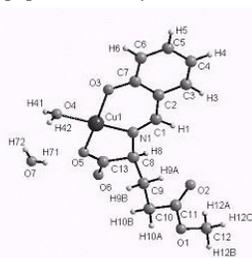


CRYSTAL AND ELECTRONIC STRUCTURE OF AQUA(N-SALICYLIDENE-METHYLESTER-L-GLUTAMATO)Cu(II) MONOHYDRATE

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The crystal structure of aqua(N-salicylidene-methylester-L-glutamato)copper(II) monohydrate has been determined. The structure was refined by SHELXL-97 to R = 0.0344 for 5318 unique reflections taken at the temperature 183 K, 229 parameters being refined. The crystal structure consists of the molecular units [Cu(N-sal-5-met-L-glu)(H₂O)] connected by three dimensional network of hydrogen bonds. The coordination polyhedron in the complex is approximately square-pyramidal with the pentacoordinated Cu(II) atom. The base of the pyramid is formed by the phenolic O3, carboxylic O5 and azometine N1 atoms of the Schiff-base anion and by O4 atom of the water molecule. The apex of the pyramid contains weakly bonded O6 atom of the carboxylic group of another molecule. The base of the pyramid bond distances are 1.9267(14), 1.9492(14), 1.9312(16) and 1.9715(14) Å, respectively. The apical bond length is 2.3929(15) Å. The quantum chemical calculations of the electron structure were done by Gaussian98 program package using B3LYP/SVP method and basis set. The calculation of Mulliken population analysis, and contributions of individual atomic orbitals to Cu-O



and Cu-N bonds were done for doublet as the most stable multiplet state. Calculated bond populations indicated that while the bonds Cu1 to O3, N1 and O5 are almost equivalent (0.211, 0.228, 0.201|e|, respectively), the Cu1-O4 bond is significantly weaker (0.137|e|). Synthesis and structure determination of title compound was stimulated due to found antimicrobial activities of Cu(II) complexes containing Schiff - bases derived from salicylaldehyde and L-glutamic acid as well as its methyl and ethylesters.

Keywords: Cu(II) COMPLEX SCHIFF BASE B3LYP

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STRUCTURE AND BIOLOGICAL ACTIVITY OF Zn(II) COMPLEX WITH TRIS(BENZIMIDAZOL-2-YLMETHYL)AMINE(NTB) LIGAND

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Since the structures of superoxide dismutase (SOD) exhibit that most of the coordinated atoms around metal ions are from imidazole groups of histidines which are the primary ligands in distorted coordination geometry [1-2], an important step should be to design to synthetic models of SOD in which ligands should contain imidazole groups. In order to elucidate the properties of SOD model compounds, a new Zn (II) mononuclear complex with NTB was synthesized with stoichiometry of ZnNTB 2(NO₃) dipy dmf (dipy: 4,4-dipyridyl). The complex was characterized with element analysis, UV and IR spectra. The crystal structure was determined using X-ray diffraction method. A total of 7975 reflections were collected on a Bruker AXS Smart-1000 CCD diffractometer. 4844 observed reflections were used in the structure analysis and refinements with 514 variables. The structure was solved by direct and fourier synthesis method. The crystallographic parameters are as follows : C₃₇H₃₆N₁₂O₇Zn, a = 9.856(3), b = 12.655(4), c = 15.965(5) Å, α = 81.714(5), β = 76.601(5), γ = 81.504(5)°, Z = 2, F(000) = 856, space group P-1, R = 0.0424, wR = 0.0936, S = 1.013. The crystal structure indicates that four N atoms and one O atom coordinate to Zn (II) ion to construct a distorted trigonal-bipyramid configuration. The activity assay shows that this complex with Bipy presents certain biological activity.

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Keywords: Zn(II) COMPLEX CRYSTAL STRUCTURE BIOLOGICAL ACTIVITY

STRUCTURAL DIVERSITY OF COPPER(II) CARBOXYLATES WITH 4-AMINOPYRIDINE

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Reactions of copper(II) carboxylates with 4-aminopyridine (4-apy) were investigated and their products structurally characterized by single crystal X-ray diffraction. Reaction of Cu(II) acetate resulted in two isomers of the composition Cu(acetate)₂(4-apy)₂ with markedly different stability: the violet form - unstable in air and the blue - stable form. In both isomers the ligands are arranged around the copper atom in a *trans* mode. The 4-apy ligands lie almost in the plane in the violet form, while they are twisted with respect to each other in the blue form. Variations were observed also in the coordination of the acetate groups to the copper ion.

Monomeric complexes of the same stoichiometry were obtained also by the reaction of Cu(II) hexanoate (hex) and heptanoate (hep) with 4-apy. The violet Cu(hex)₂(4-apy)₂, and Cu(hep)₂(4-apy)₂, are isostructural and possess *trans* geometry of the ligands around the copper centre.

Reaction of 4-apy with Cu(II) octanoate lead to a formation of a novel, unprecedented basic centrosymmetric tetranuclear compound of composition Cu₄(oct)₆(OH)₂(4-apy)₂. Molecule contains bidentate bridging and monoatomic bridging carboxylate groups, triply bridging hydroxyl groups and 4-aminopyridine as a terminal ligand. In all five compounds 4-apy is coordinated through endocyclic nitrogen atom only.

Keywords: COPPER(II) COMPLEXES CARBOXYLATES AMINOPYRIDINE

THE X-RAY INVESTIGATION OF CO(III) DIOXIMATE COMPLEXES WITH BF₄⁻ OR CF₃SO₃⁻ ANIONS

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An investigation of Co(III) dioximate complexes, has shown that the reaction conditions play a determining role on their composition, structure and biological properties. X-ray analysis of five new Co(III) dioximates, with tetrafluoroborate and triflate anions, [Co(DH)₂(NH₃)₂]BF₄, [Co(MH)₂(Thio)₂]BF₄, [Co(NioxH)₂(Py)₂]2[4]₂, [Co(DH)₂(Thio)₂]CF₃SO₃ and [Co(DH)₂(Py)₂]CF₃SO₃, indicates that the metal has a normal octahedral environment. The 4-N equatorial plane (eq), formed by two residues of (DH), (MH) and (NioxH) (DH₂ dimethylglyoxime, MH₂ methylglyoxime and NioxH₂ nioxime), are coplanar within 1.2-1.6°. The mean Co-N_{eq} distance is 1.886 Å. The apical positions of the polyhedron are occupied by the nitrogen and sulphur atoms of the NH₃, Thio or Py ligands. The mean Co-N(NH₃), Co-S(Thio) and Co-N(Py) distances are 1.964, 2.281 and 1.963 Å, respectively. The DH ligands are linked by two O-H...O intramolecular hydrogen bonds, mean O...O distance of 2.52 Å. The nature of the equatorially coordinated ligand, or the different neutral ligands in the *trans* positions, does not change the configuration of the complex cation. Biological tests indicate that the tetrafluoroborate complexes have a much stronger influence on the enzymatic activity of the genera *Aspergillus niger* 33, as an amylase producer, compared to the triflate complex.

Keywords: COMPLEX, ANION, HYDROGEN BOND