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Synthesis and chemical reactivity of an Fe(III) metallacrown-6 towards *N*-donor Lewis bases

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ABSTRACT

The iron(III) 18-azametallacrown-6 $[Fe(ashz)(EtOH)]_6$ (**1**) ($ashz^{3-}$ = trianionic derivative of *N*-acetylsalicylhydrazide), prepared upon reaction of $[Fe_3(\mu_3\text{-}O)(Piv)_6(H_2O)_3](Piv)$ (Piv = Bu^tCOO^-) with H_3ashz, reacts with *N*-heterocyclic Lewis bases (B = pyridine, 4-methyl pyridine, 3-amino pyridine or imidazole), leading to the stable adducts $[Fe(ashz)(B)]_6$ (**2** to **5**, respectively) upon replacement of the labile ethanol ligand. All the compounds were characterized by elemental analysis, IR and ESI–mass spectroscopies and, for complexes **1** and the 3-amino pyridine adduct **4**, also by X-ray crystallography. In both **1** and **4**, the stereochemistry of the ligand imposes a propeller configuration of the metal cation which exhibits alternating Λ/Δ forms.

Since the first report of a metallacrown ether in 1989 [1], metallamacrocycles have attracted considerable attention due to their interesting molecular architecture, supramolecular chemistry, self-assembly, host–guest chemistry and magnetic properties [2]. Metallacrowns are structurally analogous to crown ethers in which the methylene carbons [3] are replaced by transition metal ions and nitrogen atoms, and sometimes the oxygen atoms being replaced by nitrogen atoms [4]. The ligands, which are capable to bridge two metal ions simultaneously in a cyclic way, generate the macrocyclic metal cluster. Metallacrowns are commonly of two types: one type with repeated [M–N–O] units interlinked to a cyclic structure and the other one with repeated azametallacrown [M–N–N] units. Hydroxamate and/or ketonoximate ligands are found to form $[M–N–O]_n$ metallacrowns in a rich variety of compounds, such as 9-metallacrowns-3 [5], 12-metallacrowns-4 [6] and 15-metallacrowns-5 [6d,7]. On the other hand, $[M–N–N]_n$ azametallacrowns lead to comparatively higher analogues, e.g., a Mn(III) 18-azametallacrown-6 [4a], Mn(III)/Fe(III) 30-azametallacrowns-10 [4b] and Mn(III)/Ni(II) 36-azametallacrowns-12 [8], among others. A survey of the literature reveals that there exist some stacking metallacrowns [9], a variety of dimers and also fused metallacrowns [10]. Metallacrowns can also be used as building blocks for the construction of two- or three-dimensional network structures [11]. Besides the structural interest, metallacrowns also exhibit some biological activities [12].

To design and synthesize azametallacrowns, *N*-acyl-substituted salicylhydrazide ligands have often been used; they can act as bifunctional ligands acting as *N*- and *O*-donors to the metallacrown ring metals, and the ring size and nuclearity of azametallacrowns can be controlled by the nature of the *N*-acyl substituent group [8a]. Though the synthesis and magnetic properties of metallacrowns constitute a developed research area, the study of further reactivity remains virtually unexplored.

The aim of this work was to synthesize a multinuclear cluster using the oxo-centered trinuclear iron(III) complex $[Fe_3(\mu_3\text{-}O)(Piv)_6(H_2O)_3(Piv)]$ (Piv = Bu^tCOO^-) [13] as a precursor and a potentially pentadentate pro-ligand, *N*-acetylsalicylhydrazide (H_3ashz), and study the reactivity of the cluster products. Herein we report the synthesis and reactivity study, towards N-donor Lewis bases, of an iron(III) 18-azametallacrown-6 compound derived from this pentadentate ligand.

The pro-ligand H_3ashz undergoes enolization in the presence of a metal ion in solution and can act as a tri-negative chelator being able to simultaneously encapsulate two metal ions into its two pockets, *A* and *B* (Scheme 1).

When H_3ashz reacts with $[Fe_3(\mu_3\text{-}O)(Piv)_6(H_2O)_3(Piv)]$ in ethanol at room temperature, the oxo-centered core of this precursor is destroyed and the highly stable iron(III) 18-azametallacrown-6, $[Fe(ashz)(EtOH)]_6$ (**1**) is formed. The meridional O,O,O-coordination of the ligand enforces the stereochemistry of the Fe^{3+} ions in a propeller configuration with alternating Λ/Δ forms, as known in the literature [14] for the methanol analogue $[Fe_6(ashz)_6(MeOH)_6]\cdot 8MeOH\cdot 2H_2O$, which was obtained by a route different from ours, upon reaction of ferric nitrate with H_3ashz.

The reactivity of **1** towards the heterocyclic N-donor Lewis bases (B = pyridine, 4-methyl pyridine, 3-amino pyridine and imidazole) was studied and the formation of the corresponding stable adducts

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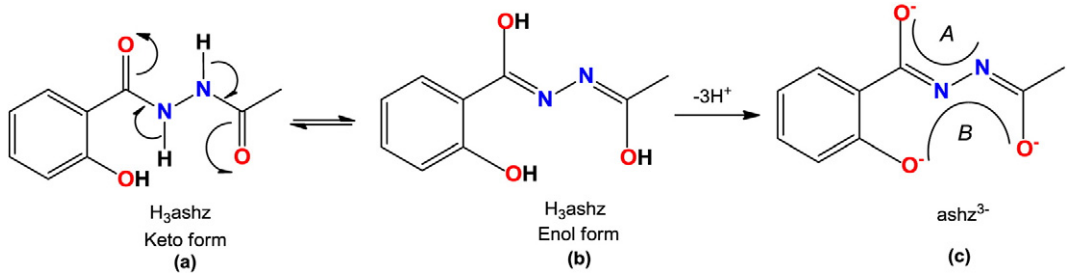


Scheme 1. Pro-ligand H_3ashz: keto form (a), enol form (b) and deprotonated form coordinated in a complex (c).

[Fe(ashz)(B)]$_6$ (**2-5**) was achieved (Scheme 2). The metallacrown complexes were characterized by elemental analysis, IR and ESI–mass spectroscopies and, in the cases of **1** and **4**, also by X-ray diffraction.

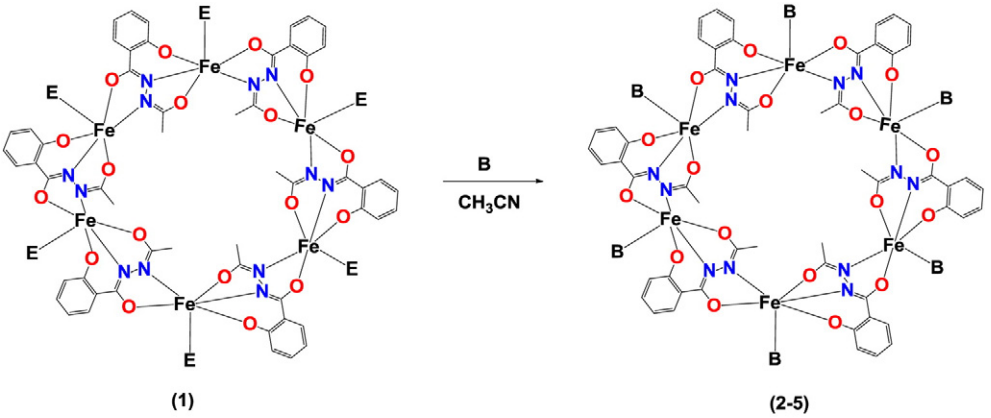
X-ray crystallographic studies have unequivocally confirmed the existence of hexanuclear neutral molecular hexagons of **1** and **4** with edge lengths Fe···Fe separation ranges of 4.863–4.883 Å (**1**) and 4.901–4.912 Å (**4**). Molecular structures and atom labeling schemes are illustrated in Figs. 1 and 2. Crystallographic data are summarized in Table 1 and selected dimensions are presented in SI, Table S1. In both compounds, the asymmetric unit contains only half of the cluster molecule and an inversion center is located in the middle of the macrocycle. The organic groups act as pentadentate $1\kappa^1N{:}\kappa^2O,2\kappa N{:}\kappa O$ chelators to the iron cations that rest in distorted octahedral N_2O_4 (**1**) or N_3O_3 (**4**) environments; therefore, each octahedral metal center has five donor atoms from two pentadentate ligands and the remaining site is occupied by an ethanol (**1**) or a 3-amino pyridine (**4**) molecule. The ligands, bridging the metal ions, enforce the stereochemistry of the Fe cations due to their type of coordination to the metal. Consequently, the chiralities of the metal centers in the clusters alternate between Λ and Δ forms generating a Λ,Δ,Λ (**1**) or a Δ,Λ,Δ (**4**) propeller configuration for the Fe1, Fe2, and Fe3 cations, respectively.

The N—N and C—N bond distances in the ashz^{-3} ligands are, in this order, formally single (*av*. 1.414 Å) and intermediate (*av*. 1.319 Å) between single and double bonds pointing to delocalization over the entire clusters. The Fe—O and Fe—N bond distances are in the 1.89–2.04 Å and 2.03–2.19 Å ranges, respectively. The longest metal–N bonds in **1** (*av*. 2.037 Å) concern the nitrogen atoms in *trans* position relative to the $O_{ethanol}$ molecules, while in **4** (*av*. 2.115 Å) such distances involve the nitrogen atoms in *trans* position relative to the $N_{pyridine}$ molecules.

While the π···π stacking interactions in both compounds are very weak (the shortest distance between centroids occurring in **1** or **4** is 3.983 or 4.073 Å, respectively), D—H···π type of interactions is important in the assembly and stability of the hexanuclear metal macrocyclic clusters, and involves not only oxygen but also carbon as donor (D) atoms engaging the aromatic rings and/or the metallacycles. For example, the former contacts can be as short as 2.54 Å (O40—H40H···*centroid*$_{Fe3-O3-C12-N3-N9}$, in **1**) and the latter 2.59 Å (C17—H17···*centroid*$_{C24>C29}$, in **1**) or 2.56 Å (C19—H19C···*centroid*$_{Fe2-O21-C21-C26-C27-N22}$, in **4**). The structures are further stabilized by intra- and intermolecular H-bond interaction, several involving carbon as donor atoms and with C—H···O separations as small as 2.731 Å (C19—H19···O13, in **1**) or 2.736 Å (C25—H25···O22, in **4**), being among the shortest H-bond contacts reported until now [15].

In summary, the reactions of the *N*-heterocyclic Lewis bases pyridine, 4-methyl pyridine, 3-amino pyridine and imidazole with the metallacrown iron(III) 18-azametallacrown-6 complex **1** in CH_3CN have been successfully carried out and yield stable adducts by replacing the loosely bound ethanol molecule. A structural comparison between the precursor **1** and the 3-amino pyridine adduct complex **4** reveals that both compounds have very stable coordinating modes of the ligand, and present propeller configurations with alternating Λ/Δ forms. In addition, stable hydrogen bond interactions are found between coordinated ethanol molecules and the phenolate oxygens of the ligands or non-coordinating solvent ethanol molecules in **1** and the amine group of the coordinated 3-aminopyridine with the phenolate oxygen of the ligand in **2**.

In these reactions, the metallacrown ring framework is preserved, but the replaceable solvent in the cluster metal centers, in principle,



Scheme 2. Reactivity of 18-azametallacrown-6 (**1**) towards several N-donor Lewis bases.