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Mn(II) complex of a di-2-pyridyl ketone-*N*(4)-substituted thiosemicarbazone: Versatile biological properties and naked-eye detection of Fe^{2+} and Ru^{3+} ions

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ABSTRACT

A novel manganese(II) complex of a di-2-pyridyl ketone *N*(4)-phenyl thiosemicarbazone (HL) was synthesized and characterized. Single crystal X-ray diffraction studies revealed that the asymmetric unit of the triclinic unit cell contained two independent $Mn(L)_2$ molecules together with two water molecules of crystallization and a DMF molecule. DNA binding studies of the ligand and its complex were conducted using absorption titrations, fluorescent intercalator displacement assays and viscosity measurements. Both the ligand and the complex were found to show good DNA binding abilities and actively displaced the standard intercalator ethidium bromide. In addition to the DNA binding studies, antimicrobial activities of the compounds were also determined and the complex exhibited higher antibacterial activity compared to the ligand HL. Another interesting property exhibited by the manganese complex was its colorimetric sensing, making it an excellent probe for naked-eye detection of Fe^{2+} and Ru^{3+} ions, with a visible color change from yellow to colorless. The recognition ability of the ions by the probe was quantitatively analyzed using a titration [ion]/[complex] ratio of 0–2.

1. Introduction

Manganese is regarded as one of the important trace elements and an essential biometal, working as the active centre of many enzymes. Manganese compounds, like Teslascan and SC-52608, are well known for their role in diagnostic and therapeutic fields [1]. The Mn(II) ion can provide antioxidant backup for Cu-SOD [2] and hydrated Mn(II) ions are able to interact with biomolecules like DNA. Some manganese complexes have shown remarkable antibacterial, anticancer and antifungal activities [3,4]. Mn(II) complexes are important in anticancer treatment, mainly because of their low toxicity compared to Pt(II) and Ru(II) complexes, but also due to their environmental friendliness and potentially fewer side effects [5,6]. As ligands, thiosemicarbazones are known to coordinate to metals in their neutral form or in the deprotonated form through NNS atoms, but there are few studies on the crystal structure features of Mn(II) complexes of N-(4)-substituted thiosemicarbazones [7,8]. Many thiosemicarbazones have been evaluated to have chemotherapeutic activities against a broad spectrum of tumors [9,10]. However, in spite of all the biological properties of Mn(II) ions, only a few reports have been published on their DNA interaction effects and nuclease activity, and much fewer about the bioactivity of Mn(II) thiosemicarbazone complexes [5,11–14]

Metal complexes are reported to interact with mammalian DNA either reversibly through covalent interactions or through irreversible interactions, notably intercalation which causes damage to the double helix, thereby inducing the apoptosis of cells [15–17]. In vitro studies to establish the activity of complexes towards cancer cell DNA are usually performed using titrations of complex solutions with that of DNA. The interactions are usually investigated by different techniques, like absorption and fluorescence titrations, viscosity, cyclic voltammetric measurements, time resolved infrared methods, circular dichroism, electrophoresis etc. [18,19]. These studies can reveal the mode of binding of the complexes to DNA, which is invaluable for the design and preparation of modified clinically active drugs.

The biological activity of complexes can further be established by antimicrobial studies, where the ability of complexes to inhibit the microbial growth in a culture can be tested and quantified. The activities against Gram negative (*Escherichia coli, Klebsiella,*

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