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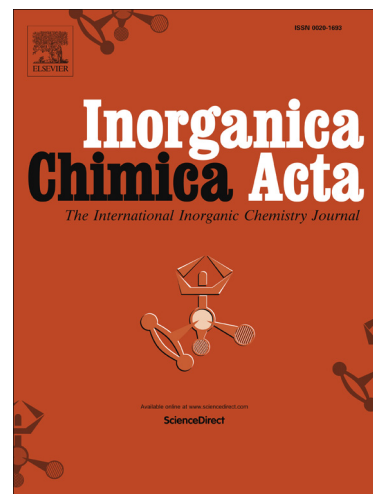
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Cytosine and 1-Methylcytosine Mg(II) complexes: structural insights on the reactivity of magnesium(II) toward nucleic acid constituents†

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Abstract. The synthesis and crystal structure of the compounds $[\text{Mg}(\text{H}_2\text{O})_6(1\text{-Mecyt})_2]\text{Br}_2$ (**1**), $[\text{Mg}(\text{cyt})_2(\text{H}_2\text{O})_4]\text{X}_2$, [X = Br (**2**), Cl (**3**)], $[\text{Mg}(\text{cyt})_4(\text{H}_2\text{O})_2]\text{X}_2$ [X = Br (**4**), Cl (**5**)], and $[\text{Mn}(\text{cyt})_4(\text{H}_2\text{O})_2]\text{Br}_2$ (**6**) (where 1-Mecyt = 1-Methylcytosine and cyt = cytosine) are reported. Compounds **1** consist of hexa-aquo cations, 1-Mecyt molecules and bromide anions self-assembled through an extended network of hydrogen-bonding interactions. Compound **2**, **3** and **4**, **5** are made of $[\text{Mg}(\text{cyt})_2(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Mg}(\text{cyt})_4(\text{H}_2\text{O})_2]^{2+}$ cations, with the cyt molecules directly coordinated to the metal centers through the O(2) atom. Compound **6** is isostructural to **4**, containing Mn(II) instead of Mg(II) ions. In compounds **2-6** the electro-neutrality is achieved by means of bromide (**2**, **4**, **6**) or chloride ions (**3**, **5**). When crystals of **2** and **3** were left in their mother solutions, they disappeared over time and crystals of different size and shape, corresponding to compounds **4** and **5**, respectively, appeared in their place.

Introduction

Many research efforts focused on metal ion-nucleic acid interactions and related crystallographic studies have experienced a rapid development over the last four decades.

Several works have been dedicated to the rational design, synthesis and detailed characterization of biomimetic systems based on the interaction of fragments or constituents of DNA, such as nucleobases and their derivatives, with a wide variety of metal ions.[1–10] There are two basic explanations to this. Firstly, it was crucial to clearly establish the binding mode of a specific nucleobase toward a metal ion, which mostly depends on the metal ion hardness/softness, the basicity of the donor site of the nucleobase and, of course, on auxiliary ligands coordinated to the metal center, if any.[7]

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