Supplementary Data

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Copper(II) Complexes with 2NO and 3N Donor Ligands: Synthesis, Structures and Chemical Nuclease and Anticancer Activities

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Synthesis of Ligands

All the six ligands L1 - L6 were prepared using known procedures, which involve the reaction of salicylaldehyde, 5-methylsalicyaldehyde, pyridine-2-carboxaldehyde, imidazole-2-carboxaldehyde, and quinoline-2-carboxaldehyde with 2-aminoethylbenzimidazole hydrochloride and 2-aminoethylpyridine to form Schiff bases. 2-Aminoethylbenzimidazole dihydrochloride[41] was prepared according to methods reported in the literature.

Synthesis of 2-(2-(1*H*-benzimidazol-2-yl)ethyliminomethyl)phenol H(L1)

This ligand was synthesized by reported procedure.[42] 2-Aminoethylbenzimidazole dihydrochloride (1.35 g, 5 mmol) dissolved in water (20 ml) was added with stirring to aqueous K_2CO_3 solution (0.83 g, 6 mmol). A solution of salicylaldehyde (0.610 g, 5 mmol) in methanol (10 ml) was then added dropwise to this solution over 1 h. During this period, yellow colored solid H(L1) separated out slowly. The solid was filtered off, washed thoroughly with water and then dried in vacuum at room temperature. It was finally recrystallized from methanol. Yield: 1.06 g (80%).

Synthesis of 2-(2-(1*H*-benzimidazol-2-yl-ethylimino)methyl)-4-methylphenol H(L2)

2-Aminoethylbenzimidazole dihydrochloride (1.35 g, 5 mmol) dissolved in water (20 ml) was added with stirring to aqueous K_2CO_3 solution (0.83 g, 6 mmol). A solution of 5-methyl-salicylaldehyde (0.680 g, 5 mmol) in methanol (10 ml) was then added dropwise to this solution over 1 h. During this period, yellow colored solid H(L2) separated out slowly. The solid was filtered off, washed thoroughly with water and then dried in vacuum at room temperature. It was finally recrystallized from methanol. Yield: 1.12 g (81%).

Synthesis of (2-pyridin-2-yl-ethyl)pyridin-2-ylmethyleneamine L3

This ligand was synthesized by reported procedure[43] by treating 2-aminoethylpyridine (0.61 g, 5 mmol) with pyridine-2-carboxaldehyde (0.535 g, 5 mmol) and stirring the reaction mixture for 18 h and the solvent removed under reduced pressure. The product L3 obtained as pale yellow oil was used without further purification for isolation of the copper(II) complex. Yield: 0.84 g (80%).

Synthesis of 2-(1*H*-benzimidazol-2-yl)ethyl)pyridin-2-ylmethyleneamine L4

This ligand was synthesized by reported procedure[44] by treating 2-Aminoethylbenzimidazole dihydrochloride (1.35 g, 5 mmol) dissolved in water (20 ml) was added with stirring to aqueous K_2CO_3 solution (0.83 g, 6 mmol). A solution of pyridine-2-carboxaldehyde (0.535 g, 5 mmol) in methanol (10 ml) was then added dropwise to this solution over 1 h. During this period a colorless solid L4 separated out slowly. The solid was filtered off, washed thoroughly with water and dried in vacuum at room temperature. It was finally recrystallized from methanol. Yield: 0.93 g (75%).

Synthesis of 2-(1*H*-benzimidazol-2-yl)ethyl)(1*H*-imidazol-2-ylmethylene)amine L5

The ligand L5 was prepared by the same method adopted for the preparation of L4 except that imidazole-2-carboxaldehyde (0.48 g, 5mmol) was used instead of pyridine-2-carboxaldehyde.Yield: 0.87 g (73%).

Synthesis of 2-(1*H*-benzimidazol-2-yl)ethyl)-(4,4a-dihydroquinolin-2-ylmethylene)- amine L6

The ligand L6 was prepared by the same method adopted for the preparation of L4 except that quinoline-2-carboxaldehyde (0.79 g, 5 mmol) was used instead of pyridine-2-carboxaldehyde.Yield: 1.05 g (70%).

Synthesis of Complexes

Synthesis of [Cu(L1)Cl] 1

A methanolic solution (10 ml) of copper(II) chloride dihydrate (0.17 g, 1 mmol) was added to a solution of H(L1) (0.265 g, 1 mmol) in methanol with constant stirring. Green color clear solution was obtained. Single crystals suitable for X-ray diffraction was obtained by slow evaporation of the complex in methanol:acetonitrile solvent mixture. Yield: 0.290 g (84%). Anal. Calcd for $CuC_{16}H_{14}N_3ClO$: C, 52.90; H, 3.88; N, 11.57. Found: C, 52.76; H, 3.84; N, 11.52%. ESI-MS m/z = 327 $[Cu(L1)]^+$.

Synthesis of [Cu(L2)Cl] 2

A methanolic solution (10 ml) of copper(II) chloride dihydrate (0.17 g, 1 mmol) was added to a solution of H(L2) (0.279 g, 1 mmol) in methanol with constant stirring. A clear green colored solution was obtained. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanolic solution of the complex. Yield: 0.320 g (85%). Anal. Calcd for $CuC_{17}H_{16}N_3ClO$: C, 54.11; H, 4.27; N, 11.14. Found: C, 53.97; H, 4.22; N, 11.10%. ESI-MS *m/z* = 341 $[Cu(L2)]^+$.

Synthesis of [Cu(L3)Cl$_2$] 3

Copper(II) chloride dihydrate (0.17 g, 1 mmol) was dissolved in methanol (10 ml) was added with constant stirring to a methanolic solution of L3 (0.211 g, 1 mmol). The green color precipitate formed was filtered off, washed with cold methanol and diethyl ether, and then dried under vacuum. Yield: 0.260 g (75%). Anal. Calcd for $CuC_{13}H_{13}N_3Cl_2$: C, 45.16; H, 3.79; N, 12.15. Found: C, 45.12; H, 3.76; N, 12.15%. ESI-MS *m/z* = 309 $[Cu(L3)Cl]^+$.

Synthesis of [Cu(L4)Cl$_2$] 4

To a methanolic solution of L4 (0.250 g, 1 mmol) was added a solution of copper(II) chloride dihydrate (0.17 g, 1 mmol) dissolved in methanol (10 ml) with constant stirring. The green colored precipitate formed was filtered off, washed with cold methanol and diethyl ether, and then dried under vacuum. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanolic solution of the complex. Yield: 0.290 g (75%). Anal. Calcd for $CuC_{15}H_{14}N_4Cl_2$: C, 46.83; H, 3.67; N, 14.56. Found: C, 46.78; H, 3.63; N, 14.55%. ESI-MS *m/z* = 348 $[Cu(L4)Cl]^+$.

Synthesis of [Cu(L5)Cl$_2$] 5

A methanolic solution (10 ml) of copper(II) chloride dihydrate (0.17 g, 1 mmol) was added to a solution of L5 (0.239 g, 1 mmol) in methanol with constant stirring. The green colored precipitate formed was filtered off, washed with cold methanol and diethyl ether, and then dried under vacuum. Yield: 0.260 g (70%). Anal. Calcd for $CuC_{13}H_{13}N_5Cl_2$: C, 41.78; H, 3.51; N, 18.74. Found: C, 41.74; H, 3.48; N, 18.73%. ESI-MS *m/z* = 337 $[Cu(L5)Cl]^+$.

Synthesis of [Cu(L6)Cl_2] 6

A methanolic solution (10 ml) of copper(II) chloride dihydrate (0.17 g, 1 mmol) was added to a solution of L6 (0.300 g, 1 mmol) in methanol with constant stirring. The green colored complex formed was filtered off, washed with cold methanol and diethyl ether, and then dried under vacuum. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanolic solution of the complex. Yield: 0.300 g (70%). Anal. Calcd for $CuC_{19}H_{16}N_4Cl_2$: C, 52.48; H, 3.71; N, 12.89. Found: C, 52.44; H, 3.68; N, 12.88%. ESI-MS *m/z* = 398 $[Cu(L6)Cl]^+$.

Table S1: Calculated and observed ESI-MS data for complexes **1** – **6**.

Complex	Molecular ion	m/z (Found/Calculated)	Relative intensity
1	$[CuC_{16}H_{14}N_3O]^+$ (**1**)	327/327.053	100%
2.	$[CuC_{17}H_{16}N_3O]^+$ (**2**)	341/341.069	100%
3	$[CuC_{13}H_{13}N_3Cl]^+$ (**3**)	309/309.019	100%
4	$[CuC_{15}H_{14}N_4Cl]^+$ (**4**)	348/348.030	100%
5	$[CuC_{13}H_{13}N_5Cl]^+$ (**5**)	337/337.026	100%
6	$[CuC_{19}H_{16}N_4Cl]^+$ (**6**)	398/398.046	100%