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## The structural study of metal complexes of bisphosphonate amide ester

Jonna Jokiniemi<sup>a</sup>, Eija Vuokila-Laine<sup>a</sup>,  
Jouko J. Vepsäläinen<sup>b</sup>, Sirpa Peräniemi<sup>b</sup>, Markku Ahlgrén<sup>a</sup>

<sup>a</sup>University of Joensuu, Department of Chemistry, P.O.Box 111, 80101 Joensuu, Finland. E-mail: Jonna.Jokiniemi@joensuu.fi <sup>b</sup>University of Kuopio, Department of Chemistry, P.O.Box 1627, 70211 Kuopio, Finland

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As a class of materials, metal phosphonates have been known for almost 30 years, but in recent years the research has expanded rapidly due to the important applications of metal bisphosphonate compounds in industrial processes such as ion-exchange, catalysis and sorption [1-3]. Recently, several metal complexes of clodronate, (dichloromethylene)-bisphosphonate, Cl<sub>2</sub>MBP, which is one of the best-documented bisphosphonates used effectively in medical applications, and its symmetrical dialkyl ester derivatives, have been prepared for studying the properties of solid materials [4]. The arrangement of metal complexes of bisphosphonates is dependent on the size of the organic group connected to the phosphonate groups, and also on the number of donor atoms of the ligand and on the degree of protonation of the phosphonate group [2]. In this study, a new, selective and simple method for the preparation of amide ester derivatives of Cl<sub>2</sub>MBP, has been developed. Four metal complexes of one of these synthesized ligands, P-piperidinium-P-methyl-(dichloromethylene)bis-phosphonate have been prepared in order to study the effect of the cyclic amine group on the complexing properties of the ligand and on the dimensionalities of its metal complexes. The compounds were crystallised by the gel method, and the structures of the complex crystals were characterized by single crystal X-ray diffraction methods, elemental analyses and thermal analyses. The methyl ester of piperidine derivative of Cl<sub>2</sub>MBP ligand forms the first wheel-like metal complex of bisphosphonate; the packing of the copper complex consist of channels occupied by aqua ligands and lattice water molecules. The complex, which has a unique hexameric structure, differs from rather common heptanuclear transition metal clusters such as Cu<sub>6</sub>Na, Co<sub>6</sub>Na, Fe<sub>6</sub>Na, Zn<sub>7</sub>, Mn<sub>7</sub> and Cu<sub>7</sub>, where the seventh metal ion occupies the central position as a cation template. The other three compounds are polymers; Mg, Zn and Cd complexes consist of one-dimensional chains with different composition. In addition, in the case of the zinc complex, the coordinated Na<sup>+</sup> cations hold the chains together forming a two-dimensional layered construction. Divalent metal cations are capable of forming different compounds with the methyl ester of piperidine derivative of clodronic acid. These kinds of structures provide new information about the ability of the amino derivatives of clodronic acid to form polymeric structures and microporous materials that can be utilized in chemical applications.

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## Synthesis, Crystal Structure and Spectral Studies of M(hsm)<sub>2</sub>(sac)<sub>2</sub> complexes (M=Cu, Ni and Cd)

Gökhan Kastan<sup>a</sup>, Hümeýra Pasaođlu<sup>a</sup>, Iclal Bulut<sup>b</sup>

<sup>a</sup>Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, TR-55139, Kurupelit, Samsun, Turkey <sup>b</sup>Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Chemistry, TR-55139, Kurupelit, Samsun, Turkey

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The mixed metal-saccharine (sac) complexes of histamine (hsm), M(hsm)<sub>2</sub>(sac)<sub>2</sub>, (M=Cu, Ni and Cd) have been synthesized and characterized by IR spectra and single crystal X-ray diffraction. The complexes crystallize in monoclinic P2<sub>1</sub>/c (for Cu and Cd) and triclinic P1̄ space groups. In all complexes the metal ions have a distorted octahedral coordination with two bidentate hsm ligands and with monodentate sac ligands (Fig. 1). The results of vibrational spectra are also supported by the crystallographic results. For all complexes the crystal packing is mainly stabilized by N-H...O type hydrogen bonds. Among these, the Ni(hsm)<sub>2</sub>(sac)<sub>2</sub> complex has also shown a polymeric structure constructed by N-H...O hydrogen bond.

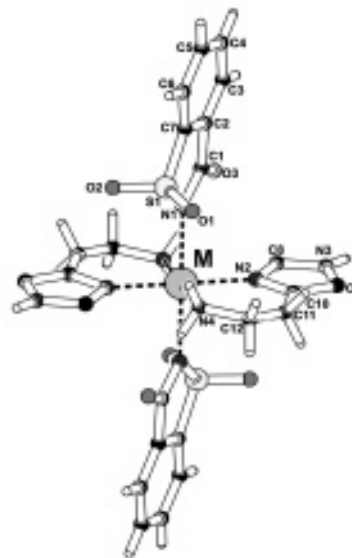


Figure 1. Perspective view and atom labeling scheme of M(hsm)<sub>2</sub>(sac)<sub>2</sub> complexes.