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**Supplementary material**

**Ordering a selected Zn(II), Cu(II), Pd(II) and Co(III) complex compounds. Their separately and combinedly antibacterial therapy and DNA-binding studies**

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**Procedures for the synthesis of the metal complexes**

 The metal complexes were synthesized according to the literature methods with some modifications in our laboratory. Characterization data for each compound have been given at the end of its synthetic procedure.

**a)** Synthesis of K3[Co(ox)3]·3H2O (**I**)

 This complex was synthesized as previously described in our literature (Khosravi & Mansouri-Torshizi, 2018).

**b)** Synthesis of [Cu(phen)2Cl]Cl·6.5H2O (**II**)

 0.500 g (2 mmol) of CuSO4·5H2O and 0.296 g (4 mmol) of KCl were dissolved in 50 mL of distilled water, stirred with magnetic stirrer at 50 ºC for 10 min. Then, 0.792 g (4 mmol) of 1,10-phenanthroline monohydrate was dissolved in 10 mL of ethanol; this was added slowly to the warm solution above. While it was continuously stirred, the whole mixture was heated to 80 ºC for 30 min. Green shining precipitate formed as the residue. After cooling the reaction mixture to room temperature, the resulting product was filtrated and recrystallized in ethanol−water mixture (1:4 v/v) to achieve green shining crystals. The crystals were isolated by filtration and were dried at 40 °C (Onawumi, Adekunle, Ibrahim, Rajasekharan, & Odunola, 2010). The yield of this complex was 1.060 g (87%) which decomposed at 150−154 °C. Selected FT-IR bands (cm−1): 3384 (*ν*(O−H)), 1626 and 1585 (*ν*(C=N)), 1428 (*ν*(C=C)) and 723 (*δ*(C−H)) (Adelaide, Abidemi, & Olubunmi, 2013). Electronic spectra exhibited four bands in the range 200−400 nm. The bands at 203 (log ε = 5.23), 224 (log *ε* = 5.25), 270 (log *ε* = 5.18) and 294 (log *ε* = 4.67) may be assigned to intraligand *π*→*π*\* transitions of phen ligand. The broad band centered at 681 nm (log *ε* = 1.99) assigned to *d*-*d* transitions (Murphy, Nagle, Murphy, & Hathaway, 1997). Elemental analysis calculated for C24H29N4O6.5Cl2Cu (MW = 611.5): C, 47.10; H, 4.74; N, 9.16. Found: C, 46.97; H, 4.77; N, 9.26. Molar conductance measurement for the complex is 115 Ω−1mol−1cm2 indicating 1:1 electrolytes (Angelici, 1969).

**c)** Synthesis of [Zn(phen)3]Cl2 (**III**)

 In a 100 mL beaker, 1.620 g (9 mmol) of 1,10-phenanthroline was added to 75 mL of distilled water. Concentrated HCl was then added to dissolve the phen (~20 drops). To this solution, 0.408 g (3 mmol) of zinc chloride was added and stirred to get clear and colorless solution. The solution was neutralized with aqueous 1.0 M NaOH. Stirring continued at 50 °C to reduce the volume to 20 mL. The warm solution was filtered and the filtrate evaporated to 5 mL at 30−35 °C. This solution was cooled to room temperature and the needle-shaped crystals was isolated by filtration, washed with chilled water and acetone and dried at 50 °C (Dollberg, 2004). The yield of this complex was 1.836 g (90%) which decomposed at 202−204 °C. Selected FT-IR bands (cm−1): 1619 and 1587 (*ν*(C=N)), 1427 (*ν*(C=C)), 728 and 846 (*δ*(C−H)) (Arounaguiri, Easwaramoorthy, Ashokkumar, Dattagupta, & Maiya, 2000). 1H-NMR (250 MHz, D2O, ppm, s = singlet, d = doublet, sb = singlet broad, t = triplet and dd = doublet of doublet): 8.915 (H-a, d, 6H), 8.33 (H-d, s, 6H), 7.64 (H-b, dd, 6H), 7.78 (H-c, d, 6H) (Fig. 1) (Mudasir, Yoshioka, & Inoue, 1999). Electronic spectra exhibited three bands in the range of 200−400 nm. The band at 226 (log *ε* = 5.30), 268 (log *ε* = 5.19) and 292 (log *ε* = 4.75) could be assigned to intraligand *π*→*π*\* transitions of coordinated 1,10-phenanthroline ligand (Arounaguiri et al., 2000). Elemental analysis calculated for C36H24N6Cl2Zn (MW = 676.4): C, 63.86, H, 3.55; N, 12.41. Found: C, 63.88; H, 3.58; N, 12.36. Molar conductance measurement for the complex is 253 Ω−1mol−1cm2 indicating 1:2 electrolytes (Angelici, 1969).

**d)** Synthesis of [Pd(phen)2](NO3)2 (**IV**)

 [Pd(phen)Cl2] (1.070 g, 3 mmol) was suspended in 180 mL acetone−water mixture (2:1 v/v), and (1.020 g, 6 mmol) of AgNO3 was added to it with constant stirring. This reaction mixture was heated with stirring under dark for 7 h at 60 ºC and then for 6 h at room temperature (30 ºC). The AgCl precipitate was filtered through Whatman 42 filter paper. To the clear yellow filtrate containing [Pd(phen)(H2O)2](NO3)2, a solution of 0.541 g (3 mmol) 1,10-phenanthroline in 10 mL ethanol was added slowly. The obtained precipitate was stirred at 40 ºC for another 1 h and was filtered. Then, obtained precipitate was dissolved in 250 mL water and the clear yellowish orange solution was evaporated at 35−40 ºC to give yellowish orange needle-shaped crystals. The crystals were isolated by filtration, washed with acetone and dried at 40 °C (Islami-Moghaddam, Mansouri-Torshizi, Divsalar, & Saboury, 2009). The yield of this complex was 1.430 g (81%) which decomposed at 271−273 °C. Selected FT-IR bands (cm−1): 1586−1636 (*ν*(C=N)), 1434 (*ν*(C=C)), and 781–856 (*δ*(C−H)) (Kannan & Arumugham, 2012). The sharp band at 1384 cm−1 was assigned to an uncoordinated NO3− ion (Song, Wang, Zheng, Liu, & Tan, 2007). 1H-NMR (250 MHz, D2O, ppm): 8.98 (4H, sb, H-a), 8.68 (4H, sb, H-d) and 7.93 (8H, sb, H-b and H-c) (Fig. 1) (Mital, Srivastava, Parekh, & Chitnis, 1991). Electronic spectra exhibited three bands in the range of 200−800 nm. The bands at 206 (log *ε* = 5.26), 266 (log *ε* = 4.94) and 282 (log *ε* = 4.90) could be assigned to intraligand *π*→*π*\* transitions of phen ligand. Elemental analysis calculated for C24H16O6N6Pd (MW = 590.4): C, 48.78; H, 2.71; N, 14.22. Found: C, 48.62; H, 2.75; N, 14.29. Molar conductance measurement for the complex is 236 Ω−1mol−1cm2 indicating 1:2 electrolytes (Angelici, 1969).

**References**

Adelaide, O. M., Abidemi, O. O., & Olubunmi, A. D. (2013). Synthesis, characterization and antibacterial studies of some copper(II) complexes of 2,2ʹ-bipyridine and 1.10-phenanthroline. *Journal of Chemical and Pharmaceutical Research*, *5*, 69–73.

Angelici, R. J. (1969). *Synthesis and Techniques in Inorganic Chemistry*. London: Saunders.

Arounaguiri, S., Easwaramoorthy, D., Ashokkumar, A., Dattagupta, A., & Maiya, B. G. (2000). Cobalt(III), nickel(II) and ruthenium(II) complexes of 1,10-phenanthroline family of ligands: DNA binding and photocleavage studies. *Journal of Chemical Sciences*, *112*(1), 1–17.

Dollberg, C. L. (2004). Zinc and ruthenium quinone diimine complexes: Synthesis and photophysical properties. Columbus, OH: The Ohio State University.

Islami-Moghaddam, M., Mansouri-Torshizi, H., Divsalar, A., & Saboury, A. A. (2009). Synthesis, characterization, cytotoxic and DNA binding studies of diimine platinum(II) and palladium(II) complexes of short hydrocarbon chain ethyldithiocarbamate ligand. *Journal of the Iranian Chemical Society*, *6*(3), 552–569.

Kannan, D., & Arumugham, M. N. (2012). Synthesis, characterisation, DNA-binding studies and antimicrobial activity of copper(II) complex with 1,10-phenanthroline, L-tyrosine and urea as ligands. *International Journal of Research in Controlled Release*, *2*(4), 10–17.

Khosravi, F., & Mansouri-Torshizi, H. (2018). Antibacterial combination therapy using Co3+, Cu2+, Zn2+ and Pd2+ complexes: Their calf thymus DNA binding studies. *Journal of Biomolecular Structure and Dynamics*, *36*(2), 512–531.

Mital, R., Srivastava, T. S., Parekh, H. K., & Chitnis, M. P. (1991). Synthesis, characterization, DNA binding, and cytotoxic studies of some mixed-ligand palladium(II) and platinum(II) complexes of *α*-diimine and amino acids. *Journal of Inorganic Biochemistry*, *41*(2), 93–103.

Mudasir, Yoshioka, N., & Inoue, H. (1999). Iron(II) and nickel(II) mixed-ligand complexes containing 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline. *Transition Metal Chemistry*, *24*(2), 210–217.

Murphy, G., Nagle, P., Murphy, B., & Hathaway, B. (1997). Crystal structures, electronic properties and structural pathways of four [Cu(phen)2Cl][Y] complexes (phen = 1,10-phenanthroline; Y= BF4−·0.5 H2O, PF6−, CF3SO3−·H2O or BPh4−). *Journal of the Chemical Society, Dalton Transactions*, (15), 2645–2652.

Onawumi, O. O., Adekunle, F. A., Ibrahim, A. O., Rajasekharan, M. V, & Odunola, O. A. (2010). Synthesis, Characterization, and Crystal Structures of [Cu(phen)2Cl]Cl· 6.5H2O and [Cu(phen)2Br]Br. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, *40*(2), 78–83.

Song, X.-Q., Wang, Y.-W., Zheng, J.-R., Liu, W.-S., & Tan, M.-Y. (2007). Synthesis and spectroscopic properties of lanthanide nitrate complexes with a new amide-based quinoxaline-2,3-dione ligand. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *68*(3), 701–704.