SUPPLEMENTARY MATERIAL TO

**Synthesis, crystal structure and biological activity of copper(II) complex with**

**4-nitro-3-pyrazolecarboxylic ligand**

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*Results of CSD search*

*Cu(II) complexes with the unsubstituted 3-pyrazolecarboxylato ligands*.In the case of Cu(II) complexes with the parent 3-pyrazolecarboxylato ligand, the CSD search reveals mononuclear (CSD refcode: DABRUW1), binuclear (CSD refcodes: BEQGIQ2, BOYBOI3, RUNXOO4 and OJUKOU5) and polynuclear complexes (CSD refcodes: BOYBUO3, LAGNIT6, QOFLAA7); only in mononuclear DABRUW1 the Cu(II) is found in an octahedral coordination environment. In all binuclear complexes the Cu(II) is placed in a square pyramidal coordination environment, where fully deprotonated ligands bridge and chelate the pair of Cu(II) centers to form the square base of a polyhedron. Among these complexes the binuclear BEQGIQ complex, can be considered as a five-coordinated analogue of the title octahedral complex, with one axial H2O ligand less in Cu(II) coordination sphere.2

In general, regardless of different coordination geometry the binuclear, octahedral [Cu2(4-nitro-3pc)2(H2O)6]·2H2O complex and the extracted square pyramidal 3-pyrazolecarboxylato Cu(II) complexes exhibit number of common features. All complexes are characterized by the similar, approximately flat ring system composed of six-membered ring and five-membered chelate rings placed in the base plane of a polyhedron. The N1–Cu–O1 bite angle of chelating pz ligand shows small variation, from 81.1 in RUNXOO4 (where square base is completed by imidazole ligand) to 82.5° in OJUKOU5 (square base is completed by DMSO ligand). In title octahedral complex the pz ligand bite angle is 81.24(5)°. In all cases, the pyrazolecarboxylato ligand is characterized by an asymmetrical coordination which is mainly reflected in dissimilar Cu1–N1–N2 and Cu1–N2–N1 angles of the central, six membered ring. The difference between two angles ranges form 13.9 in RUNXOO4 to 16.8° in BEQGIQ.2 In title octahedral complex this difference is 12.8°.

In comparison to [Cu2(4nitro-3pzc)2(H2O)6]·2H2O the Cu–N1 and Cu–N2 coordination bonds in analogue square pyramidal BEQGIQ are notably shorter (1.952 and 1.962 Å), while Cu–O has similar length (1.990 Å). Such bond distribution may be responsible for the above mentioned increased difference between Cu1–N1–N2 and Cu1–N2–N1 angles of BEQGIQ in comparison to [Cu2(4nitro-3pc)2(H2O)6]·2H2O. The Cu–N coordination bonds in square pyramidal complexes show considerable variation in lengths which seems to depend of the size of additional equatorial ligand. Thus in BOYBOI3 and RUNXOO4, which contain pyridine and imidazole ligand respectively, the bonds are longer than those in [Cu2(4nitro-3pc)2(H2O)6]·2H2O (Cu–N1 and Cu–N2 lengths: 1.974 and 1.983 in BOYBOI, while 1.970 and 1.984 in RUNXOO). The described redistribution of bond distances and angles suggests that the rigid 3-pyrazolecarboxylato ligand displays considerable adjustments in coordination in order to preserve approximately planar form of the condensed ring system. Sum of the angles in each central six-membered ring is very close to 720° of an ideal hexagon.

*Octahedral binuclear complexes with 3-pyrazolecarboxylato ligands***.** In recently reported crystal structures of [Co2(4-nitro-3pc)2(H2O)6]·2H2O8 and [Ni2(3pc)2(H2O)6]·2H2O complexes (refcode: LAGNOZ)6 the corresponding metal ions were found in the octahedral coordination environment, equivalent to that of Cu(II) in [Cu2(4nitro-3pc)2(H2O)6]·2H2O. The corresponding M–N coordination bond distances increase from those in Cu(II) complex [1.971(1) and 1.972(1) Å] to Ni(II) [2.039 and 2.024 Å] and Co(II) [2.0729 (7) and 2.0679 (7) Å] complexes. The N2–M–O1 bite angle shows opposite trend [81.24(5), 79.3 and 76.55(3)°], as well as the distance to the axial water ligand [2.47, 2.15 and 2.12 Å in average in Cu, Ni and Co complex, respectively]. Somewhat different octahedral surrounding was found for Zn(II) in the mixed ligand complex [Zn2(3pc)2(bipy)(H2O)]·2H2O [refcode XORVUX].9 Coordinated next to bipyridine ligand, the pz bridge forms M–N bonds of comparable lengths to above complexes [2.063 and 2.079 Å]. It is interesting to notice that the crystal packing of each octahedral complex is characterized by the presence of solvent water molecules which significantly influence the hydrogen bonding pattern. Nevertheless, each crystal structure is dominated by the similar O–H...O hydrogen bonding motif where two coordinated water donors interact with the pair of carboxyl O acceptors and directly bond the complex units.

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