sites for guest species. The inverted piano-stool motif, a characteristic synthon of half-sandwich ruthenium units, is always observed here, generating well defined layers of host molecules. Both polycatenated and host–guest systems were generated in order to achieve a compact packing.

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1. Introduction

In the field of materials chemistry a strong interest is focused on the design of new compounds able to incorporate small molecules in their crystalline network through heterogeneous solid–gas reactions [1]. These materials can find important applications in several strategic fields, such as gas storage, gas-sensing, or heterogeneous catalysis. Literature counts a lot of examples of metallorganic frameworks (MOF) that in the solid-state give rise to porous networks, with potential receptor sites for guest species [2]. In this context, we are particularly interested on the construction of crystalline molecular solids, since they allow to exert a great control over the intermolecular host–host and host–guest interactions, thanks to the basic principles of crystal engineering and to the numerous structures available on the CSD (Cambridge Structural Database). The control over the crystal packing of the host species is of fundamental importance in order to predict the intermolecular host–guest interactions which will be in action once the crystalline host comes in contact with suitable gaseous guests. Our interest is not directed onto materials with an intrinsic porosity, but rather to the design of metal-containing complexes showing a dynamic behavior in the solid state, that is, able to undergo a network

rearrangement in response to an external stimulus, such as exposure to guest vapors. Recently our group developed a series of hybrid organic–inorganic systems, called wheel-and-axle diols (waad) [3], where the coordinating metal Pd(II) is the center of the linear rigid axle, while the bulky ends are occupied by the ligand α -(4-pyridyl)benzhydrol (called LOH) (Fig. 1a). Their irregular shape frustrates the achievement of a unique compact stable packing, that rather may be realized by inclusion of suitable small molecules that fill the voids. The formation of host–guest systems was observed simply by solvent vapor exposure of the host compounds, with a simultaneous rearrangement of its crystal structure (Fig. 1b,c); the 3D packing analysis shows that the apohost is preorganized for inclusion and that solvent uptake/release involves a “venetian blinds” mechanism based on concerted oscillations of the complex molecules around the palladium atoms (Fig. 1b). These molecules are organized in layers with practically invariant metrics, and the oscillation occurs with slight conformational rearrangements; this process turned out to be fully reversible and the starting host was restored by thermal treatment of the solvate complex.

A reverse synthetic strategy for wheel-and-axle (waa) systems takes into account bulky metal-containing units at the ends, while the central spacer can be constructed either by a bidentate divergent ligand granting a covalent rigid axle (covalent waa), or by a robust supramolecular synthon (supramolecular waa) (Scheme 1) occurring between suitable dimerizing functions present on an organic ligand bound to the metal [4].

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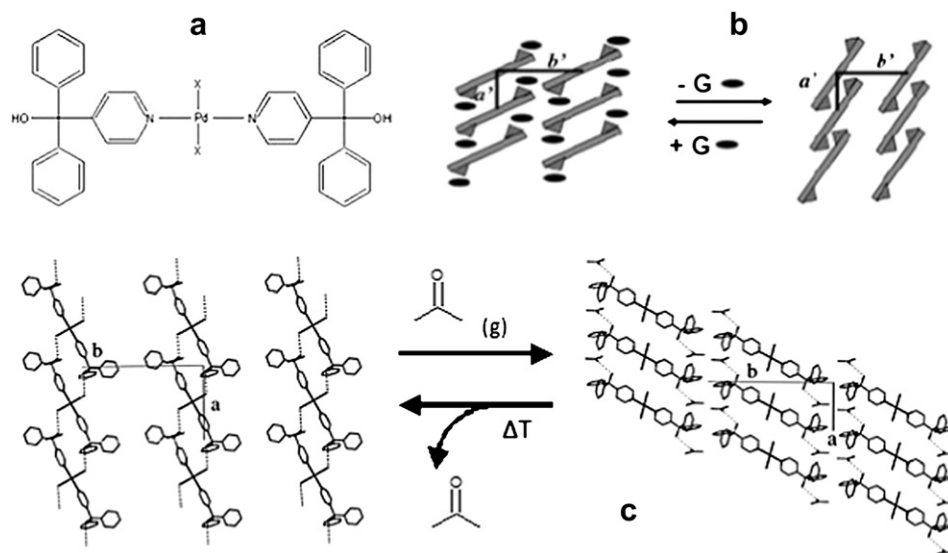


Fig. 1. (a) Scheme of $\text{Pd}(\text{LOH})_2\text{X}_2$. (b) Representation of “venetian blinds” rearrangement mechanism (the host is sketched with bars, while ovals represent the guest). (c) Structure rearrangements occurring after exposure of the apohost to acetone vapors and thermally induced extrusion of acetone.

Two half-sandwich Ru(II) units were chosen as wheels, thus giving rise to wheel-and-axle metallorganic (waamo) systems by which it is possible to exploit the metal center as potential site of interactions with guest molecules, taking into account that ruthenium is widely used in catalysis for its capacity to activate several substrates. Furthermore, the propensity of half-sandwich ruthenium(II) compounds to associate in a pseudo-centric dimeric supramolecular entity, called the inverted piano-stool dimer [5], can be exploited in order to engineer crystal networks based on the alignment of half-sandwich Ru units along arrays that can generate columnar pores when exposed to guests. In literature there is a large number of examples in which these units are used as building blocks for the design of supramolecular architectures [6].

In a previous work [7] we reported the synthesis and the structural characterization of two supramolecular waamo systems (Scheme 2) containing aminic functions: [(*p*-cymene)Ru(4-aminobenzoic acid) Cl_2] (**Ru4aba**) and [(*p*-cymene)Ru(4-aminocinnamic acid) Cl_2] (**Ru4aca**). Both compounds showed the expected 3D packing, based on the carboxylic supramolecular dimerization and on the inverted piano-stool motif, but their behavior toward potential guests revealed to be very different. Several attempts aimed at synthesizing and crystallizing **Ru4aba** by different solvents always brought to the same anhydrous form, thus revealing a very robust pattern with a complete hydrogen bond balance; on the contrary, **Ru4aca**, bearing a longer spacer between the metal centers, was obtained in three different crystalline solvate forms. This is probably due to the higher conformational freedom of the cinnamic group with respect to the benzoic group, that promotes the achievement of a favorable condition for the guest interaction.

In the present paper we describe the synthesis and the solid-state behavior of a series of new covalent waamo complexes containing the [(*p*-cymene)Ru Cl_2] units and organic ligands with two different coordinating groups, often used in the design of MOFs [2]:



Scheme 1. Scheme of the covalent and supramolecular waa.

pyridine and nitrile. A general scheme of the ligands and corresponding Ru-complexes is reported in Scheme 3. In particular, our attention will be directed onto the supramolecular interactions which dictate the observed crystal packings with the aim at verifying the construction of the desired structural motifs described above. Then, we will examine the propensity of complexes **1–4** to generate solvate-species, both by crystallization experiments as well as solid-gas uptake experiments of volatile organic guests. The different length of the organic spacers allows to evaluate the importance of this parameter toward the clathrating properties of the organometallic species, taking into account what observed with the supramolecular waamo [7].

2. Results and discussion

2.1. Synthesis and characterization of complexes **1–3**

{[(*p*-Cymene)Ru Cl_2] $_2$ (4,4'-bipyridyl)} (**1**) and {[(*p*-cymene)Ru Cl_2] $_2$ (1,2-di(4-pyridyl)ethylene)} (**2**) were obtained by reaction between [Ru(*p*-cymene) Cl_2] $_2$ and 4,4'-bipyridyl or 1,2-di(4-pyridyl)ethylene (molar ratio 1:1) in dry dichloromethane, under an inert atmosphere of nitrogen. The instantaneous precipitation of microcrystalline solids was observed just when the two reactants were put in contact. The products were isolated in good yields and their purity was confirmed by elemental analysis. Ruthenium is at the center of a distorted octahedron, where the η^6 -coordinated *p*-cymene occupies three coordination sites, while the remaining sites are occupied by two chloride ligands and by the pyridine ring of the organic spacer. The IR-ATR spectra of complexes **1** and **2** show the expected signal at 1609 cm^{-1} and 1607 cm^{-1} , respectively, due to the $\text{C}\equiv\text{N}$ stretching of the pyridine ring. Both complexes are insoluble in most of the common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran, acetonitrile, toluene, methanol, ethanol, acetone, *t*-butyl methyl ether, diethyl ether, ethyl acetate as well as water. The solubility slightly improves in dioxane and nitromethane, while it is complete in dimethyl sulfoxide and in dimethylformamide. In the last two cases, however, dissolution occurs by dissociation of the pyridine function from the metal, with formation of the solvato complexes [(*p*-cymene)Ru(*S*) Cl_2] (*S* = DMF or DMSO) and free ligand [8]. The ^1H NMR

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