Electronic Supplementary Data

DNA cleavage activity and cytotoxicity of mononuclear and trinuclear Cu(II) complexes containing 1H-pyrazole-3,5-dicarboxylic acid as ligand

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Synthetic method and characterization of complexes (1) and (2).

Synthesis of complex \([\text{Cu}(\text{H}_2\text{pdc})_2(\text{H}_2\text{O})_2]\) 1

A solution of \(\text{H}_3\text{pdc}\) (0.184g, 1.00 mmol) in water and methanol containing NaOH (0.040 g, 1.00 mmol) was added to a solution of \(\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}\) (0.242 g, 1.00 mmol) in water (5.0 mL). The reaction mixture was then heated at 90°C for 12 h. Rectangular shaped blue crystals were isolated. Yield: 54%, M.P. 220°C, elemental analysis calculated for \(\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_{12}\text{Cu}\) (%): C, 26.94; H, 3.17; N, 12.57. Found (%): C, 27.09; H, 3.25; N, 12.18. IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1}\) 3436 (OH, H\(_2\)O), 3086 (CH, Ph), 1704 (COO\(^{-}\) uncoordinated), 1636 \(\nu_{\text{as}}\)(COO\(^{-}\) coordinated), 1461 \(\nu_{\text{s}}\)(COO\(^{-}\) coordinated). UV-vis. absorptions: \(\lambda_{\text{max}}\) (DMSO, 10\(^{-4}\)M/nm \(\varepsilon\times10^{-4} / \text{M}^{-1} \text{cm}^{-1}\)) 239 (1.29) and 652 (0.009).

Synthesis of complex \([\text{Cu}_3(\text{pdc})_2(\text{bpy})_2(\text{H}_2\text{O})_2]\) 2

A solution of \([\text{Cu(bpy)}(\text{NO}_3)_2]\)· 2\(\text{H}_2\text{O}\) (0.365g, 1.00 mmol) in water (5.0 mL) was added to an alkaline solution of \(\text{H}_3\text{pdc}\) (0.087g, 0.5 mmol) in methanol:water (1:4 ml). It was then heated at 90°C for 3 h. Cuboidal crystals of green colour were isolated and washed with hexane. Crystals were soluble in hot DMSO. Yield: 43%, M.P. >230 °C, elemental analysis calculated for \(\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_{12}\text{Cu}_3\) (%): C, 40.89; H, 2.97; N, 12.72. Found (%): C, 41.00; H, 3.07; N, 12.31. R (KBr): \(\nu_{\text{max}}/\text{cm}^{-1}\) 3440 (OH, H\(_2\)O), 3033 (CH, Ph), 1649 \(\nu_{\text{as}}\)(COO\(^{-}\) uncoordinated), 1603 (2, 2’ bpy), 1429 \(\nu_{\text{s}}\)(COO\(^{-}\) coordinated). UV-vis. absorptions: \(\lambda_{\text{max}}\) (DMSO, 10\(^{-5}\)M/nm \(\varepsilon\times10^{-4} / \text{M}^{-1} \text{cm}^{-1}\)) 241 (2.9), 301 (2.3) and 666 (0.019). Complex 2 was reported earlier, by the reaction of \(\text{Cu(ClO}_4)_2\cdot6\text{H}_2\text{O}\), \(\text{H}_3\text{pdc}\), 2,2’-bpy, \(\text{Et}_3\text{N}\) in stainless steel reactor with Teflon liner at 160°C [1]. This method clearly follows difficult route and raises the possibility of purification and explosion too as perchlorate salts are generally explosive on heating. Therefore present synthetic route was found easy and also it avoid of explosion if any during the reaction.

Synthesis of complex \([\text{Zn}(\text{H}_2\text{pdc})_2(\text{H}_2\text{O})_2]\) 3

The reaction condition for the synthesis of complex 3 was similar to that used for the synthesis of complex 1 except that \(\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}\) was used in place of \(\text{Cu(NO}_3)_2\cdot6\text{H}_2\text{O}\). Hexagonal tiny white crystals were isolated and washed with diethyl ether. Crystals were found insoluble in common organic solvents. Yield: 54%, M.P. 220 °C, elemental analysis calculated for \(\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_{12}\text{Zn}\) (%): C, 40.44; H, 2.05; N, 15.73. Found (%): C, 41.24; H, 2.17; N, 16.21. UV-vis. absorptions: \(\lambda_{\text{max}}\) (solid state)/nm 301. IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1}\) 3436 (OH, H\(_2\)O), 3077 (CH, Ph), 1701 (CO), 1633 \(\nu_{\text{as}}\)(COO\(^{-}\) coordinated), 1465 \(\nu_{\text{s}}\)(COO\(^{-}\) coordinated).

Reference
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Table S1  – Parameters of weak interactions

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<th>D-H···A</th>
<th>D-H (Å)</th>
<th>H···A (Å)</th>
<th>D···A (Å)</th>
<th>DHA (°)</th>
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