



SUPPLEMENTARY MATERIAL TO  
**Synthesis, crystal structure and biological activity of a  
copper(II) complex with a 4-nitro-3-pyrazolecarboxylic  
ligand**

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RESULTS OF CSD SEARCH

*Cu(II) complexes with unsubstituted 3-pyrazolecarboxylato ligands*

In the case of Cu(II) complexes with the parent 3-pyrazolecarboxylato ligand, the CSD search revealed mononuclear (CSD refcode: DABRUW<sup>1</sup>), binuclear (CSD refcodes: BEQGIQ,<sup>2</sup> BOYBOI<sup>3</sup> and RUNXOO<sup>4</sup>) and polynuclear complexes (CSD refcodes: BOYBUO,<sup>3</sup> LAGNIT,<sup>5</sup> QOFLAA<sup>6</sup>). Only in the mononuclear DABRUW<sup>1</sup> is the Cu(II) 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) centres 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 H<sub>2</sub>O ligand less in Cu(II) coordination sphere.<sup>2</sup>

In general, regardless of the different coordination geometry, the binuclear, octahedral [Cu<sub>2</sub>(4-nitro-3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]2H<sub>2</sub>O complex and the extracted square pyramidal 3-pyrazolecarboxylato Cu(II) complexes exhibit a number of common features. All complexes are characterized by a similar, approximately flat ring system composed of a six-membered ring and five-membered chelate rings placed in the base plane of a polyhedron. The N1–Cu–O1 bite angle of the

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chelating pz-ligand shows small variation, from 81.1 in RUNXOO (where square base is completed by an imidazole ligand) to 82.5° in OJUKOU (the square base is completed by a DMSO ligand). In the 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 the dissimilar Cu1–N1–N2 and Cu1–N2–N1 angles of the central, six membered rings. The difference between the two angles ranges from 13.9 in RUNXOO<sup>4</sup> to 16.8° in BEQGIQ.<sup>2</sup> In the title octahedral complex, this difference is 12.8°.

In comparison to [Cu<sub>2</sub>(4nitro-3pzc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O, the Cu–N1 and Cu–N2 coordination bonds in the analogue square pyramidal BEQGIQ are notably shorter (1.952 and 1.962 Å), while the Cu–O bond has a similar length (1.990 Å). Such bond distribution may be responsible for the above-mentioned increased difference between the Cu1–N1–N2 and Cu1–N2–N1 angles of BEQGIQ in comparison to [Cu<sub>2</sub>(4nitro-3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O. The Cu–N coordination bonds in square pyramidal complexes show considerable variation in lengths, which seems to depend of the size of the additional equatorial ligand. Thus, in BOYBOI<sup>3</sup> and RUNXOO,<sup>4</sup> which contain a pyridine and imidazole ligand, respectively, the bonds are longer than those in [Cu<sub>2</sub>(4nitro-3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O (Cu–N1 and Cu–N2 lengths: 1.974 and 1.983 in BOYBOI, while they are 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 the approximately planar form of the condensed ring system. The sum of the angles in each central six-membered ring is very close to the 720° of an ideal hexagon.

#### *Octahedral binuclear complexes with 3-pyrazolecarboxylato ligands*

In recently reported crystal structures of [Co<sub>2</sub>(4-nitro-3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O<sup>7</sup> and [Ni<sub>2</sub>(3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O complexes (refcode: LAGNOZ)<sup>5</sup> the corresponding metal ions were found in an octahedral coordination environment, equivalent to that of Cu(II) in [Cu<sub>2</sub>(4nitro-3pc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>H<sub>2</sub>O. The 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 the 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 on average in the Cu, Ni and Co complex, respectively]. A somewhat different octahedral surrounding was found for Zn(II) in the mixed ligand complex [Zn<sub>2</sub>(3pc)<sub>2</sub>(bipy)(H<sub>2</sub>O)]<sub>2</sub>H<sub>2</sub>O [refcode XORVUX].<sup>8</sup> Coordinated next to bipyridine ligand, the pz-bridge forms M–N bonds of comparable lengths to the above complexes [2.063 and 2.079 Å]. It is interesting that the crystal packing of each octahedral complex is characterized by the presence of a solvent water molecule that significantly influences the hydrogen-bonding pattern. Nevertheless, each

crystal structure is dominated by a similar O–H···O hydrogen-bonding motif in which two coordinated water donors interact with the pair of carboxyl O acceptors and directly bond the complex units.

TABLE S-I. Crystal data, data collection and refinement details

Chemical formula	[Cu <sub>2</sub> (4nitro-3pzc) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]2H <sub>2</sub> O
Temperature, K	200
<i>Mr</i>	290.68
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)
<i>a</i> / Å	10.181(2)
<i>b</i> / Å	6.447(1)
<i>c</i> / Å	14.451(3)
$\beta$ / °	93.35(3)
<i>V</i> / Å <sup>3</sup>	946.9(3)
Crystal size, mm <sup>3</sup>	0.10 × 0.10 × 0.15
Reflections collected / unique	5485 / 2877
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2692
<i>R</i> <sub>int</sub>	0.0117
<i>R</i> -indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0215, <i>wR</i> <sub>2</sub> = 0.0578
<i>R</i> -indices (all data)	<i>R</i> <sub>1</sub> = 0.0240, <i>wR</i> <sub>2</sub> = 0.0588
Goodness-of-fit, <i>S</i>	1.068
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ / e Å <sup>-3</sup>	0.453, -0.473

TABLE S-II. FTIR ATR band positions and band assignments for [Cu<sub>2</sub>(4nitro-3pzc)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]2H<sub>2</sub>O. References used are given in the text.  $\nu$  = stretching,  $\delta$  = deformation in-plane bending,  $\gamma$  = out-of-plane bending, sh = shoulder, pz = pyrazole ring,  $\omega$  = ring stretching (N–N, N–C, C–C)

Band position, cm <sup>-1</sup>	Band assignment
3507	pz $\nu$ (N–H), $\nu$ (H <sub>2</sub> O)
3234 ( $\approx$ 2800–3600)	$\nu$ (H <sub>2</sub> O)
3157	pz $\nu$ (C–H), $\nu$ (H <sub>2</sub> O)
$\approx$ 1675 sh	$\nu$ (C=O)
1604	$\delta$ (H <sub>2</sub> O)
1535	pz $\omega$
1506	$\nu$ (NO <sub>2</sub> ) <sub>antisym.</sub>
1461	pz $\omega$
1401, 1391	pz $\omega$
1354	$\nu$ (NO <sub>2</sub> ) <sub>sym.</sub>
1298	$\nu$ (C–O)
1207	pz $\delta$ (C–H), $\omega$
1137, 1110	pz $\omega$
1007	pz $\delta$ (C–H), $\omega$
858	$\delta$ (NO <sub>2</sub> )
806	$\delta$ (O=C–O)
750	pz $\gamma$ (C–H)

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