

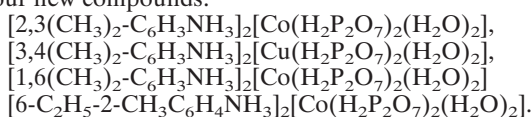
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## Crystal Chemistry and Structure of $M^{II}$ Organic Diphosphate Hydrates ( $M^{II} = \text{Co}, \text{Cu}$ )

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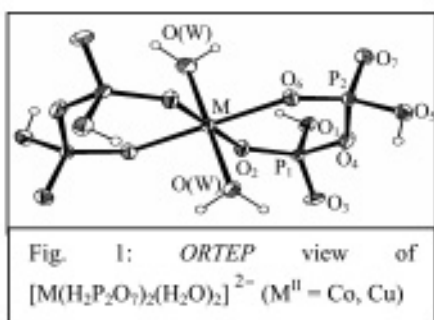
**Keywords:** organic-inorganic hybrid materials, crystal structure, transition-element compounds

Synthesis of inorganic-organic hybrid phosphates template by transition metal continues to be a focus subject in chemistry and material science for their great potential applications in diverse areas, such as magnetism, luminescence, non-linear optic [1-3]. In these compounds, the transition metal seems to play a key role in the richness of the structural chemistry. During the study of  $M^{II}$ -organic-diphosphate systems, we have isolated four new compounds:



Crystal preparation and structures are reported here. Their isotypical atomic arrangement can be described by inorganic layers  $[\text{M}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]_n^{2n-}$ , parallel to the *ab* plane, and built up from the transition metal  $M^{II}$  (Co, Cu), the diphosphate anions  $\text{H}_2\text{P}_2\text{O}_7^{2-}$  and the water molecules. The organic cations are displayed in the inter-layer spaces by establishing H-bonds, to successfully participate with electrostatic and Van der Waals interactions to the cohesion of the network.

In these structures, the coordination polyhedra of  $M^{II}$  (Co, Cu) are slightly distorted  $\text{MO}_6$  octahedra, located around the inversion centres. Four corners are oxygen atoms of diphosphate anions,  $\text{H}_2\text{P}_2\text{O}_7^{2-}$ , and the remaining corners are oxygen atoms of the water molecules. The diphosphate group acts as a bidentate ligand to  $M^{II}$ , thus producing a fairly bent  $\text{P}_2\text{O}_7$  group. An ORTEP view of the  $[\text{M}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]^{2-}$  complex anion is depicted in Fig. 1.



[1] A. K. Cheetham, G. Férey, and T. Loiseau, *Angew. Chem.* 38 (1999) 3268-3292.

[2] S. Natarajan, *Indian Acad. Sci. (Chem. Sci.)*, 112 (2000), 249-272.

[3] C N R RAO, *Indian Acad. Sci. (Chem. Sci.)*, 113 (2001), 363-374.

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## Crystal chemical Role of Oxalate and Malonate Ions

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Crystal chemical analysis of oxalate and malonate ions role in inorganic and coordination compounds was carried out. More than 800 oxalates and 100 malonates became the object of our investigation. The primary structure information was selected from the Cambridge Structural Database [1] and Inorganic Crystal Structure Database [2]. Coordination numbers of all atoms were determined by intersected spheres method included in the TOPOS package [3].

The compounds under discussion contain 1400 oxalate and 151 malonate crystallographically different ions. The oxalate and malonate ions can be mono-, bi-, three- and tetradentate ligands with respect to metal atoms. These anions show 15 and 11 coordination types. Bidentate cyclic coordination type is most extended. In that case oxalate and malonate ions form pentagonal and hexagonal cycles with metal atom, respectively. Note that the malonate ions form quadrangle cycle with metal atom more often than oxalate ions.

Dihedral angle ( $\varphi$ ) between both carboxy-groups is equal to  $0^\circ$  in the oxalic acid molecule; on the other hand it amounts to  $95^\circ$  in the malonic acid molecule. The average values  $\varphi$  are equal to  $4(6)^\circ$  and  $41(18)^\circ$  for oxalate and malonate ions, respectively. In this connection the influence of coordination type of  $\text{C}_2\text{O}_4^{2-}$  and  $(\text{CH}_2)\text{C}_2\text{O}_4^{2-}$  on its geometric features was discussed in details. It was discovered that some oxalate-containing compounds have  $\varphi = 90^\circ$ . The reason of non-planar structure for oxalate ions is the coordination type when anion does not form pentagonal cycles with metal or hydrogen atoms. Value of dihedral angle in malonate ions changes from  $6$  to  $90^\circ$ .

The coordination influence on the anion geometry was considered. The basic characteristics of Voronoi-Dirichlet polyhedron of the carbon and oxygen atoms were determined.

[1] Cambridge structural database system. November 2005 Release.

[2] Inorganic crystal structure database. FIZ Karlsruhe & NIST Gaithersburg. 2005.

[3] Blatov V.A., Shevchenko A.P. & Serezhkin V.N. // *Russ. J. Coord. Chem.* 1999. V. 25. N° 7. P. 453 - 456.