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Research paper

Treatment of cadmium(II) and zinc(II) with N_2-donor linkages in presence of β-diketone ligand; supported by structural, spectral, theoretical and docking studies

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ABSTRACT

Five compounds, {(μ-OAc)(DPPD)Cd(μ-PYZ)Cd(DPPD)(μ-OAc)}$_n$ (**1**); HDPPD: 1,3-diphenylpropane-1,3-dione; PYZ: pyrazine, {Cd(μ-4,4′-Bipy)(DPPD)$_2$}$_n$ (**2**) Bipy: bipyridine [(DPPD)$_2$Zn(μ-4,4′-Bipy)Zn(DPPD)$_2$] (**3**), {Cd(μ-DPP)(DPPD)$_2$}$_n$ (**4**); DPP: 1,3-di(pyridin-4-yl)propane and (*Z*)-3-hydroxy-1,3-bis(4-methoxyphenyl)prop-2-en-1-one (*Z*-HMPP), were prepared and identified by elemental analysis, FT-IR, ^{1}H NMR spectroscopy and single-crystal X-ray diffraction. **1**,**2** and **4** form 1D coordination polymers whereas 3 adopts a binuclear structure with the zinc atom in a distorted square-pyramidal geometry. In addition to these complexes, the enolic structure of the *Z*-HMPP is reported. The ability of compounds to interact with the nine biomacromolecules (BRAF kinase, CatB, DNA gyrase, HDAC7, rHA, RNR, TrxR, TS and Top II) is investigated by the Docking calculations (for **3** and its ligands). The charge distribution pattern of the optimized structure of **3** was studied by NBO analysis. The Polymer Stability Slope for pentameric chain (PSS^5, new parameter which is proposed in this paper) of the coordination polymers of **1**, **2** and **4** were calculated to investigate the variation of energy level during the growing the polymeric chain in the solid phase.

1. Introduction

Coordination polymers are interesting metal-organic hybrid materials in which metal ions or metal-containing clusters act as nodes and organic ligands act as spacers; both units are linked via coordination bonds to form one-, two- or three-dimensional extended structures [1]. This class of compounds has been used as electrodes in supercapacitors [2], gas storage/separation and ion exchange [3–8], biological and material science [9,10], sensing [11–15], precursors for the preparation of nano-materials [16], magnetism [17–21], luminescent materials nonlinear optics [22–25], catalysis [26–29],.

Aromatic β-diketones are frequently used as chelating ligands for Lewis acids and to produce complexes used in many applications such as catalysis [30], vapour deposition [31], luminescent compounds [32,33], near infrared organic light emitting devices [34,35] and optoelectronics [36]. For example, difluoroboron diketonates [37] have lately received tremendous attention due to their mechanochromic luminescence (ML) [38] and room-temperature phosphorescence properties [39–41]. Some 1D-, 2D- and 3D-coordination polymers containing β-diketone derivatives have been reported [42,43].

In order to extend the chemistry of these coordination polymers, in this work, the synthesis of compounds including, {(μ-OAc)(DPPD)Cd(μ-PYZ)Cd(DPPD)(μ-OAc)}$_n$ (**1**); HDPPD: 1,3-diphenylpropane-1,3-dione (Scheme 1); PYZ: pyrazine (Scheme 1), {Cd(μ-4,4′-Bipy)(DPPD)$_2$}$_n$ (**2**); Bipy: bipyridine (Scheme 1), [(DPPD)$_2$Zn(μ-4,4′-Bipy)Zn(DPPD)$_2$] (**3**), {Cd(μ-DPP)(DPPD)$_2$}$_n$ (**4**); DPP: 1,3-di(pyridin-4-yl)propane (Scheme 1) and (*Z*)-3-hydroxy-1,3-bis(4-methoxyphenyl)prop-2-en-1-one (*Z*-HMPP), are described, along with the characterization and theoretical study of the compounds.

In addition to the expected biological properties of compounds containing β-diketons [44,45] and pyridine derivatives [46–49], binding of the zinc(II) ion to this unit make these complexes as a good choice for biologically active compounds [50–52], thus docking calculations were run to investigate the possibility of interaction between

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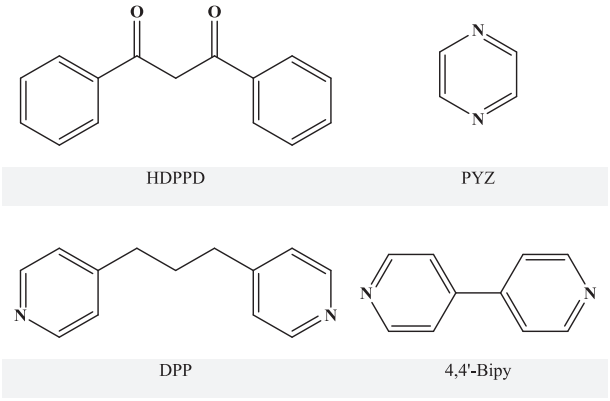

Scheme 1. Structures of the 1,3-diphenylpropane-1,3-dione (HDPPD), pyrazine (PYZ), 4,4′-bipyridine (4,4′-Bipy) and 1,3-di(pyridin-4-yl)propane (DPP) ligands.

3 and its ligands (4,4′-bipyridine and DPPD) with the nine protein targets, including: BRAF kinase, Cathepsin B (CatB), DNA gyrase, Histone deacetylase (HDAC7), recombinant Human albumin (rHA), Ribonucleotide reductases (RNR), Thioredoxin reductase (TrxR), Thymidylate synthase (TS), Topoisomerase II (Top II). These proteins are used in this project either due to their reported roles in the cancer growth or as transport agents that affect drug pharmacokinetic properties (e.g., rHA). Also, DNA gyrase was included to study the possibility of the compounds also acting as antimalarial agents [53].

2. Experimental

2.1. Materials and instrumentation

All starting chemicals and solvents were reagent or analytical grade and used as received. Infrared spectra in the range 4000–400 cm^{-1} were recorded on KBr pellets with a FT-IR 8400-Shimadzu spectrometer. ^1H NMR spectra were recorded on a Bruker spectrometer at 250 MHz; chemical shifts δ are given in parts per million, relative to TMS as an internal standard. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

2.1.1. Synthesis of {(μ-OAc)(DPPD)Cd(μ-PYZ)Cd(DPPD)(μ-OAc)}$_n$ (1)

HDPPD (0.135 g, 0.6 mmol), pyrazine (0.072 g, 0.9 mmol) and Cd $(OAc)_2{\cdot}2H_2O$ (0.080 g, 0.3 mmol) were placed in the large arms of a branched tube (see ref [54]). Ethanol was carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a bath at 60 °C while the other arm was maintained at ambient temperature [55]. After a few days, the colorless crystals deposited in the cooler arm were filtered off and dried in air. Yield: 0.058 g, 45%; m. p. 212–217 °C. Anal. Calcd for $C_{19}H_{16}CdNO_4$ (434.73): C, 52.49; H, 3.71; N, 3.22. Found: C, 52.62; H, 3.75; N, 3.19%. IR (KBr, cm^{-1}): 3105 w (ν CH)^{ar}, 3063 w (ν CH)$^{\beta\text{-diketone}}$, 2997 w (ν CH), 1592 s (ν C═C + ν C═O)$^{\beta\text{-diketone}}$, 1580 m (ν C═N), 1543 m (ν_{as} COO)^{OAc}, 1522 m (ν C═O + ν C═C), 1456 w (ν C═C^{ar} and/or δ_{as} CH_3), 1434 m (ν_s COO^{Oac} and/or δ CH + ν C═C$^{\beta\text{-diketone}}$), 1343 w (δ_s CH_2), 674 (δ OCO)^{OAc}. ^1H NMR (250 MHz, DMSO-d_6, ppm, Hz): δ = 8.64)s, 2 H, pyrazine), 7.40–7.91)m, 10 H, phenyl-DPPD), 6.54)s, 1 H, β-diketone), 1.82)s, 3H, OAc).

2.1.2. Synthesis of {Cd(μ-4,4′-Bipy)(DPPD)$_2$}$_n$ (2)

The procedure for synthesis of **2** was similar to **1** except that pyrazine was replaced by 4,4′-bipyridine (0.141 g, 0.9 mmol) using the MeOH/H_2O in a ratio of 3:1. Yield: 0.028 g, 13%; m. p. 204–214 °C. Anal. Calcd for $C_{40}H_{30}CdN_2O_4$ (715.06): C, 67.18; H, 4.23; N, 3.92. Found: C, 67.32; H, 4.28; N, 4.01%. IR (KBr, cm^{-1}): 3091 w (ν CH)^{ar}, 3056 w (ν CH)$^{\beta\text{-diketone}}$, 1597 s (ν C═C + ν C═O)$^{\beta\text{-diketone}}$, 1552 m (ν C═O + ν C═C)$^{\beta\text{-diketone}}$, 1513 m (ν C═N), 1477 m (ν C═C)^{ar}, 1454 s (δ CH + ν C═C)$^{\beta\text{-diketone}}$. ^1H NMR (250 MHz, DMSO-d_6, ppm, Hz): δ= 8.69–8.71)d, 4 H, 4,4′-bipy), 7.90–8.17)m, 8 H, DPPD), 7.79–7.81)d, 4 H, 4,4′-bipy), 7.33–7.66)m, 12H, DPPD), 6.54)s, 2 H, β-diketone).

2.1.3. Synthesis of [(DPPD)$_2$Zn(μ-4,4′-Bipy)Zn(DPPD)$_2$] (3)

The procedure for synthesis of **3** was similar to **2** except that Cd $(OAc)_2{\cdot}2H_2O$ was replaced by $Zn(OAc)_2{\cdot}2H_2O$ (0.066 g, 0.3 mmol) using the MeOH/EtOH in a ratio of 3:1. Yellowish crystals were formed after a few days in the cooler arm and filtered. Yield: 0.026 g, 15%; m. p. 237–238 °C. Anal. Calcd for $C_{70}H_{52}N_2O_8Zn_2$ (1179.87): C, 71.25; H, 4.44; N, 2.37. Found: C, 71.51; H, 4.53; N, 2.35%. IR (KBr, cm^{-1}): 3102 w (ν CH)^{ar}, 3066 w (ν CH)$^{\beta\text{-diketone}}$, 1606 m (ν C═C + ν C═O)$^{\beta\text{-diketone}}$, 1555 m (ν C═O + ν C═C)$^{\beta\text{-diketone}}$, 1544 m (ν C═N), 1474 s (ν C═C)^{ar}, 1458 s (δ CH + ν C═C)$^{\beta\text{-diketone}}$. ^1H NMR (250 MHz, DMSO-d_6, ppm, Hz): δ = 8.73)d, 2H, 4,4′-bipy), 8.02–8.05)d, 8 H, DPPD), 7.80–7.82)d, 2 H, 4,4′-bipy), 7.46–7.48)m, 12 H, DPPD), 6.76)s, 2 H, β-diketone).

2.1.4. Synthesis of {Cd(μ-DPP)(DPPD)$_2$}$_n$ (4)

The procedure for synthesis of **4** was similar to **1** except that pyrazine was replaced by DPP (0.178 g, 0.9 mmol) using the MeOH/EtOH in a ratio of 1:3. After one week, the reaction mixture was filtered and then colorless crystals suitable for X-ray diffraction studies were obtained by slow evaporation after a few days. Yield: 0.017 g, 8%; m. p. 215 °C. Anal. Calcd for $C_{43}H_{36}CdN_2O_4$ (757.14): C, 68.21; H, 4.79; N, 3.70. Found: C, 67.94; H, 4.77; N, 3.71%. IR (KBr, cm^{-1}): 3087 w (ν CH)^{ar}, 3060 w (ν CH)$^{\beta\text{-diketone}}$, 2945 w (ν CH_2), 1594 s (ν C═C + ν C═O)$^{\beta\text{-diketone}}$, 1547 m (ν C═O + ν C═C)$^{\beta\text{-diketone}}$, 1515 m (ν C═N), 1478 m (ν C═C)^{ar}, 1455 s (δ CH + ν C═C)$^{\beta\text{-diketone}}$, 1406 s (δ_{as} CH_2), 1301 w (δ_s CH_2). ^1H NMR (250 MHz, DMSO-d_6, ppm, Hz): δ = 8.43–8.45)d, 4H, DPP), 7.89–7.91)d, 8H, DPPD), 7.41)m, 12 H, DPPD), 7.22–7.24)m, 4 H, DPP), 6.53)s, 2 H, β-diketone), 2.56–2.63 (t, 4 H, DPP), 1.87–1.93 (m, 2 H, DPP).

2.1.5. Preperation of (Z)-3-hydroxy-1,3-bis(4-methoxyphenyl)prop-2-en-1-one (Z-HMPP)

The procedure for synthesis of *Z*-HMPP was similar to **3** except that HDPPD and pyrazine was replaced by 1,3-bis(4-methoxyphenyl)propane-1,3-dione, HMPP (0.171 g, 0.6 mmol), and 1,2-di(pyridin-4-yl) ethane, DPE (0.164 g, 0.9 mmol), using the MeOH. After a few days, yellow crystals that were deposited in the cooler arm were filtered off and dried in air. Yield: 0.050 g; m. p. 222 °C. Anal. Calcd for $C_{17}H_{16}O_4$ (284.30): C, 71.82; H, 5.67. Found: C, 71.96; H, 5.66%. IR (KBr, cm^{-1}): 3060 w (ν CH)^{ar}, 2962 w (ν CH_3), 1604 s (ν C═O)^{enol}, 1545 w (ν C═C)^{enol}, 1491 m and 1458 w (ν C═C)^{ar}, 1438 m (δ_{as} CH_3), 1303 m (ν C−O^{enol} and/or δ_s CH_3). ^1H NMR (250 MHz, DMSO-d_6, ppm, Hz): δ = 8.10–8.13)d, 4 H, Ph), 7.51)s, 1 H, β-diketone), 7.17)s, 1 H, OH), 7.05–7.08)d, 4 H, Ph), 3.82–3.84 (s, 6 H, methoxy).

2.2. Crystal structure determination

Suitable crystals of **1**–**4** and *Z*-HMPP were chosen and their X-ray analysis were done using Apex-II Duo CCDC diffractometer with fine-focus sealed tube graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å) at room temperature. The data was processed with SAINT and corrected for absorption using SADABS [56]. The structures were solved by direct method using the program SHELXTL [57] and were refined by full-matrix least squares technique on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. Diagrams of the molecular structure and unit cell were created using Ortep-III [58,59] and Diamond [60] softwares. Details of crystal data, data collection, structure solutions and refinements are given in Table 1. Selected bond lengths and angles of complexes are listed in Table 2 and hydrogen bond geometries in Table S2 (Supplementary Materials).