

Investigation of the Zinc Chloride / Methyl(2-pyridyl)ketone Oxime Reaction System: A Mononuclear Complex and an Inverse 12-Metallacrown-4 Cluster

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This paper is dedicated to the memory of Dimitris Katakis, Professor of Inorganic Chemistry in the Chemistry Department of the University of Athens

The reactions of methyl(2-pyridyl)ketone oxime, (py)C(Me)NOH, with zinc chloride have been investigated. An excess of the ligand in EtOH/MeCN affords the mononuclear complex [ZnCl₂{(py)C(Me)NOH}₂] (**1**) in moderate yield. The metal ion is coordinated by two chloro ligands and two *N,N'*-chelating (py)C(Me)NOH molecules. The six-coordinate molecule is the *cis-cis-trans* isomer considering the positions of the coordinated chlorine, pyridyl and oxime nitrogen atoms, respectively. The reaction between equimolar quantities of ZnCl₂, (py)C(Me)NOH and LiOH · H₂O in EtOH/MeCN leads to the tetranuclear cluster [Zn₄(OH)₂Cl₂{(py)C(Me)NO}₄] (**2**) in high yield. The molecule lies on a crystallographic inversion center and has an inverse 12-metallacrown-4 topology. Two triply bridging hydroxides are accommodated within the metallacrown ring. Each (py)C(Me)NO[−] ligand adopts the 2.111 coordination mode (Harris notation), chelating one Zn^{II} ion and bridging a Zn^{II}₂ pair. Two metal ions are in a distorted O₂N₄ octahedral environment, whereas the other two are in a severely distorted tetrahedral O₃Cl environment. Complex **2** joins a small family of structurally characterized zinc(II) metallacrown complexes. The IR data are discussed in terms of the nature of bonding and the structures of the two complexes.

Key words: Crystal Structures, Infrared Spectra, Inverse 12-Metallacrown Complexes,
Methyl(2-pyridyl)ketone Oxime Complexes, Zinc(II) Chloro Complexes