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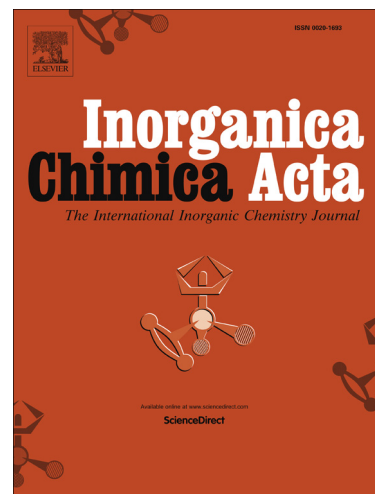
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# Manganese(II) complexes of tolfenamic acid or naproxen in polymeric structures or encapsulated in [15-MC-5] manganese(III) metallacrowns: Structure and biological activity

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## Abstract

The interaction of MnCl<sub>2</sub> with the non-steroidal anti-inflammatory drugs tolfenamic acid (Htolf) or naproxen (Hnap) in the presence of salicylhydroxamic acid (H<sub>3</sub>shi) leads to the formation of the hexanuclear mixed-valence Mn<sup>II</sup>Mn<sup>III</sup><sub>5</sub> clusters [Mn<sub>6</sub>(tolf)<sub>2</sub>(shi)<sub>6</sub>(py)<sub>6</sub>], **1** and [Mn<sub>6</sub>(nap)(Hsal)(shi)<sub>6</sub>(py)<sub>6</sub>], **2** (where H<sub>2</sub>sal = salicylic acid) which are characterized as 15-metallacrown-5 complexes accommodating the Mn(II) ion and the monoanionic carboxylato ligands tolf<sup>-1</sup>, nap<sup>-1</sup> and Hsal<sup>-1</sup>. The interaction of Mn(II) with deprotonated naproxen led to formation the polymeric Mn(II) complex [Mn(nap)<sub>2</sub>(CH<sub>3</sub>OH)]<sub>n</sub>, **3**. All three complexes were characterized by physicochemical and spectroscopic techniques and by single-crystal X-ray crystallography. The *in vitro* cytotoxic effects of the complexes were evaluated against three cancer cell lines (HeLa, MCF-7 and A549 cells) as well as their combinatory activity with the well-known chemotherapeutic drugs irinotecan, cisplatin, paclitaxel and 5-fluorouracil. The interaction of complexes **1-3** with calf-thymus (CT) DNA and bovine serum albumin (BSA) was investigated *in vitro* by diverse techniques. In addition, the cytotoxic activity of the previously reported polymeric complex [Mn(tolf)<sub>2</sub>(DMF)<sub>2</sub>]<sub>n</sub>, **4** was also investigated and its behavior towards CT DNA and BSA was compared to that of complexes **1-3**.

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