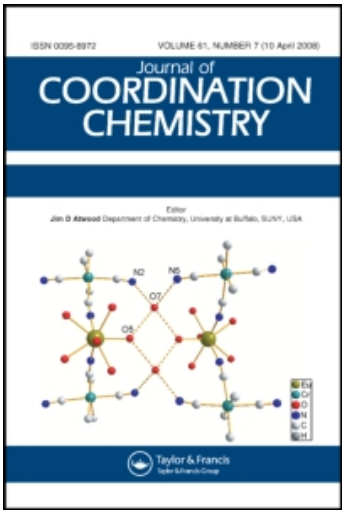

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Synthesis, characterization, and antibacterial activity of yttrium(III) complexes with 2,6-pyridinedicarboxylate and pyridine

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Synthesis, characterization, and antibacterial activity of yttrium(III) complexes with 2,6-pyridinedicarboxylate and pyridine

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A series of metal coordination complexes of yttrium(III) containing 2,6-pyridinedicarboxylate and pyridine have been prepared with different molar ratios of yttrium(III) to 2,6-pyridinedicarboxylate in aqueous pyridine solutions, and characterized by elemental analysis, infrared spectra, nuclear magnetic resonance, and thermal analyses. The *in vitro* antibacterial activities of the complexes have also been investigated against microorganisms such as Gram-negative bacteria *Bacillus coli* and Gram-positive bacteria *Staphylococcus aureus* by the disc diffusion method in DMSO. When compared to previous results, the yttrium(III) complexes of 2,6-pyridinedicarboxylate and pyridine have a moderate effect on microorganisms due to the presence of the pyridine group.

Keywords: Yttrium; 2,6-Pyridinedicarboxylate; Pyridine; Antibacterial activity; Coordination complex

1. Introduction

2,6-Pyridinedicarboxylic acid ($pydcH_2$) and its anions ($pydcH^-$, $pydc^{2-}$) have been proved to be well-suitable for construction of multidimensional frameworks with simple metal ions and nonmetal cations [1] due to the presence of heterocyclic nitrogen and two carboxylate groups functioning as monodentate [2], bidentate [3], tridentate [4], and bridging [5] ligand. Research in metal complexes coordinated with 2,6-pyridinedicarboxylate (pydc) has attracted a great deal of attention [6–9] due to their magnetic [10–12], luminescence [13–15], and antibacterial activity [16, 17]. Some rare earth metal complexes such as La(III), Ce(III), Eu(III), and Gd(III) coordinated with 2,6-pyridinedicarboxylate were synthesized and characterized for their potent antibacterial activity [18]. However, the rare earth metal ions with different ligands have varying antibacterial activities against bacterial species; and the antibacterial activities of these rare metal complexes are not very notable. Thus, more studies have focused on

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preparation of complexes from different rare metal ions coordinated with binary or ternary mixed ligands [19, 20].

We recently reported synthesis, structure, and antibacterial activities of two yttrium(III) compounds based on 2,6-pyridinedicarboxylate [21]. As continuation of our research, we prepared other yttrium(III) coordination complexes with 2,6-pyridinedicarboxylate and pyridine (py). Herein, we report the synthesis, structure, and thermal properties of four complexes of yttrium(III) coordinated with 2,6-pyridinedicarboxylate and pyridine. All complexes are also investigated for their antibacterial activities against Gram-negative bacteria *Bacillus coli* and Gram-positive bacteria *Staphylococcus aureus*.

2. Experimental

2.1. *Reagents and materials*

2,6-Pyridinedicarboxylic acid (99%) was purchased from Sigma-Aldrich Chemical Company. Yttrium(III) oxide (99.99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Other analytical grade chemical reagents were purchased commercially and used without purification. *Bacillus coli* (8099) and *S. aureus* (ATCC 6538; ATCC, American Type Culture Collection) were provided by Shanghai Drug Institute, the Chinese Academy of Sciences.

2.2. *Synthesis of metal complexes*

An aqueous solution of $Y(NO_3)_3$ ($0.6\,mol\cdot L^{-1}$) was prepared. Yttrium oxide (1.70 g, 7.53 mmol) was dissolved in 10 mL nitric acid ($6\,mol\cdot L^{-1}$) by heated to accelerate yttrium(III) oxide dissolution and to get rid of excessive nitric acid, and then diluted to 25 mL with distilled water.

All the complexes were synthesized following the same general procedure except different molar ratios of yttrium(III) to $pydcH_2$ (Supplementary material). In the preparation procedure, pyridine was in excess. However, the process of dealing with the filtrate and obtaining powders is slightly different.

2.2.1. $Y_2(pydc)_3(py)\cdot 4H_2O$ (1). An aqueous solution of $Y(NO_3)_3$ (0.6 mmol, 5 mL) was slowly added to an aqueous solution of $pydcH_2$ (0.6 mmol, 30 mL) and stirred for 10 min at 60°C. To the mixture, pyridine (2 mL) was added and stirring continuously for 4 h. Upon cooling, a white precipitate was isolated by filtration, washed with water, and dried in an oven. The yield of **1** was 67.5%.

2.2.2. $Y_2(pydc)_3(py)_2\cdot 2H_2O$ (2). Complex **2** was prepared in a similar manner to **1** from an aqueous solution of $Y(NO_3)_3$ (0.6 mmol, 5 mL) and $pydcH_2$ (0.9 mmol, 30 mL) giving a white precipitate in 76.2% yield.

2.2.3. $Y(pydc)_2(pyH) \cdot H_2O$ (3). Complex **3** was prepared in a similar manner to **1** from an aqueous solution of $Y(NO_3)_3$ (0.6 mmol, 5 mL) and $pydcH_2$ (1.2 mmol, 30 mL) giving a white precipitate in 78.4% yield.

2.2.4. $Y(pydc)_3(pyH)_3 \cdot 4H_2O$ (4). Complex **4** was prepared in a similar manner to **1** from an aqueous solution of $Y(NO_3)_3$ (0.6 mmol, 5 mL) and $pydcH_2$ (1.8 mmol, 30 mL) giving a colorless transparent solution. White powder was collected by slowly evaporating the liquid at room temperature, filtered, washed with ethanol, and dried (yield, 78.6%).

2.3. *Physical measurements*

The carbon, hydrogen, and nitrogen contents were determined by elemental analysis using a CHN Vario EL III analyzer. Yttrium(III) content was determined by an IRIS 1000 inductively coupled plasma-atomic emission spectrometry (ICP-AES). Data are given in table 1. FT-IR spectra of complexes were recorded from 4000 to 400 cm^{-1} using a 5700 Nicolet spectrometer. The samples were prepared as KBr discs. ^{1}H-NMR spectra were obtained on a Bruker DRX 500 Fourier transform spectrometer operating at 500 MHz using dimethyl sulfoxide-d_6 (DMSO-d_6) as solvent. The thermal stability of complexes was determined in air using a WRT-2P TGA and a CRY-2 DTA thermal analysis instruments. Samples ranging between 7.00 and 9.00 mg were heated in Al_2O_3 crucibles to 650°C at a heating rate of 10°C · min^{-1} in static air.

2.4. *Procedure for antibacterial activity*

In vitro antibacterial activities of free ligands and metal complexes were tested against the Gram-negative bacteria *B. coli* and Gram-positive bacteria *S. aureus* by the disc diffusion method. The bacterial strains were picked with inoculating loop and inoculated in 2 mL liquid medium at (37 ± 1)°C for 12 h, and 0.2 mL of the liquid containing strains was coated uniformly on the surface of the solid medium plate. Five minutes later, filter paper discs (5 mm in diameter) were soaked in 20 μL DMSO solution containing 0.005 mol · L^{-1} yttrium(III) complexes or ligands and incubated for 16–24 h at (37 ± 1)°C. The diameter of inhibition zone around each disc was measured with a vernier caliper after 16–24 h. Every sample was paralleled three times.

Table 1. Elemental analysis data of yttrium complexes containing pydc and py.

		Y (%)		C (%)		N (%)		H (%)	
Complexes	Molecular weight	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Y_2(pydc)_3(py) \cdot 4H_2O$	824.29	21.60	21.14	37.86	37.81	6.80	6.78	2.67	2.75
$Y_2(pydc)_3(py)_2 \cdot 2H_2O$	867.36	20.53	20.29	42.91	42.87	8.07	8.02	2.65	2.68
$Y(pydc)_2(pyH) \cdot H_2O$	517.24	17.21	17.05	44.10	44.06	8.12	8.06	2.71	2.85
$Y(pydc)_3(pyH)_3 \cdot 4H_2O$	896.61	9.93	9.77	48.21	48.07	9.38	9.40	3.91	3.79

3. Results and discussion

3.1. *FT-IR spectra*

To confirm the composition of the prepared complexes and to determine the metal–ligand coordination, infrared (IR) spectra of $pydcH_2$ and the prepared complexes were recorded. The FT-IR spectra of yttrium(III) complexes are very similar, but different from the free ligands (table 2).

In the prepared yttrium(III) complexes, the characteristic absorption bands of –COOH groups of free $pydcH_2$ at 1692 cm^{-1} disappear, and bands of asymmetrical (ν_{as}) and symmetrical (ν_s) vibrations of COO^- appear at 1622–1614 and 1593–1582 cm^{-1}, and 1443–1431 and 1392–1381 cm^{-1} [22]. The separation value ($\Delta\nu = 180\,cm^{-1}$) of ν_{as}(COO) and ν_s(COO) indicates participation of the ionic bond and strong monodentate coordination of the carboxylate oxygen to yttrium(III) [23]. The asymmetrical (ν_{as}) and symmetrical (ν_s) bands of COO^- are split suggesting that COO^- groups are bonded in different ways in the same molecule. Bands of Y–O appear at 438–416 cm^{-1} [24]. Bands of C–N in the pyridine ring appear at 1271–1283 and 1061–1077 cm^{-1} in the prepared complexes, whereas the bands of C–N vibrations appear at 1291 and 1082 cm^{-1} in 2,6-pyridinedicarboxylate, and 1216 and 1067 cm^{-1} in pyridine; this indicates that the pyridyl nitrogens are coordinated to yttrium [25]. Absorptions of C–N in the prepared complexes are different from the absorptions of free pyridine, indicating that the pyridines are combined with 2,6-pyridinedicarboxylate or yttrium(III). The appearance of characteristic absorption bands at 2500–2000 cm^{-1} and the disappearance of absorption at 3200–2500 cm^{-1} show that a hydrogen bond has been formed between nitrogen of py and hydrogen of $pydcH_2$ [26]. Broad absorptions at 3431–3203 cm^{-1} assigned to ν(OH) indicate that water is found in the prepared complexes [27], confirmed in thermal analyses.

3.2. *^{1}H-NMR spectra*

^{1}H-NMR spectra of free pyridine and $pydcH_2$ and the yttrium(III) complex were obtained in DMSO-d_6 and the chemical shift data are given in table 3.

In ^{1}H-NMR spectra, two characteristic sets of resonances indicate the presence of two different pyridine rings. The first set is located at 7.72–7.84 and 8.62–8.76 ppm assigned to the pyridine ring of py, while the second set at 8.06–8.31 ppm is assigned to the pyridine ring of pydc. The sharp resonance of –COOH appearing at 13.24 ppm disappears in the ^{1}H-NMR spectra of yttrium(III) complexes, indicating no free –COOH group exists in the complexes. The decreasing chemical shift of ^{1}H-NMR for $pydc^{2-}$ confirm that $-COO^-$ is coordinated with Y^{3+}, and the increasing chemical shifts for py suggest that pyridine groups are combined with Y^{3+} ions in **1** and **2** and combined with $pydc^{2-}$ groups in **3** and **4**. In other words, hydrogen bonds are formed through the oxygen and hydrogen of carboxyl groups and/or water and the nitrogen of py in **3** and **4**. Furthermore, the disappearance of –COOH at 13.24 ppm suggests that the pyridine molecules are protonated in **3** and **4**.

3.3. *Thermal analyses*

The thermal decomposition behaviors of **1**, **2**, **3**, and **4** have been studied by TGA and DTA in static air at a heating rate of 10°C min^{-1} (Supplementary material), and the

Table 2. Frequencies of the most important absorption bands for IR spectra of $pydcH_2$, py, and complexes (cm^{-1}).

Complexes	$\nu_{(OH)}$		$\delta_{(OH)}$		$\nu_{(CO)}$	$\nu_{as(COO)}$		$\nu_{s(COO)}$		$\nu_{(C-N)}$				$\nu_{(C-H)}$		$\nu_{(N-H)}$		$\nu_{(Y-O)}$
$pydcH_2$					1692		1572	1412		1291		1082		994	514			
py											1216	1067		991	603			
$Y_2(pydc)_3(py)\cdot 4H_2O$	3430	3271	1194	1151		1614	1590	1443	1385	1283	1219	1077	1024	926	531			438
$Y_2(pydc)_3(py)_2\cdot 2H_2O$	3424	3203	1192	1150		1619	1591	1438	1392	1282	1218	1074	1024	920	532			427
$Y(pydc)_2(pyH)\cdot H_2O$	3431	3250	1189	1148		1619	1593	1434	1392	1279	1254	1069	1024	918	523	2532	2035	416
$Y(pydc)_3(pyH)_3\cdot 4H_2O$	3431	3271	1192	1151		1622	1582	1431	1381	1271	1253	1061	1030	917	520	2512	2041	419

Table 3. ^{1}H-NMR data of ligands and complexes (ppm in DMSO-d_6).

Compounds	H (py) (δ, ppm; J, Hz)	H ($pydc^{2-}$) (δ, ppm; J, Hz)	H (–COOH) (δ, ppm; J, Hz)
$pydcH_2$	–	8.30 (m, 2H) 8.27 (m, 1H)	13.24 (br, s, 2H)
py	8.59 (d, 1H, 8.60) 7.62 (t, 2H, 7.61) 7.23 (t, 2H, 7.22)	–	–
$Y_2(pydc)_3(py)\cdot 4H_2O$	8.62 (d, 1H, 8.58) 7.82 (t, 2H, 7.78) 7.72 (t, 2H, 7.68)	8.23 (m, 2H) 8.14 (m, 1H)	–
$Y_2(pydc)_3(py)_2\cdot 2H_2O$	8.63 (d, 1H, 8.62) 7.83 (t, 2H, 7.82) 7.74 (t, 2H, 7.72)	8.23 (m, 2H) 8.16 (m, 1H)	–
$Y(pydc)_2(pyH)\cdot H_2O$	8.75 (d, 2H, 8.82) 7.84 (t, 2H, 7.86) 7.75 (t, 2H, 7.60)	8.25 (m, 2H) 8.17 (m, 1H)	–
$Y(pydc)_3(pyH)_3\cdot 4H_2O$	8.76 (d, 2H, 8.86) 7.84 (t, 2H, 7.82) 7.75 (t, 2H, 7.66)	8.25 (m, 2H) 8.19 (m, 1H)	–

data on dehydration and decomposition are given in table 4, and exhibit good agreement with the chemical formulae.

Four yttrium(III) complexes first lose their water molecules and pyridines when heated, then complexes with 2,6-pyridinedicarboxylate begin to decompose, and finally give stable Y_2O_3. The thermal decomposition of yttrium(III) complexes are analyzed taking **4** as an example.

$Y(pydc)_3(pyH)_3\cdot 4H_2O$ first loses three water molecules accompanied by a weak endothermic effect when heated from room temperature to 110°C, then loses one water molecule and three pyridines accompanied by a moderate endothermic effect from 110°C to 240°C. Further weight loss corresponding to organic components is observed between 240°C and 560°C. This stage includes two steps accompanied by a moderate endothermic effect on $pydcH^-$ decomposition and a strong exothermic effect on combustion of organic groups, such as $pydc^{2-}$ and other intermediate products; the intermediate products are visible and unstable, continuing to lose weight with increase in temperature. The final decomposition product is Y_2O_3, identified by IR spectroscopy.

The results indicate that the thermal decompositions of yttrium complexes occur as follows:

$$Y_2(pydc)_3(py)\cdot 4H_2O \rightarrow Y_2(pydc)_3(py) \rightarrow Y_2(pydc)_3 \rightarrow Y_2O_3,$$

$$Y_2(pydc)_3(py)_2\cdot 2H_2O \rightarrow Y_2(pydc)_3(py)_2 \rightarrow Y_2(pydc)_3 \rightarrow Y_2O_3,$$

$$Y(pydc)_2(pyH)\cdot H_2O \rightarrow Y(pydc)_2(pyH) \rightarrow Y(pydcH)(pydc) \rightarrow Y_2O_3,$$

$$Y(pydc)_3(pyH)_3\cdot 4H_2O \rightarrow Y(pydc)_3(pyH)_3\cdot H_2O \rightarrow Y(pydcH)_3 \rightarrow Y_2O_3.$$

Table 4. Data on dehydration and decomposition of yttrium complexes containing pydc and py.

Complexes	Temperature range of dehydration (°C)		Mass loss (%)		Loss of H_2O (mol)	Temperature range of loss py (°C)		Mass loss (%)		Temperature range of decomposition (°C)		Y_2O_3 (%)	
			Calcd	Found				Calcd	Found			Calcd	Found
$Y_2(pydc)_3(py)\cdot 4H_2O$	22	105	8.74	8.96	4	115	250	9.59	9.81	410	575	27.43	28.08
$Y_2(pydc)_3(py)_2\cdot 2H_2O$	22	90	4.15	3.96	2	110	250	18.22	18.58	386	574	26.07	27.06
$Y(pydc)_2(pyH)\cdot H_2O$	22	110	3.57	3.48	1	110	185	15.28	15.01	402	560	21.86	21.50
$Y(pydc)_3(pyH)_3\cdot 4H_2O$	22	110	6.03	6.04	3	110	240	28.46[a]	27.84[a]	240	550	12.61	12.98

[a]Including 1 mol L^{-1} water molecule.

Table 5. Antibacterial activity *in vitro* expressed as diameter of growth inhibition zone.

Compounds	Concentration ($mol\,L^{-1}$)	Diameter of growth inhibition zone (mm)	
		B. coli 8099	*S. aureus* ATCC 6538
DMSO	0.005	–	–
$pydcH_2$	0.005	5.2	5.4
py	0.005	12.5	12.0
$Y(NO_3)_3$	0.005	10.0	7.2
$Y_2(pydc)_3(py)\cdot 4H_2O$ (**1**)	0.005	12.8	12.3
$Y_2(pydc)_3(py)_2\cdot 2H_2O$ (**2**)	0.005	13.6	13.1
$Y(pydc)_2(pyH)\cdot H_2O$ (**3**)	0.005	–	6.5
$Y(pydc)_3(pyH)_3\cdot 4H_2O$ (**4**)	0.005	–	6.2

–, No inhibition of zone. All the compounds were dissolved in DMSO.

3.4. *Antibacterial activity*

The antibacterial results of four yttrium(III) complexes and their ligands against Gram-negative bacteria *B. coli* and Gram-positive bacteria *S. aureus* are given in table 5. To clarify any participating role of DMSO in the antibacterial test, separate studies were carried out for solutions without the complexes and they showed less or no activity against bacteria.

The diameters of inhibition zones of yttrium(III) complexes at $0.005\,mol\,L^{-1}$ against *B. coli* and *S. aureus* are all less than 14 mm, which indicates that the antibacterial effect of yttrium(III) complexes is not very notable. Nonetheless, free pyridine and $Y(NO_3)_3$ have more activity than **3** and **4** but less activity than **1** and **2** against the tested bacteria. Generally, the antibacterial action mechanism proposed is that yttrium(III) complexes with 2,6-pyridinedicarboxylate and pyridine interfere with the transport of substrates and ions through cell membrane resulting in antibacterial activity [28]. It can be concluded that yttrium(III) and ligands have a cooperative antibacterial effect in **1** and **2**, whereas **3** and **4** having less activity can be attributed to protonation of pyridine leading to the inactivation on tested bacteria. Comparing the antibacterial activities with other coordination complexes containing 2,6-pyridinedicarboxylate [18, 29], the yttrium(III) complexes containing 2,6-pyridinedicarboxylate and pyridine are similar to the lanthanide complexes coordinated with 2,6-pyridinedicarboxylate and α-picolinic acid. The unimpressive antibacterial activities of these coordination complexes may be attributed to the low antibacterial activities of ligands, such as 2,6-pyridinedicarboxylate, α-picolinic, and pyridine, or the low antibacterial activities of metal ions, such as yttrium(III), lanthanum(III), and gallium(III). However, the relationship between molecular structure and antibacterial mechanism needs to be confirmed. Comparing the antibacterial results of four yttrium(III) complexes, it is risky to correlate the coordination complexes of yttrium(III) containing 2,6-pyridinedicarboxylate and pyridine with the high antibacterial activity just based on the limited present complexes.

4. Conclusion

Four yttrium(III) complexes have been synthesized by the reaction of $Y(NO_3)_3$ with $pydcH_2$ in different molar ratios in an aqueous solution containing pyridine, and

characterized by elemental analysis, FT-IR, ^{1}H-NMR, TGA, DTG, and DTA. The antibacterial activities against *B. coli* and *S. aureus* for the four yttrium complexes presented in this study are $Y_2(pydc)_3(py)_2 \cdot 2H_2O > Y_2(pydc)_3(py) \cdot 4H_2O > py > Y(NO_3)_3 > Y(pydc)_2(pyH) \cdot H_2O > Y(pydc)_3(pyH)_3 \cdot 4H_2O$.

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