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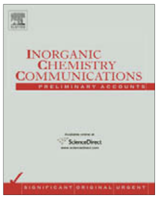

Synthesis, structures and antibacterial activities of two complexes of yttrium (III) with 2,6-pyridinedicarboxylate

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ABSTRACT

Two novel complexes, $Na_3Y(pydc)_3\cdot 12H_2O$ (**1**) and $Y_2(pydc)(OH)_4\cdot 3H_2O$ (**2**) (pydc = 2,6-pyridinedicarboxylate), were synthesized by yttrium (III) nitrate and $pydcH_2$ with different molar ratios. The elemental analysis, IR spectra and single crystal X-ray diffraction were used to determine the structure of complexes. The thermal decompositions and antimicrobial activities against *Bacillus coli* and *Staphylococcus aureus* were recorded and interpreted for both.

In the last decades, metal–organic coordination complexes have attracted extensive interest in virtue of their structural diversities, promising perspectives toward new functional materials [1] and potential applications in the fields of catalysis [2], conductivity [3], magnetism [4], optical behaviors [5], ion exchange [6] and adsorption [7]. Much work are focused on transition metal coordination polymers with multi-carboxyl ligands [8], such as 2,6-pyridinedicarboxylate [9], 2,5-pyridinedicarboxylate [10], 3,5-pyridinedicarboxylate [11], 2,4-pyridinedicarboxylate [12], and 3,4-pyridinedicarboxylate [13]. The multi-carboxyl ligands are good spacers for the formation of 1D, 2D or 3D frameworks owing to their rich coordination modes. The coordination complexes constructed from lanthanide and pyridinedicarboxylate have become a notable topic in literature [14]. However, the complexes of yttrium (III) (lanthanide element) with pyridinedicarboxylate have less been studied [15], especially on their crystal structures and antibacterial activities. In actuality, it is difficult to obtain the single crystal complexes of yttrium (III) with organic ligands for the special outer electron structure and radius of yttrium atom differing from other rare earth metal atoms. So it is significant to synthesize the single crystal complexes of yttrium (III) with pyridinedicarboxylate and determine the structures and other properties of them.

The 2,6-pyridinedicarboxylic acid ($pydcH_2$), known as dipicolinic acid, has biological activity [16]. It is possible for $pydcH_2$ to form bridging or hydrogen bonds coordination complexes with other metals or ligands owing to its diverse functional groups in self-assembly process [17]. The heat resistance of the spores of several gram-positive eubacteria during sporulation is attributed to the presence of the calcium 2,6-pyridinedicarboxylate. Its complexes of iron are found to play the role of electron carriers in some model biological systems [18] and are recognized as specific molecular tools in DNA cleavage [19]. On the other hand, the less toxicity of yttrium than other rare earth metals make it possible to be used as antineoplastic drugs and antibacterial medicaments [20]. This leads us to study novel complexes of yttrium (III) with $pydc^{2-}$ and to disclose their structures, components, antibacterial activities and so on. Here we mainly report the synthesis, structural characterizations, thermal decompositions and antibacterial activities of two novel complexes, $Na_3Y(pydc)_3\cdot 12H_2O$ (**1**) and $Y_2(pydc)(OH)_4\cdot 3H_2O$ (**2**).

An aqueous solution of yttrium (III) nitrate (0.6 mmol, 10 mL) was dropped into 30 mL aqueous solution of $pydcH_2$ (0.6 mmol, 0.9 mmol, 1.2 mmol, 1.8 mmol, respectively) under stirring at 60 °C. Then the mixture was adjusted to pH 6.0 by 1.0 mol L^{-1} NaOH. After 4 h, the resultant was cooled to room temperature and filtered. The colorless crystals of complex $Na_3Y(pydc)_3\cdot 12H_2O$ (**1**) suitable for X-ray diffraction were obtained by slowly evaporating the filtered liquor at room temperature in 40%, 42%, 45% and 72% yield, respectively. The white precipitate residues $Y_2(pydc)(OH)_4\cdot 3H_2O$ (**2**) were obtained by washing with water and vacuum drying for 24 h at 60 °C in 38%, 35%, 30% and zero yield, when the molar ratios of yttrium (III) nitrate to $pydcH_2$ were about 1:1, 1:1.5, 1:2 and 1:3, respectively. Anal. Calcd. for $C_{21}H_{33}N_3Na_3O_{24}Y$: C, 29.00; H, 3.80; N, 4.83; Y, 10.47. Found: C, 28.98; H, 3.75; N, 4.82; Y, 10.24%. Anal. Calcd. for $C_7H_{13}NO_{11}Y_2$:

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C, 18.04; H, 2.69; N, 3.02; Y, 38.06. Found: C, 18.06; H, 2.80; N, 3.01; Y, 38.28%.

In IR spectra, the ligand pydcH_2 shows stretching bands attributed to $\upsilon(CO)$, υ_{as}(OCO), υ_s(OCO), υ(CN) and υ(CH) at 1697, 1575, 1415, 1299 and 1082, and 997 and 513 cm^{-1}, respectively. In complex **1**, the absence of characteristic absorption band at 1697 cm^{-1} and the appearance of the absorption bands at 1627 and 1393 cm^{-1} assigned to υ_{as}(OCO) and υ_s(OCO) are observed. The separation value ($\Delta\upsilon = 234\ cm^{-1}$) of υ_{as}(OCO) and υ_s(OCO) indicates a notable participation of the ionic bond and a strong mono-dentate coordination of the oxygen atom of carboxyl with the yttrium (III) ion centre. This is confirmed by the band around 434 cm^{-1} assigned to Y–O bond [16]. Compared to the ligand, the bands of υ(CN) and υ(CH) of complex **1** shift to 1280 and 1080 cm^{-1}, and 920 and 520 cm^{-1}, respectively. This indicates the pyridyl nitrogen is coordinated to yttrium atom. The broad absorption bands attributed to υ(OH) at 3700–2900 cm^{-1} are reasonably attributable to coordinated H_2O molecules. In complex **2**, the broad absorption bands of υ(OH) and υ(CO) appear at 3490–3410 cm^{-1} and 1628 cm^{-1}, respectively. The characteristic absorption band of Y–O bond appears at 487 cm^{-1}. The absorption band of C–N in complex **2** is shifted insignificantly compared to pydcH_2, which indicates the nitrogen atom of the pyridine ring does not take parting in the coordination of Y^{3+} ions.

Complex **1** crystallizes in the monoclinic system and space group P2(1)/c [21]. A diagram of the crystal structure of complex **1** is presented in Fig. 1. The deprotonated ligand pydc^{2-} acts as a tridentate ligand combining with Y^{3+} ion through two carboxyl oxygen atoms and one nitrogen atom, which leads to two five-member chelating cycles formed through pyridine ring. Y(1) ion centre is coordinated by three pairs of chelating oxygen atoms and three pyridyl nitrogen atoms from three pydc^{2-} ligands. The Y–O (carboxyl) bond distances range from 2.372(3) to 2.408(3) Å with a mean value of 2.391 Å, and the Y–N bond distances range from 2.473(4) to 2.489(4) Å with a mean value of 2.479 Å. The summation of bond angle of N(1)–Y(1)–N(2), N(1)–Y(1)–N(3) and N(2)–Y(1)–N(3) is 359.90°, which indicates that Y(1) is located in the centre of N(1)N(2)N(3) base plane. Three oxygen atoms O(1), O(5) and O(9) have formed a triangle and another three oxygen atoms O(3), O(7) and O(11) have formed another triangle around the Y(1) ion. Three Na^+ ions act as counter ions with symmetrical centre. Thus complex **1** exhibits a 3D infinite framework structure through Na^+ counter ions interaction with O atoms of carbonyls and O atoms of water molecules (Fig. 2). Our efforts to crystallize complex **2** and obtain single crystals suitable for X-ray diffraction studies are not successful. To sum up all of arguments, we figure out that the possible structure of anhydrous complex **2** is listed as Fig. 3.

In order to study the thermal stabilities of two complexes, the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are performed at a heating rate of 10 °C min^{-1} with air as the static atmosphere in the range 30–700 °C. In Fig. 4, the TGA curve of complex **1** shows the decomposition in four stages. The first weight loss is about 18.26% (calcd. 18.64%) in the range of 30–100 °C, corresponding to nine non-coordinated water molecules. Immediately followed by another 5.74% (calcd. 6.21%) weight loss in the range of 100–182 °C, it is corresponding to three coordinated water molecules. The third weight loss is about 26.83% (calcd. 26.58%) corresponding to three pydc^{2-} molecules, to form the intermediate products of $Na_2C_2O_4$ and $Y_2(C_2O_4)_3$ around 440 °C, then immediately followed by another 32.18% (calcd. 32.65%) weight loss corresponding to oxalates, ultimately giving stable compounds Na_2CO_3 and Y_2O_3 at approximate 650 °C. It is consistent with two strong exothermic peaks around 490 °C and 610 °C in the DTA curve of complex **1**. In Fig. 5, the TGA curve of complex **2** shows the decomposition in two stages. The first weight loss is about 11.14% (calcd. 11.61%) in the range of 30–150 °C, corresponding to three water molecules. The second weight loss is about

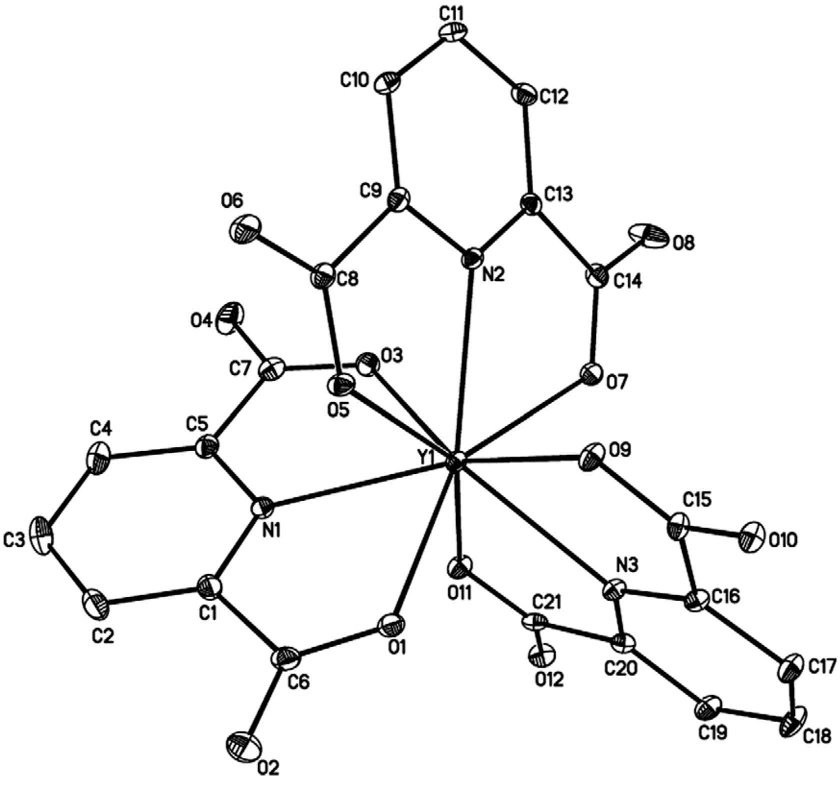

Fig. 1. Perspective view of complex $Na_3Y(pydc)_3 \cdot 12H_2O$, all hydrogen atoms and solvent molecules have been omitted for clarity.