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Research paper

Template synthesis and X-ray structure of the tris-glyoximate iron(II) clathrochelates with terminal reactive groups

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ABSTRACT

One-pot template condensation of glyoxime with the corresponding functionalized phenylboronic acids on an iron(II) ion as a matrix afforded 3- and 4-substituted phenylboron-capped tris-glyoximate iron (II) clathrochelates with terminal amine, formyl (acetal) and vinyl groups; those with acetal groups were converted into the formyl-terminated cage complexes using H^+-catalyzed hydrolysis. The complexes obtained were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV–Vis, ^1H and ^{13}C NMR spectroscopies, and by single crystal X-ray diffraction (for three of these clathrochelates). Their molecules possess a geometry intermediate between a trigonal prism (TP) and a trigonal antiprism (TAP) and the bite angles α remain almost constant being in the range 77–79°, whereas the heights h of FeN_6-coordination polyhedra depend on the distortion angle φ values (from 12.2 to 20.7°) thus being in the range 2.36–2.37 Å. An encapsulated iron(II) ion is situated almost in the centre of cage frameworks and the average chelate C—C bonds in these tris-glyoximate frameworks are substantially shorter than those for their aliphatic and aromatic analogs. The crystal packings are governed by weak supramolecular hydrophobic interactions and an absence of the steric hindrances between the ribbed substituents (hydrogen atoms) allowed to form intermolecular π…π interactions.

As follows from single crystal X-ray diffraction data, the synthesized macrobicyclic tris-glyoximates with reactive terminal groups, which the macrobicyclic molecules contain no bulky ribbed substituents, have large ligand aspect ratio and, therefore, they seem to be promising syntones and building blocks for preparation of covalent (including imine and amine) and coordination metallomacrocycles, MOFs and cages (capsules) with big voids and cavities as hosts, suitable for inclusion of various organic and inorganic guests.

1. Introduction

Cage metal complexes (clathrochelates [1]) with the ribbed and apical terminal reactive, donor and biologically relevant groups are chemically robust, three-dimensional molecular platforms and building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs as well. In particular, clathrochelate molecules with pendant substituents containing reactive terminal HO-, H_2N- and HS-groups [2–5], have been widely used for modification of various materials (in particular, through their covalent immobilization on a surface of the working electrodes, Scheme 1, **a**). This allowed to elaborate new types of molecular switches [2], electrocatalysts for hydrogen evolution reaction [5], mediators of electron transfer and clathrochelate-modified gold electrodes for amperometric determination of hydrogen peroxide [4]. On the other hand, clathrochelate complexes with inherent donor amine and thiol substituents in *vic*-position of the same chelate fragment are reported to be suitable mono- and *cis*-bidentate macrobicyclic ligands towards to platinum(II, IV) [6] and copper(II) [7,8] ions. For example, the reaction of a bis-methylsulfide iron(II) clathrochelate with $PtCl_4^{2-}$ dianion gave polynuclear platinum(II) complexes of the corresponding dithiolate macrobicyclic ligand (see an exampling compound **b** on Scheme 1) as a result of unusual demethylation process with elimination of CH_3Cl [6]. The monoribbed-functionalized iron(II) cage complex with two inherent NH_2-groups undergoes deprotonation in the presence of strong bases thus giving a clathrochelate dianion, which have been used [7] as an acido-ligand towards to

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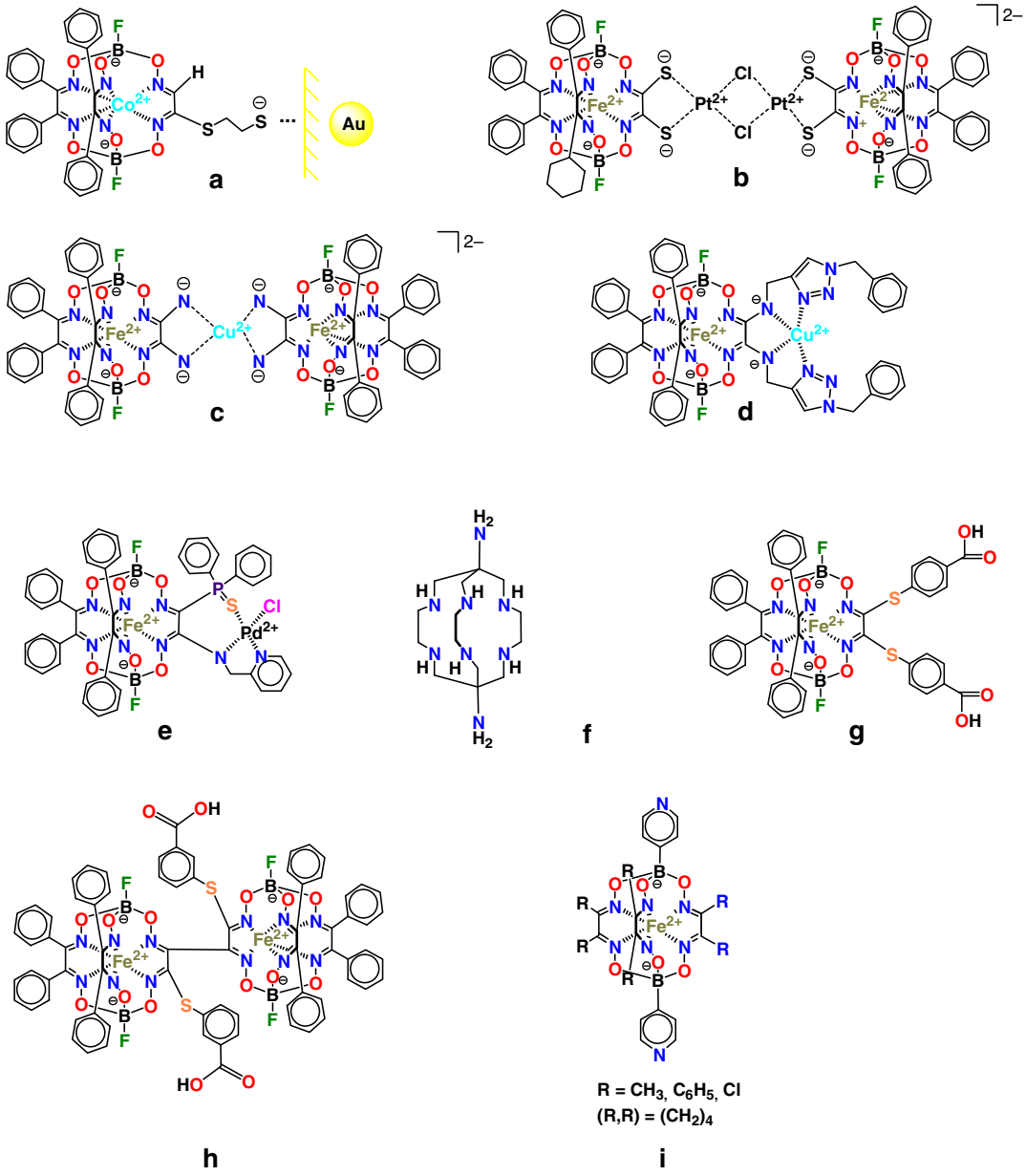

Scheme 1. Clathrochelates with the ribbed reactive groups.

copper(II) ion giving a Cu, Fe-heteronuclear compound **c** (Scheme 1) with $Cu(N^{-})_4$- and FeN_6-coordination polyhedra. The analogous dipropargylamine-functionilized iron(II) macrobicyclic complex is reported in [8] to undergo copper(I)-catalyzed "click" reaction with benzyl azide thus giving the unexpected binuclear compound **d** (Scheme 1): in its molecule, central Cu^{2+} ion coordinates two deprotonated amino groups and two donor azaheterocyclic fragments of the ribbed substituents at a quasiaromatic macrobicyclic framework. Moreover, the *P,N*-substituted iron(II) mono- and bis-clathrochelates as cage and bis-cage ligands, respectively, with the donor diphenylthiophosphine and pyridyl groups are reported in [9] to form Pd, Fe-binuclear 1: 1 complexes (see exampling compound **e** on Scheme 1), which are efficient and structure-dependent catalysts of the model Suzuki cross-coupling reaction.

The reactivity of apical amino groups of polyamine macrobicyclic ligands (see exampling sarcophagine **f**, Scheme 1) and their complexes have been widely used for the synthesis of radioactive cage metal compounds with biologically relevant (for example, specific peptide) vector groups that bind to specific molecular targets *in vivo* thus allowing to use these clathrochelates for radiation therapy and diagnostics [10–34]. The ribbed-functionalized clathrochelates and bis-clathrochelates with biorelevant iono- and protonogenic terminal groups [35], such as the monoribbed-functionalized carboxyphenylsulfide iron(II) cage and bis-cage complexes (Scheme 1, **g** and **h**, respectively) are reported to be the efficient transcription inhibitors (topological drugs) and antifibrillogenic agents as well; these results are recently highlighted in a review [36].

4-Pyridinylboron-capped iron(II) aliphatic, aromatic and halogenoclathrochelates **i** (Scheme 1) are described in [37] to be a suitable macrobicyclic precursors for Bubnov diallylation reaction, giving the allylated apical groups at a cage framework. Donor ability of apical 3- and 4-pyridyl substituents of aliphatic macrobicyclic iron(II) tris-dioximates allowed to obtain a wide range of polyclathrochelate metallamacrocycles, coordination polymers