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Synthesis and characterization of Cu(II) complexes of pyrazine-2,3-dicarboxylicacid

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ABSTRACT

Four copper(II) coordination polymers, $\{[Cu(pz(COO)_2)(H_2O)]_4{\cdot}HBr\}_n$ (**1**), $\{[Cu(pz(COO)_2)(NH_3)_2]{\cdot}H_2O\}_n$ (**2**), $\{[Cu_3H_2(pz(COO)_2)_4(H_2O)_3]{\cdot}2H_2O\}_n$ (**3**) and $\{[Cu_2(pz(COO)_2)_2(NH_3)_2(H_2O)_3][Cu(pz(COO)_2)(NH_3)(H_2O)_2][Cu(pz(COO)_2)(NH_3)(H_2O)]{\cdot}2H_2O\}_n$ (**4**) were synthesized using pyrazine-2,3-dicarboxylic acid, $CuBr_2$, 2-(2-aminoethylamino)ethanol/triethanol amine/ammonia in a methanol:water (1:1) solution, and the mixed ligand complexes were characterized by spectroscopic methods, thermal and elemental analysis, and magnetic susceptibility. Complexes **2** and **4** were also characterized by means of single crystal X-ray crystallography. The characterizations show that the complexes have polynuclear molecular structures, except for complex **2**, and all of the complex structures form polymeric chains. Complex **4** has a pseudo-merohedral twin structure.

1. Introduction

Pyrazine-2,3-dicarboxylic acid (H_2pzdc) and its complexes are the subject of many studies in which coordination polymers with special electronic and magnetic properties have been synthesized as linear chains or infinite networks. Pyrazine [1–5] itself and carboxylate groups are used to bridge transition metal atoms to form binuclear or polynuclear complexes [6–11]. Thus, one, two or three dimensional molecular structures can be constructed. Pyrazine-2,3-dicarboxylic acid bears both kinds of bridging species and is capable of building polynuclear complexes [12–14]. It is a dianionic tetradentate ligand with two potential nitrogens of pyrazine and two carboxylate-oxygens. The other two oxygens of carboxylate groups also may participate in bridging. The coordination modes as well as the hydrogen bonding between monomeric units determine the kind of polymerization.

An aqueous solution of Na_2pzdc and $Cu(ClO_4)_2$ gives a one dimensional polymeric chain built up by pentacoordinated Cu(II) ions, pzdc as a bridging ligand and water molecules, $[Cu(pzdc)_2(H_2O)_2]{\cdot}H_2O$, in which lattice water molecules give rise to a 3D structure via hydrogen bonding [15]. The lack of one of the carboxylic acid protons, as in the case of the mono methyl ester of H_2pzdc, with aqueous $CuCl_2$ causes the formation of a two dimensional coordinating polymer with CuL_2 monomeric units [16]. However, H_2pzdc reacts with aqueous $CoCl_2$ solution to give $Co(Hpzdc)_2$ $(H_2O)_2$ in which mononuclear units are bridged only by hydrogen bonds through pyrazine–carboxylate ligands [12,13].

Although there are a number of bis-bidentate complexes of H_2pzdc with two copper atoms, only one example of a ladder-like polymeric manganese(II) complex, $[Mn(pzdc)(H_2O)_2]_n$, has been reported. The ladder-like chain is formed via bridging the two Mn(II) atoms with one of the carboxylates of two parallel pzdc units and the chains are linked by hydrogen bonds of water molecules [14].

Pyrazine-2,3-dicarboxylic acid reacts with $CuCl_2$ in 6 N HCl to give a one dimensional coordination polymer [12] with monomeric $Cu(pzdc){\cdot}HCl$ units, in which Cu(II) is pentacoordinated and the ligand coordinates to two Cu atoms in a bis-bidentate mode. The acid hydrogen of one carboxylic acid moiety forms intramolecular hydrogen bonds with another carboxylate oxygen.

H_2pzdc, Cu(II) and bidentate ligands with nitrogen atoms give ligand coordinated mono-, di- and polynuclear complexes, which lead to polymer chains [17–20]. In continuation of our work on polynuclear complexes [21], now we report the results of the $CuBr_2$–H_2pzdc interaction in weakly alkaline and neutral solutions to give polynuclear coordination oligomers, which react with 5 N NH_3 solution to give ammonia coordinated complexes.

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2. Experimental

2.1. Physical and chemical measurements

2.1.1. UV–Vis and IR

The electronic and infrared spectra were recorded on Shimadzu UV–Vis 240, Varian Cary Eclipse Fluorescence and Hyper IR Shimadzu Infrared (KBr disc) spectrophotometers, respectively.

Thermogravimetric analysis experiments were performed using a Netzsch STA 409C/CD in a nitrogen atmosphere with a nitrogen flow rate of 50 mL min^{-1} in the temperature range 20–400 °C, with a 5 °C min^{-1} heating rate.

Magnetic susceptibility measurements were carried out at room temperature on a magnetic balance of the Faraday type with $Hg[Co(SCN)_4]$ as the standard.

Elemental analyses and mass measurements were performed in the analytical laboratory, Tübitak, Ankara on a LECO CHNS 932 Analyzer and the LC/MS system of an Agilent1100 MSD spectrometer, respectively.

Copper analysis was carried out with an Analytikjena Zeenit 700 AAS.

Melting points were measured by using a Gallenkamp melting point apparatus.

Single crystal X-ray structural analyses were performed on a STOE IPDS 2 diffractometer with graphite monochromated Mo Kα radiation at 296 and 110 K.

2.2. Syntheses

2.2.1. Reagents

Pyrazine-2,3-dicarboxylic acid was from Fluka and $CuBr_2$ was from Riedel-de Haen. The solvents used in the preparations were all Merck p.a. products.

2.2.2. Preparation of $\{[Cu(pz(COO)_2)(H_2O)]_4{\cdot}HBr\}_n$ (**1**)

$CuBr_2$ (4.46 g, 0.02 mol), pyrazine-2,3-dicarboxylic acid (3.36 g, 0.02 mol), 2-(2-aminoethylamino)ethanol or triethanolamine (approx. 0.02 mol) were dissolved in 20 mL methanol/water (1/1), and the solution was heated at 70–80 °C for 2 h with continuous stirring under a reflux condenser. The green precipitate obtained in the powder form was filtered, washed with chloroform and dried in air.

Yield: 4.97 g (93%), Mw: 1071.524 g mol^{-1}, m.p.: >250 °C, μ_{eff} = 3.27 BM. TGA data (°C) (weight loss%) (calcd. weight loss%): 129 (6.94) (6.72; calcd. for – $4H_2O$): 129–269 (45.22) (45.64; –HBr, $-8CO_2$, $-2N_2$). UV (nm) (H_2O): 388; 533; 634. IR (KBr, ν/cm^{-1}): 3418 (m, br, O–H str.), 3090, 3067 (m, pz-C–H str.), 1680 (m, COO^-), 1643 (s, C=N), 1580 (m, asym. COO^- str.), 1329 (s, sym. COO^- str.), 889 (m, H_2O), 853 (m, C–H bend. of ring), 496 (m, Cu–N str.), 231 (s, Cu–N). Mass (positive pol., *m*/*e*): 1028.4 (1%, m*-CO_2 + H); 740.5 (0.7%, $[pz(COO)_2Cu(H_2O)]_3$–2H); 495.6 (2.6%, $[pz(COO)_2Cu{\cdot}H_2O]_2$); 284.3 (100%, $pz(COOH)CuBr{\cdot}H_2O^+$); 230.3 (8.3%, $Hpz(COO)_2Cu^+$). *Anal.* Calc. for $C_{24}H_{17}N_8O_{20}Cu_4B$: C, 26.90; H, 1.60; N, 10.46; Cu, 23.72. Found: C, 27.42; H, 1.14; N, 11.05; Cu, 22.57%.

2.2.3. Preparation of $\{[Cu(pz(COO)_2)(NH_3)_2]{\cdot}H_2O\}_n$ (**2**)

$Cu_4[pz(COO)_2]_4{\cdot}HBr{\cdot}4H_2O$ (0.5 g, 1.78 mmol) (**1**) was dissolved in 20 mL 5 N NH_4OH and 25% of the solution was evaporated at atmospheric pressure. Green needles of $\{[Cu(pz(COO)_2)(NH_3)_2](H_2O)\}_n$ crystallized out on cooling down to room temperature. The green crystals were filtered and washed with chloroform.

Yield: 0.24 g (88%), Mw: 281.72 g mol^{-1}, m.p.: >300 °C, μ_{eff} = 2.05 BM. TGA data (°C) (weight loss%) (calcd. weight loss%): 137–270 (56.44) (54.7; $-H_2O$, $-2NH_3$, $-2CO_2$, –N); 270–400 (1.48). IR (KBr, ν/cm^{-1}): 3462 (m, br, O–H str. of H_2O), 3090 (m, pz-CH str.), 3321 (s), 3274 (m), 3239 (m) (N–H str. of NH_3), 3171 (m, pz-C–H str.), 1659 (s, C=N ring), 1628 (m, sh, O–H bend of H_2O), 1591 (s, asym. COO^- str.), 1450 (m, C=C ring), 1386 (s, sym. COO^- str.), 1350 (m, sym. COO^- str.), 1313, 1265 (m, sym. deform.mode of N–H of coord. NH_3), 888 (m, H_2O), 845 (m, C–H bend of ring), 735 (rocking mode of N–H of coord. NH_3), 547 (w, H_2O), 471 (m, Cu–N str.), 448 (m, Cu–N of NH_3), 259 (s, Cu–O asym. str.). UV (nm) (H_2O): 389; 487; 532; 631. Mass (negative pol., *m*/*e*): 841 (0.2%, m*-4H), 283.2 (36.3%, $pz(COOH)_2Cu(NH_3)_2{\cdot}H_2O$); 281.1 (32.5%, $pz(COO)_2Cu(NH_3)_2{\cdot}H_2O$); 255.2 (100%), 253.30 (46%). *Anal.* Calc. for $C_6H_{10}N_4O_5Cu$: C, 25.58; H, 3.58; N, 19.89; Cu, 22.55. Found: C, 25.90; H, 3.13; N, 19.74; Cu, 21.91%.

2.2.4. Preparation of $\{[Cu_3H_2(pz(COO)_2)_4(H_2O)_3]{\cdot}2H_2O\}_n$ (**3**)

$CuBr_2$ (0.5025 g, 2.3 mmol) and pyrazine-2,3-dicarboxylic acid (0.5040 g, 3 mmol) were dissolved in 20 mL methanol/water (1/1) and the solution was heated at 70–80 °C for 2 h with continuous stirring under a reflux condenser. The light green precipitate obtained in the powder form was filtered, washed with chloroform and dried in air.

Yield: 0.61 g (88%). Mw: 947.092 g mol^{-1}, m.p.: >250 °C. μ_{eff} = 3.4 BM. TGA data (°C) (weight loss%) (calcd. weight loss%): 132 (4.32) (3.80; $-2H_2O$); 132–261 (14.66) (15.00; $-2CO_2$–$3H_2O$), 261–280 (35.44) (35.48; $-7CO_2$, $-N_2$); 280–400 (4.17%) (4.43%; $-3/2N_2$). IR (KBr, ν/cm^{-1}): 3385 (m, br, O–H str. of H_2O), 3231 (m, br, O–H str. of COOH), 3090, 3067 (m, pz-C–H str.), 2650–2500 (O–H str., bonded), 1674 (m, COO^-), 1651 (s, C=N), 1640 (s, O–H bending), 1584 (s, asym. COO^- str.), 1425 (s, C=C ring), 1354, 1333 (s, sym. COO^- str.), 889 (s, H_2O), 853 (m, C–H bend. of ring), 538 (m, H_2O), 494 (m, Cu–N str.), 423 (w, Cu–O–aqua complex), 260 (s, Cu–O). UV (nm) (H_2O): 391; 533; 630. Mass (positive polarity) (*m*/*e*): 715.2 (1.5%, m*-$[pz(COO)_2Cu + 2H]$), 503.9 (21.7%, m*-$[(pz(COO)_2)_2Cu + CO_2 + 4H]$); 425.0 (53.6%, m*-$[(pz(COO)_2)_2Cu + HpzCOOH + 2H]$); 423.0 (100%); 323.9 (26.5%, m*-$[(pz(COO)_2)_2\text{-}Cu_2 + pz(COO)_2\text{–}2H]$); 321.9 (22.4%); 258.3 (5.2%, m*-$[pz(COO)_2]_3\text{-}Cu_3$); 79.2 (61.2%, HPz). *Anal.* Calc. for $C_{24}H_{20}N_8O_{21}Cu_3$: C, 30.44; H, 2.13; N, 11.83; Cu, 20.13. Found: C, 30.48; H, 1.36; N, 12.02; Cu, 19.96%.

2.2.5. Preparation of $\{[Cu_2(pz(COO)_2)_2(NH_3)_2(H_2O)_3][Cu(pz(COO)_2)(NH_3)(H_2O)_2]\ [Cu(pz(COO)_2)(NH_3)(H_2O)]{\cdot}2H_2O\}_n$ (**4**)

$\{[Cu_3H_2(pz(COO)_2)_4(H_2O)_3]{\cdot}2H_2O\}_n$ (0.3 g, 0.33 mmol) (**3**) was dissolved in 10 mL 5 N NH_4OH solution and 25% of the solution was evaporated at atmospheric pressure. Light blue crystals were filtered, washed with chloroform, and methanol/water (1/1) and dried in air. Complex **4** was also obtained via the addition of $CuBr_2$ and 5 N ammonia solution (75–80 °C, 1 h) to the 2-(2-aminoethylamino)ethanol salt of pyrazine-2,3-dicarboxylic acid, which was isolated from a dimethylsulfoxide solution of the reactants. The mixture yields bright blue crystals in a month.

Yield: 0.063 g (68%). Mw: 1130.81 g mol^{-1}, m.p.: >300 °C. μ_{eff} = 3.19 BM. TGA data (°C) (weight loss%) (calcd. weight loss%): 72–182 (12.10) (12.74, $-8H_2O$); 182–252 (40.40) (40.87; $-4NH_3$, $-8CO_2$, $-3/2N_2$); 252–400 (4.09 (3.72; $-3/2N_2$). IR (KBr, ν/cm^{-1}): 3449 (m, br, O–H str. of H_2O), 3343 (s), 3262 (m), 3180 (m, N–H str. of NH_3), 3067 (m, pz-CH str.), 1650 (s, C=N ring), 1643 (s, N–H bend), 1635, 1622 (m, sh, O–H bend of H_2O), 1580 (s, asym. COO^- str.), 1454 (m, C=C ring), 1387 (s, sym. COO^- str.), 1350 (m, sym. COO^- str.), 1305, 1283, 1265 (w, sym. deform. mode of N–H of coord. NH_3), 893 (m, H_2O), 849 (s, C–H bend. of ring), 756 (rocking mode of N–H of coord. NH_3), 559 (w, H_2O), 486 (w, Cu–N str.), 448 (w, Cu–N of NH_3), 274 (s, Cu–O asym.str.). UV (nm) (H_2O): 388, 534, 634; UV (nm) (solid): 390, 479, 532, 632. Mass (positive pol.) (*m*/*e*): 1127 (0.2%, m-4), 1053 (0.3%, m*-($NH_{3+}3H_2O$), 1026 (0.5%, m*-($3NH_3 + 3H_2O$), 954 (0.4%, m*-($4NH_3 + 6H_2O$–H),