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1D, 2D and 3D cadmium(II) polymeric complexes with quinoline-4-carboxylato anion, quinazoline and 2,5-dimethylpyrazine

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Abstract

Three new cadmium(II) complexes, namely $[Cd(Qux)_2(H_2O)]_n$ (**1**), $[Cd(Quz)_2(N_3)_2]_n$ (**2**) and $[Cd(dmpz)(N_3)_2]_n$ (**3**) (Qux = quinoline-4-carboxylato anion, Quz = quinazoline, dmpz = 2,5-dimethylpyrazine), have been synthesized and characterized by spectroscopic and crystallographic methods. The structure of **1** contains CdO_6 slightly distorted octahedral geometry around the Cd(II) atoms, axialy coordinated to two bridging water molecules forming the 1D chain and four oxygen atoms from four different μ-O,O′-bridging caboxylato groups of (Qux) in the equatorial plane. The 1D chains are further held together through hydrogen bonds between the μ-aqua molecule and the meta non-coordinated nitrogen atom of the quinoline moiety. In complex **2**, two quinazoline ligands are linked to the central Cd(II) ion in a *trans* position through the meta hetero nitrogen atom and di(EE), ($\mu_{1,3}$-N_3) groups and show a two dimensional (2D) topology. In complex **3** the central cadmium(II) atom is simultaneously coordinated to di(EE), ($\mu_{1,3}$-N_3) groups (N–Cd–N, 180.0°) forming a sheet structure in the *bc* plane and further bridging μ-*N*,*N*′-dimethylpyrazine ligand in the *a*-direction (N–Cd–N, 180.0°) giving rise to a 3D network structure. The IR spectra of the three complexes were measured and they confirm the X-ray structural data.

Keywords: Cadmium(II); Quinazoline; Quinoline-4-carboxylate; Azido; Aqua complexes; IR; X-ray structure

1. Introduction

The pursuit of polymeric crystalline assemblies extending across a wide variety of organic–inorganic hybrid compounds has been motivated by creating structures with new topologies, cavities and channels of potential use in gas adsorption and storage, ion exchange, non-linear optical and magnetic materials [1]. Synthesis and studies of hybrid architecture via combination of organic bridging ligands and metallic nodes provides complexes with systematically tunable properties of interest [2]. In this context, the μ-aqua and azido-bridged complexes have became of high interest, due to the coordination versatility of the aqua and azido bridging modes. We have focused on the magnetic diversity of the complexes where azide ion can link two or more metal ions in various modes and mediate magnetic exchange of different nature and magnitude [3–5] (Scheme 1).

These modes may simultaneously exist in the same compound in various alternating sequences or coexist with other bridging groups. An increasing number of 2D and sometimes 3D systems have been obtained by this strategy, and the second bridging ligands used thus far have been pyridyl-based ditopic ligands such as pyrazine, 4,4′-bipy and their analogues, with some exceptions that contain carboxylate groups [6].

On the other hand, although ligands used in this work (see Scheme 2) are interesting from the structural point of view and can exhibit novel bridging networks different from other pyridine and quinoline derivatives, there are

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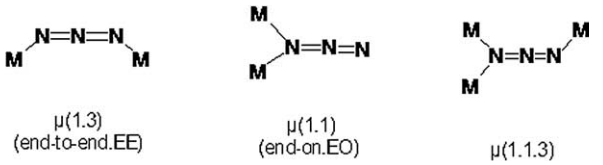
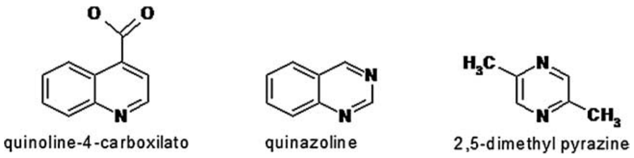


Scheme 1. Different bridging modes of the azido ion.



Scheme 2. Some pyridyl-based ditopic ligands.

only few known crystal structures. 2,5-dimethyl pyrazine as simultaneously bridging ligand through its $\mu(N,N')$ atoms was found in some copper(II) complexes [7–9], nickel(II) complex [10] and silver(I) complex [11] or coordinated through only one hetero nitrogen atom as in Ru(II) complex [12]. Also quinazoline was presented as $\mu(N,N')$ bridging in Cu(II) and Cu(I) halide complex [13]. While quinoline-4-carboxylato shows an enormous amount of complexes in the literature, although very few solved structures appear in the CCDC with Sn(II) and Re(II) [14]. Therefore, we extend our work to explore the different possible systems arising with these ligands. As part of our investigation on metal azides, we have recently reported a number of cadmium(II) azido and thiocyanato coordination polymers with some pyridine derivative ligands containing different bridging modes of $[Cd(N_3)_2]_n$ and $[Cd(NCS)_2]_n$ chains to construct coordination supramolecular frameworks [15–17]. Compared to the relatively large number of the azido-bridged polymers with Mn(II), Ni(II) and Cu(II) reported in the literature, the Cd(II) polymers are still very rare. Although diamagnetic, the cadmium systems are interesting from the structural point of view, since the systems can exhibit novel bridging networks different from other metal complexes [18]. Here, we present the reactions of cadmium(II) ions with quinoline-4-carboxylic acid, quinazoline and 2,5-dimethylpyrazine in presence of azide ions, and we isolated three complexes; 1:2:1 Cd:quinoline-4-carboxylato:H_2O (**1**), 1:2:2 Cd:quinazoline:azide (**2**) and a 1:1:2 Cd:dimethylpyrazine:azide (**3**) complexes.

2. Experimental

2.1. Material and instrumentation

Elemental analyses C, H, N were carried out using a Perkin–Elmer analyzer, Cd^{2+} was analyzed by a Perkin–Elmer Analyst 300, AAS atomic absorption spectrometer. Infrared spectra were recorded on a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. Quinoline-4-carboxylic acid, quinazoline and 2,5-dimethylpyrazine were purchased from Aldrich Company and other chemicals were of analytical grade quality and used as received.

Caution: Metal azide complexes are potentially explosives. Only a small amount of material should be prepared and should be handled with caution.

2.2. Synthesis

The complexes **1**, **2** and **3** have been synthesized in a similar way as reported [17], where an aqueous solution (20 cm^3) of $3CdSO_4 \cdot 8H_2O$ (0.77 g, 1.0 mmol, 3 mmol in Cd^{2+}) was prepared then the organic ligand (0.34 g, 2 mmol, Qux, 0.26 g, 2 mmol, Quz or 0.22 g, 2 mmol, dmpz) dissolved in ca. 15–20 cm^3 of methanol or (methanol/water) were added, followed by a dropwise addition of aqueous solution of NaN_3 (0.65 g, 10 mmol) with continuous stirring. The turbid mixtures were heated, filtered off, boiled again and the final clear mixtures were allowed to cool gradually to room temperature then placed in a refrigerator for several days. Colourless crystals of **1** and **2** with a yield (0.14 g, $\sim$30% and 0.23 g, $\sim$50%), respectively and pale yellow crystals of **3** with a yield (0.49 g, $\sim$80%) with respect to the ligand, suitable for X-ray measurements were collected and dried in air. *Anal.* Calc. for complex **1**: C, 50.60; H, 2.97; N, 5.90; Cd, 23.67. Found: C, 50.40; H, 2.88; N, 6.05; Cd, 23.59%. IR, KBr (cm^{-1}): 3573 vs, 3360 s, 2923 w, 2852 w, 2610 w, 2540 w, 2332 w, 2153 vs, 2056 w, 2038 w, 1601 s, 1577 s, 1536 w, 1458 br, 1428 w, 1403 m, 1373 m, 1340 w, 1319 s, 1227 w. 1191 br, 1110 br, 961 w, 886 br, 856 w,802 m, 683 br, 618 vs, 595 vs, 433 s, 369 s, 298 vs. *Anal.* Calc. for complex **2**: C, 42.07; H, 2.64; N, 30.66; Cd, 24.60. Found: C, 42.16; H, 2.47; N, 30.90; Cd, 24.49%. IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 3353 m, 2850 m, 2613 m, 2352 w, 2321 w, 2068 vs, 2036 vs, 1618 s, 1576 s, 1536 w, 1518 w, 1490 s, 1411 m, 1376 s, 1332 s, 1306 s, 1254 w, 1211 s, 1154 s, 1135 s, 1066 s, 954 s, 923 s, 867 m, 834 m, 787 s, 747 vs, 680 w, 634 s, 593 br, 522 m, 470 m, 442 br, 408 m, 387 m, 365 m, 342 m, 315 m, 293 m, 269 s, 233 s. *Anal.* Calc. for complex **3**: C, 23.66; H, 2.64; N, 36.78; Cd, 36.90. Found: C, 23.48; H, 2.72; N, 36.66; Cd, 36.43%. IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 3427 w, 3382 m, 3114 w, 3032 m, 2928 m, 2306 br, 2251 br, 2064 vs, 2006 w, 1838 w, 1627 w, 1552 w, 1535 w, 1502 vs, 1449 s, 1382 s, 1334 vs, 1269 br, 1159 vs, 1070 vs, 1035 s, 987 m, 896 m, 746 w, 641 m, 622 m, 594 w, 433 vs, 410 w, 387 w, 366 w, 342 w, 317 m, 290 w, 271 s, 232 s.

2.3. X-ray crystallography

All diffraction data were collected using a Siemens SMART CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The crystals were cooled to 173(2) K by a flow of nitrogen gas using the LT-2A device. Full spheres of reciprocal lattices were scanned by 0.3° steps in ω with a crystal-to-detector