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Synthetic procedures and structural features of new di- and tri-nuclear chelate compounds of Cd(II) with sulfur and nitrogen donor ligands

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ABSTRACT

$Cd(dmpymt)_2$ reacts with $CdCl_2$, $CdBr_2{\cdot}4H_2O$, CdI_2, 2,2′-bipyridine and 1,10-phenanthroline to give the dimeric chelates $[Cd(dmpymt)(bpy)Cl]_2$ and $[Cd(dmpymt)(phen)Cl]_2$, as well as the tri-nuclear complexes $[Cd_3(dmpymt)_4(bpy)_2Br_2]$ and $[Cd_3(dmpymt)_4(bpy)_2I_2]$ (dmpymtH = 4,6-dimethylpyrimidine-2-thione; bpy = 2,2′-bipyridine; phen = 1,10-phenantroline). In all complexes the Cd(II) centers present the coordination number six. The new compounds are examples of the managing of the final aggregation state of thiolate metal complexes by introducing co-ligands to block specific coordination sites of the metal center.

1. Introduction

The study of heterocyclic thione donor ligands and their metal complexes has received increasing attention because of several important features: the tautomeric species pyrimidine-2-thione, for example, is present in soluble ribonucleic acid [1,2]; metal complexes of heterocyclic thione ligands seem to be relevant as models of active sites in metalloenzymes [3], and thiolate complexes are structurally correlated with biologically active reaction centers such as nitrogenase or metallothioneins [4–6]. From the (coordination) chemical point of view, metal thiolate complexes adopt a great variety of nuclearities, as well as remarkable structural complexities, because thiolate ligands present a noteworthy tendency to bridge metal centers yielding oligo or polymeric species. Sousa and co-workers [7] have early pointed out that the aggregation state of thiolate metal complexes may be limited by providing steric constraints by means of appropriated ligand design or introducing co-ligands to block a certain number of coordination sites.

Regarding to the influence of the ligand on the aggregation state of the final products, the tautomeric ligand 4,6-dimethylpyrimidine-2-thione (dmpymtH), represented in Scheme 1, is one of the most versatile and functional sulfur donors, because it can act as a neutral monodentate [8], bridging [9] or chelating [10,11] ligand.

The deprotonation of the SH group yields a donor, tridentate anionic ligand, with two nitrogen atoms at the pyrimidine ring which support the stereochemical requisites for many unusual bonds. This behavior should explain why the ligand properties of the anion $dmpymt^-$ represent the major goal in this investigation field. An example of the versatility of the anion $dmpymt^-$ is the reaction of $dmpymt^-Na^+$ with $[CpCr(NO)_2Cl]$ [12] to give $[CpCr(NO)(dmpymt)]$ ($Cp = \pi\text{-}C_5H_5$) and NaCl, which occurs with displacement of NO followed by Cl^- elimination [13].

Although the chelating ability of anionic $dmpymt^-$ is centered in the sulfur–nitrogen pair, the sulfur atom itself can perform bridging bonds, *with* [7,14] or *without* [15] the involvement of the partner nitrogen. Recently, we have also shown that the sulfur atom can link two different metal centers, with both N atoms of the pyrimidine ring performing simultaneously a reinforced μ_2-bridge [16]. This reaction yielded α- and β-$[Cd(dmpymt)_2]_n$, the first cadmium complexes exhibiting a polymeric chain structure, with the polymerization arising exclusively due primary metal–ligand bonds, without the participation of secondary interactions.

The reactions of transition metal complexes with heterocyclic thiones, and PPh_3 [17–19] or π-allyl species [4,13,20] as co-ligands, are well known. In the same way, studies of the effects of the size of the substituents near the donor atoms of heterocyclic thiones on the polymerization of Cd^{II} complexes have been already reported [20], as well as the electrochemical synthesis of Ni^{II}/Cd^{II} [7] and Mn^{II} [21] complexes of pyrimidine-2-thione, and co-ligands such as 2,2′-bipyridine and 1,10-phenantroline.

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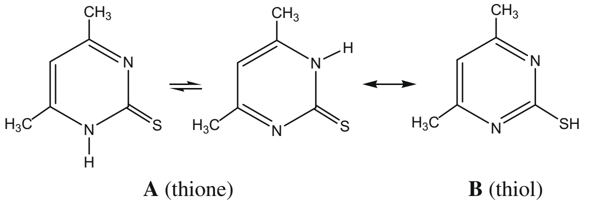

Scheme 1. Tautomeric equilibrium of 4,6-dimethylpyrimidine-2-thione (dmpymtH).

To search: (a) the behavior of cadmium(II) ions toward different stoichiometric relationships of dmpymtH, 2,2′-bipyridine and 1,10-phenantroline in the absence of electric current; (b) the introduction of co-ligands to block specific coordination sites, hence providing steric constraints in the coordination process [7], we have carried out a number of reactions whose products should contribute to enlighten this research field. We report in this communication the synthesis and the structural characterization of the new compounds [Cd(dmpymt)(bpy)Cl]$_2$ (**1**), [Cd(dmpymt)(phen)Cl]$_2$ (**2**), [Cd$_3$(dmpymt)$_4$(bpy)$_2$Br$_2$] (**3**) and [Cd$_3$(dmpymt)$_4$(bpy)$_2$I$_2$] (**4**) (dmpymtH = 4,6-dimethylpyrimidine-2-thione; bpy = 2,2′-bipyridine; phen = 1,10-phenantroline).

2. Experimental

2.1. Reagents and equipments

Cadmium chloride, cadmium iodide, cadmium bromide tetrahydrate, 2,2′-bipyridine and 1,10-phenanthroline were purchased from Sigma Aldrich®. *N*,*N*-dimethylformamide (DMF) and isopropanol were purchased from Vetec®. Cd(dmpymt)$_2$ was synthesized according to literature procedures [16]. Elemental analyses were made using a FlashEA 1112 device.

2.2. Synthesis of [Cd(dmpymt)(bpy)Cl]$_2$ (1)

To a suspension of Cd(dmpymt)$_2$ (0.039 g, 0.1 mmol) in 5 mL of DMF, CdCl$_2$ (0.018 g, 0.1 mmol) was added. After stirring of the clear suspension for 30 min at 25 °C, 0.031 g (0.2 mmol) of 2,2′-bipyridine were added, producing a white precipitate of [CdCl$_2$(bpy)]. The reaction was stirred during 1 h, and the precipitate was filtered off. The addition of an isopropanol layer to the mother solution led to the formation of white single crystals of the product, after one day. Yield: 0.006 g, 7% based on Cd(dmpymt)$_2$. Melting point: 193–195 °C. *Anal.* Calc. for $C_{32}H_{30}Cd_2Cl_2N_8S_2$ (886.46): C, 43.32; H, 3.41; N, 12.63. Found: C, 43.57; H, 3.42; N, 12.92%. IR (KBr; s, strong; m, middle; w, weak): 3049 [w, ν_s(C–H)$_{ar.}$], 2922 [w, ν_s(C–H)], 1591–1540 [s, ν_s(C=N) + ν_s(C=C)], 1439 [s, ν_{as}(C=N)], 1253 [s, ν_s(C–S)], 765 cm^{-1} [m, δ(N=C–S)].

2.3. Synthesis of [Cd(dmpymt)(phen)Cl]$_2$ (2)

According to the synthesis of **1**, with 0.036 g (0.2 mmol) of 1,10-phenanthroline in the place of 2,2′-bipyridine. The isolated precipitate was [CdCl$_2$(phen)]. Single white crystals of **2** suitable for X-ray analysis were obtained after one day, in the isopropanol layer. Yield: 0.006 g, 8% based on Cd(dmpymt)$_2$. Melting point: 246–249 °C. *Anal.* Calc. for $C_{36}H_{30}Cd_2Cl_2N_8S_2$ (934.50): C, 46.23; H, 3.23; N, 11.98. Found: C, 46.51; H, 3.18; N, 11.95%. IR (KBr): 3049 [w, ν_s(C–H)$_{ar.}$], 2918 [w, ν_s(C–H)], 1571–1541 [s, ν_s(C=N) + ν_s(C=C)], 1423 [s, ν_{as}(C=N)], 1250 [s, ν_s(C–S)], 773 cm^{-1} [m, δ(N=C–S)].

2.4. Synthesis of [Cd$_3$(dmpymt)$_4$(bpy)$_2$Br$_2$] (3)

To a suspension of Cd(dmpymt)$_2$ (0.039 g, 0.1 mmol) in 5 mL of DMF, 0.034 g (0.1 mmol) of CdBr$_2$·4H$_2$O were added. After stirring of the clear suspension for 30 min at 25 °C, 2,2′-bipyridine (0.031 g, 0.2 mmol) was added and the reaction was stirred for 1 h. Single white crystals suitable for X-ray analysis were obtained after one day, by adding a layer of isopropanol to the mother solution. Yield: 0.064 g, 94% based on Cd(dmpymt)$_2$. Melting point: 242–245 °C. *Anal.* Calc. for $C_{44}H_{44}Br_2Cd_3N_{12}S_4$ (1366.18): C, 38.65; H, 3.25; N, 12.30. Found: C, 38.94; H, 3.53; N, 12.65%. IR (KBr): 3022 [w, ν_s(C–H)$_{ar.}$], 2917 [w, ν_s(C–H)], 1575–1537 [s, ν_s(C=N) + ν_s(C=C)], 1437 [s, ν_{as}(C=N)], 1259 [s, ν_s(C–S)], 769 cm^{-1} [m, δ(N=C–S)].

2.5. Synthesis of [Cd$_3$(dmpymt)$_4$(bpy)$_2$I$_2$] (4)

According to the synthesis of **3**, with 0.037 g (0.1 mmol) of CdI$_2$ instead of CdBr$_2$·4H$_2$O. Single white crystals suitable for X-ray analysis were obtained after one day in the isopropanol layer of the mother solution. Yield: 0.066 g, 91% based on Cd(dmpymt)$_2$. Melting point: 220–223 °C. *Anal.* Calc. for $C_{44}H_{44}I_2Cd_3N_{12}S_4$ (1460.16): C, 36.16; H, 3.04; N, 11.50. Found: C, 36.24; H, 3.11; N, 11.71%. IR (KBr): 3022 [w, ν_s(C–H)$_{ar.}$], 2915 [w, ν_s(C–H)], 1575–1536 [s, ν_s(C=N) + ν_s(C=C)], 1436 [s, ν_{as}(C=N)], 1258 [s, ν_s(C–S)], 767 cm^{-1} [m, δ(N=C–S)].

2.6. X-ray structural determination

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using SHELXS [22]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [22]. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Crystal data and more details of the data collections and refinements are contained in Table 1.

3. Results and discussion

3.1. Structure

The X-ray crystal data and the experimental conditions for the analyses of [Cd(dmpymt)(bpy)Cl]$_2$ (**1**), [Cd(dmpymt)(phen)Cl]$_2$ (**2**), [Cd$_3$(dmpymt)$_4$(bpy)$_2$Br$_2$] (**3**) and [Cd$_3$(dmpymt)$_4$(bpy)$_2$I$_2$] (**4**) are given in Table 1. Selected bond distances and angles of the title compounds are listed in Tables 2 and 3. Figs. 1 and 2 represent the dimeric compounds **1** and **2**, and Figs. 3 and 4 show the molecular structure of the tri-nuclear chelate complexes **3** and **4**.

In all the obtained products the ligand 4,6-dimethylpyrimidine-2-thione (dmpymtH) undergoes deprotonation and coordinates to the metal centers through the sulfur–nitrogen pair. In the four structures the metal centers present the coordination number six, showing distorted octahedral configurations, principally in the case of the chelates **1** and **2**. The main reason for the octahedral distortion in all compounds is the small bite angle of the bidentate (dmpymt)$^-$ ligand {63.26(8), N4–Cd1–S1 (**1**); 62.79(12), N3–Cd–S (**2**); 59.98(6), S1–Cd1–N3; 63.03(7), N6–Cd2–S2 (**3**); 60.41(6), S1–Cd2–N1; 62.78(7)°, N4–Cd1–S2 (**4**)}.

In the uncommon dimeric assemblies of **1** and **2** (supported by three different ligand species), two chlorine bridges hold the cadmium(II) centers at distances of 3.8091(5) (**1**) and 3.7629(6) Å (**2**), quite longer than the sum of the van der Waals radii of two