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One-dimensional cobalt and zinc complexes involving in situ reaction of ethylenediamine and acetonitrile to form imidazoline ligand

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Abstract

The solvothermal treatment of cobalt nitrate (or zinc acetate), ethylenediamine and dicarboxylate in acetonitrile produced two onedimensional coordination polymers $[Co(mimz)_2(ox)]_n$ (1) and $[Zn(mimz)_2(ip)]_n$ (2) (mimz = 2-methylimidazoline, ox = oxalate, ip = isophthalate) which ligand involving in situ formation of imidazoline ligand by cycloaddition reaction of ethylenediamine and acetonitrile. © 2005 Elsevier B.V. All rights reserved.

Keywords: Imidazoline; Ligand reaction

The imidazole ring and its derivatives are very useful models to understand the coordination properties and the reaction mechanisms of the biologically important systems where these molecules are involved [1]. The role of the imidazole ring as metal binding site in metalloproteins is well known, and then studies of new synthesis route for these complexes are of interest [2-6]. Imidazoline, one cyclic amidine or derivative of imidazole, has attracted some attention in the field, and its formation traditionally depends on the transformation of organonitriles such as addition of nucleophiles [7] to the C=N triple bond. One of the main problems in nucleophilic addition reactions is the insufficient electrophilic activation even in the presence of very strong electron-accepting groups R at $RC \equiv N$ (R = Cl). These difficulties, however, can be overcome with the use of metal ions [8,9], in some cases even metal ions of low valence functioning strong activators toward nucleophilic attack. This activation can result in enhancement of the rate of the addition commonly in the range from 10^6 to 10^{10} [10,11]. The lanthanide(III) and Pt(II) catalytic nucleophilic additions of diamines to organonitriles have been reported [12-14], which provides an alternative synthetic route for cyclic amidines. The catalytic nucleophilic additions of diamines to organonitriles to form cyclic amidines by first-row transition metal ions such as Co(II) and Zn(II) ions have not been documented so far. It is worth noting that the above mentioned synthetic route for cyclic amidines are based on traditional organic methods, e.g., refluxing [12–14].

On the other hand, in situ ligand synthesis is of great interest in coordination chemistry and organic chemistry due to effectiveness, simplicity and environmental friendliness. Hydro(solvo)thermal method has been demonstrated to be a very promising technique to prepare complexes with novel structures and special properties, especially in growing crystals of complexes involving in situ ligand synthesis because of its relatively critical reaction conditions [15]. Based on these considerations, we tried to develop M^{2+} (M = Co, Zn) complexes of 2-methylimidazoline by solvothermal nucleophilic cyclic addition of ethylenediamine (en) and acetonitrile. We report herein two new complexes namely $[Co(mimz)_2(ox)]_n$ (1) and $[Zn(mimz)_2(ip)]_n$ (2) (mimz = 2-methylimidazoline, ox = oxalate, ip = isophthalate) which show one-dimensional structures formed by bridging of $[M(mimz)_2]^{2+}$ (M = Co, Zn) fragments via dicarboxylates.

Reaction of cobalt nitrate, oxalic acid, en, and acentonitrile in molar ratio of 2:2:1:435 in a 15 ml Teflon-lined

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stainless container at 150 °C for 72 h resulted in red blocklike crystals (45% yield based on en). Reaction of zinc acetate, isophthalic acid, en, and acentonitrile in molar of 1:2:1:435 in a 15 ml Teflon-lined stainless container at 150 °C for 72 h resulted in colourless block-like crystals (25% yield based on en). The pure complexes 1 and 2 were obtained by mechanically picking single crystals with the help of microscopy. IR and Elemental analysis confirmed the formulas of 1 and 2.

As expected, X-ray crystallography reveals that ligand 2-methylimidazoline was in situ formed in **1** and **2**. Compound **1** has a one-dimensional structure similar to that of $[Co(im)_2(ox)]$ (im = imidazole) [16]. As shown in Fig. 1, the Co(II) ion in **1** is octahedrally coordinated to four oxygen atoms from two oxalates and two nitrogen atoms from two 2-methylimidazolines. The Co–O bond lengths [2.119(3) and 2.137(3) Å] are close to those [av. 2.120(3) Å] in $[Co(im)_2(ox)]$, and the Co–N bond lengths [2.094(4) Å] are close to those [2.112(2) and 2.031(1) Å] in $[Co(im)_2(ox)]$. Two mimz ligands are located in *cis*- positions with N(1a)–Co(1)–N(1) 89.2(2)°, which is smaller



Fig. 1. Perspective view of coordination environment of Co(II) (a) and zig-zag chain (b) in 1. For clarity, the hydrogen atoms of imidazoline are omitted in (b).

than that $97.5(2)^{\circ}$ in [Co(im)₂(ox)], and three *trans*-L-Co-L angles (164.42(15)°, 175.34(14)° and 175.34(14)°), which are larger than those $[163.51(15)^\circ, 171.1(5)^\circ]$ and $169.2(5)^{\circ}$ in [Co(im)₂(ox)]. The structure of 1 is onedimensional zig-zag polymeric structure formed by $[Co(mimz)_2]^{2+}$ fragments bridged by oxalate in bis-chelate mode. In contrast, the Zn(II) ion in 2 is tetrahedrally coordinated to two oxygen atoms from two isophthalates with Zn-O bond lengths of 2.016(3) and 2.021(3) Å, and two nitrogen atoms from two imidazoline groups with Zn-N bond lengths of 1.992(4) and 2.005(6) Å. The N-Zn-N and O–Zn–O bond angles are $117.5(2)^{\circ}$ and $94.74(14)^{\circ}$, respectively. The N-Zn-O bond angles are in the range of 105.77(2)-119.21(16)° [av. N-Zn-O 110.35°]. 2 shows also one-dimensional structure consisting of $[Zn(mimz)_2]^{2+}$ fragments and dicarboxylates. However, different from the coordination mode of oxalate, isophthalate in 2 is coordinated in bis-monodentate mode. Besides, we attempted to prepare the other first-row transition metal complexes of mimz but we did not get single crystals under the similar synthetic conditions. (see Fig. 2).

The formation of imidazoline by lanthanide(III) catalytic nucleophilic additions of diamines to organonitriles has been reported, and authors suggested that the Ln^{3+} ions activate the nitriles through a predominantly electrostatic, ion–dipole interaction [12]. For Co(II) and Zn(II) ions which have lower charge, it seems that there is less possibility to activate the nitriles through electrostatic ion–dipole interaction. Considering that the acetonitrile could function as weak N-donor ligand to electrophilically activate the carbon atom, 2-methylimidazolines in **1** and **2** are presumably formed by nucleophilic attack of free ethylenediamine on the electrophilically activated carbon atom



Fig. 2. Perspective view of coordination environment of Zn(II) (a) and chain-like structure of **2** (b). For clarity, the hydrogen atoms of imidazoline are omitted in (b).

of the acetonitrile. We tried to isolate 2-methylimidazoline using catalytic amounts of metal ions but failed. Thus formation of insoluble solids **1** and **2** is less partly responsible for nucleophilic addition of diamine to organonitrile. The possible intermediate amidine undergoes rapid intramolecular ring closure.

To sum up, two one-dimensional coordination polymers of 2-methylimidazoline have been prepared by solvothermal reaction involving in situ nucleophilic cycloaddition reaction of ethylenediamine and acetonitrile to form 2-methylimidazoline. The ligand reaction described here, although not unprecedented, might open up new horizons for the preparation of unusual types of cyclic amidine ligands by use of first-row transition metal ions as catalysts [17].

Supplementary data

Additional material comprising atomic coordinates, thermal parameters, and the full bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Center (CCDC 278644 and 278645).

Note

Anal. Calc. for 1 $C_{10}H_{16}CoN_4O_4$: C, 38.11; H, 5.12; N, 17.78; O, 20.30. Found: C, 38.09; H, 5.13; N, 17.76; O, 20.32. IR (KBr,cm⁻¹): 3147s, 2423w, 1633s, 1397s, 1321m, 1286m, 1161m, 1072, 965m, 858m, 805w, 707w, 546m. Anal. Calc. for 2 $C_{16}H_{20}N_4O_4Zn$: C, 48.32; H, 5.07; N, 14.09; O, 16.09. Found: C, 48.35; H, 5.10; N, 14.10; O, 16.05. IR (KBr, cm⁻¹): 3413m, 3112s, 1700m, 1599m, 1414s, 1179m, 1027m, 977w, 948w, 860w, 523m.

Crystal data for 1 C₁₀H₁₆CoN₄O₄: monoclinic, space $M_{\rm r} = 315.20, \quad a = 11.6634(16) \,\text{\AA},$ group C2/c, b =12.2495(16) Å, c = 9.3138(13) Å, $\alpha = 90^{\circ}$, $\beta =$ 95.387(3)°, $\gamma = 90^{\circ}$, V = 1324.8(3) Å³, Z = 4, $D_c = 1.580$ g cm⁻³, F(000) = 652, $\mu = 1.311$ mm⁻¹, $T_{\text{max}} = 0.9494$, $T_{\text{min}} = 0.7794$, S = 0.950, $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}$ (e A⁻³) = 0.376/ -0.357. Crystal data for 2 C16H20ZnN4O4: monoclinic, space group $P2_1$, $M_r = 397.73$ a = 10.0973 (15) Å, b = 7.9349(11) Å, c = 11.8244(18) Å, $\alpha = 90^{\circ}$, $\beta =$ 115.098(2)°, $\gamma = 90^{\circ}$, $V = 857.9(2) \text{ Å}^3$, Z = 2, $D_c = 1.540 \text{ g}$ cm⁻³, F(000) = 412, $\mu = 1.460 \text{ mm}^{-1}$, $T_{\text{max}} = 0.9047$, $T_{\text{min}} = 0.8107$, S = 1.063, $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}$ (e A⁻³) = 0.641/ -0.498. Diffraction intensities were collected at 293 K on a Bruker Apex CCD diffractometer (Mo Κα,

 $\lambda = 0.71073$ Å). The structure was solved with the direct methods and refined with full-matrix least-squares technique (SHELX-97) [18]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were were geometrically placed and refined isotropically. For **1** the final R_1 value is 0.0624 for 87 parameters and 1387 unique reflections and the final wR_2 is 0.1154 for all 2418 reflections, and the final R_1 value is 0.0494 for 226 parameters and 3418 unique reflections and the final wR_2 is 0.1194 for all 4511 reflections for **2**.

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