第 29 卷第 7 期
2013 年 7 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.29 No.7
1557-1562

由 2,6-吡啶二羧酸根构筑的两种铈(Ⅳ)配合物的合成、结构及热性质

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摘要:采用水热法合成了 2 种铈(Ⅳ)配合物[Ce(dipic)$_3$]·(H$_2$bipy)·4H$_2$O (**1**)和[Ce(dipic)$_3$]·(H$_2$bpa)·3.5H$_2$O (**2**)(2,6-H$_2$dipic=2,6-吡啶二羧酸,bipy=4,4′-联吡啶,bpa=二(4-吡啶基)胺),并通过 X 射线单晶衍射、元素分析、FTIR 及热重分析对其结构和组成进行了表征。单晶衍射结构表明:配合物 **1** 和 **2** 的晶体都属于三斜晶系,$P\bar{1}$ 空间群。配合物的中心金属铈(Ⅳ)离子被 3 个完全去质子化的 2,6-吡啶二羧酸根环绕,配体 2,6-吡啶二羧酸的羧基均以单齿形式配位。热分析表明 2 个配合物在 64 和 50 ℃开始发生分解。

关键词:2,6-吡啶二羧酸;铈(Ⅳ)配合物;晶体结构;热性质
中图分类号:O614.33$^+$2 **文献标识码**:A **文章编号**:1001-4861(2013)07-1557-06
DOI:10.3969/j.issn.1001-4861.2013.00.211

Synthesis, Structure and Thermal Properties of Two Cerium(Ⅳ) Complexes with 2,6-Pyridinedicarboxylic Acid

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Abstract: Two cerium(Ⅳ) complexes [Ce(dipic)$_3$]·(H$_2$bipy)·4H$_2$O (**1**) and [Ce(dipic)$_3$]·(H$_2$bpa)·3.5H$_2$O (**2**) (2,6-H$_2$dipic=2,6-pyridinedicarboxylic acid, bipy=4,4′-bipyridine, bpa=Bis(4-pyridyl)amine) have been hydrothermally synthesized and structurally characterized via elemental analysis, IR spectra, TG and single-crystal X-ray diffraction. Both complexes crystallize in triclinic, space group $P\bar{1}$ with a=1.014 32(11) nm, b=1.253 64(13) nm, c=1.448 89(14) nm, V=1.662 77(6) nm^3, Z=2, R_1=0.064 1, wR_2=0.149 4 for **1**, and a=1.039 30(5) nm, b=1.604 02(8) nm, c=2.021 65(10) nm, V=3.304 5(3) nm^3, Z=2, R_1=0.039 8 and wR_2=0.104 9 for **2**. The central metal Ce(Ⅳ) ions of both complexes are surrounded by three wholly unprotonated dipicolinate groups in the usual tridentate mode. Thermogravimetric analysis shows that the two complexes are stable up to 64 and 50° C, respectively. CCDC: 856834, **1**; 856608, **2**.

Key words: 2,6-pyridinedicarboxylic acid; cerium(Ⅳ) complex; crystal structure; thermal property

The design and construction of lanthanide - organic coordination networks has recently received considerable attention because of their interesting structural motifs and potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics and molecular sensing[1-5]. Numerous one-, two- and three- dimensional complexes with interesting compositions and adsorption properties have been prepared and characterized using a variety of dipicolinate ligands. In particular, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridinedicarboxylic isomers, which contain a pyridine ring and two carboxylate groups,

收稿日期:2012-03-29。收修改稿日期:2013-03-07。
河南省高等院校自然科学研究项目(No.2009A150011)资助项目。
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can form various coordinated geometries[6-11]. Among them, 2,6-pyridinedicarboxylic acid (H_2dipic) has attracted much interest in coordination chemistry, because two carboxyl groups with a 120° angle may provide various coordination modes and form both discrete and consecutive metal complexes under appropriate synthesis conditions[12]. However, to date, only a few structural characterizations of 2,6-H_2dipic complexes containing lanthanide ions and having zero-dimensional structures, have been reported[13-14]. Moreover, most of those reported complexes contain d^{10} metal (Cu Ⅰ, Ag Ⅰ, Ni Ⅱ, Zn Ⅱ or Cd Ⅱ)[15-17]. In this study, we used different methods from the previous studies[18-19] and successfully obtained two Ce(Ⅳ)complexes **1** and **2** containing 4,4′-H_2bipy or H_2bpa counterions. Their thermal properties were also investigated.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade or better and used without further purification. The infrared (IR) spectra were recorded using a TENSOR37 spectrophotometer (Brucker AXS) and KBr pellets from 4 000 to 400 cm^{-1}. Elemental analysis (C, H, and N) was conducted on 2400LS Elemental Analyzer (PerkinElmer). The crystal structure was determined using a SMART APEX Ⅱ CCD single-crystal diffractometer (Bruker AXS). Thermogravimetric analysis was performed on a STA409PC Luxx instrument (NETZSCH) in static air atmosphere at a heating rate of 7 ℃·min^{-1}.

1.2 Synthesis of the complexes

1.2.1 Synthesis of [Ce(dipic)$_3$]·(H_2bipy)·4H_2O (**1**)

A mixture of CeO_2 (0.172 g, 1.0 mmol), CuO (0.079 5 g, 1.00 mmol), 2,6-H_2dipic (0.334 2 g, 2.00 mmol), 4,4′-bipy (0.046 9 g, 0.30 mmol), and H_2O (10 mL) was mixed in a 25 mL Teflon reactor. The pH value was adjusted to **2** with phosphoric acid. After stirring for 0.5 h, the mixture was heated at 160 ℃ for 3 d, and then cooled to room temperature. Yellowish rod-shaped crystals of **1** were filtered off and washed with distilled water in 60% yield. Anal. Calcd.(%) for $C_{31}H_{27}CeN_5O_{16}$: C, 42.97; H, 3.12; N, 8.09. Found(%): C, 42.96; H, 3.12; N, 8.08.

1.2.2 Synthesis of [Ce(dipic)$_3$]·(H_2bpa)·3.5H_2O (**2**)

A mixture of CeO_2 (0.094 7 g, 0.55 mmol), bpa (0.094 g, 0.55 mmol), 2,6-H_2dipic (0.091 8 g, 0.55 mmol), and H_2O (10 mL) was mixed in a 25 mL Teflon reactor autoclave under autogenous pressure at 160 ℃ for 3 d and then cooled to room temperature. Pure yellow massive crystals of **2** were filtered off and washed with distilled water in 75% yield. Anal. Calcd.(%) for $C_{62}H_{54}Ce_2N_{12}O_{31}$: C, 42.67; H, 3.10; N, 9.64. Found(%): C, 42.65; H, 3.09; N, 9.62.

1.3 Crystal structure determination

All measurements were made on a Bruker SMART APEX Ⅱ CCD diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The data were collected using φ-ω scans at 296(2) K and corrected for Lorentz polarization effects. The structures were solved by direct methods and refined by full matrix least squares on F^2 using the SHELX-97 program[20]. All non-hydrogen atoms were refined anisotropically. All H atoms bounded to C and N atoms were generated geometrically and refined isotropically using the riding mode, and H atoms of water molecule were placed in calculated positions. The crystal data and experimental details for the title complexes are presented in Table 1.

CCDC: 856834, **1**; CCDC: 856608, **2**.

2 Results and discussion

2.1 Synthesis of complexes

In the synthesis of title complexes, we found that two flexible ligands were protonated in acidic condition. We chosen CeO_2 and CuO as lanthanide transition metals to sythesize the heterometallic complex with 2,6-H_2dipic and 4,4′-bipy, but the structure of complex **1** does not include Cu ion. However, complex **1** has not been successfully obtained when we removed CuO from the reaction system, indicating that CuO plays a key role in the formation and crystallization of the complex **1**. The reason is unclear, and thus, further investigation is needed.

2.2 Description of crystal structures

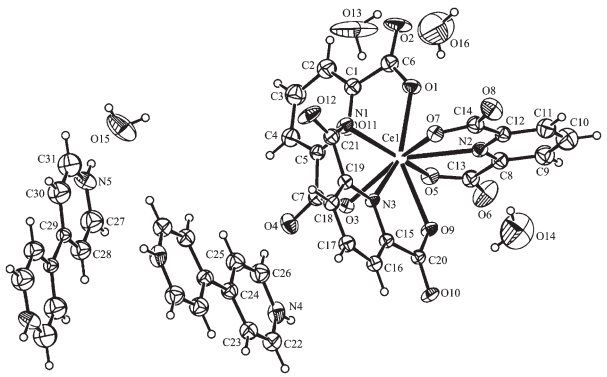
2.2.1 [Ce(dipic)$_3$]·(H_2bipy)·4H_2O (**1**)

Single-crystal X-ray diffraction analysis reveals

Table 1　Crystallographic data for the title complexes

Complex	**1**	**2**
Empirical Formula	$C_{31}H_{27}CeN_5O_{16}$	$C_{62}H_{54}Ce_2N_{12}O_{31}$
Formula weight	865.7	1743.41
Temperature / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Triclinic
Crystal size / mm	0.21×0.18×0.17	0.22×0.20×0.19
a / nm	1.014 32(11)	1.039 30(5)
b / nm	1.253 64(13)	1.604 02(8)
c / nm	1.448 89(14)	2.021 65(1)
α / (°)	104.376(2)	91.3630(1)
β / (°)	100.884(2)	93.6350(1)
γ / (°)	104.700(2)	100.540 0(1)
V / nm^3	1.662 77(6)	3.3045(3)
Z	2	2
D_c / (g·cm^{-3})	1.729	1.752
F(000)	868	1 748
θ range for data collection / (°)	2.16~25.01	1.3~25.0
μ / mm^{-1}	1.45	1.46
Absorption coefficient / mm^{-1}	1.454	1.464
Reflections collected	8 795	17 507
Independent reflections (R_{int})	5 807 (0.044)	11 570 (0.027)
Observed reflections ($I>2\sigma(I)$)	4 332	8 896
Goodness of fit on F^2	1.027	1.075
R_1, wR_2 ($I>2\sigma(I)$)	R_1=0.064 1, wR_2=0.149 4	R_1=0.039 7, wR_2=0.104 9
R_1, wR_2 (all data)	R_1=0.089 8, wR_2=0.169 9	R_1=0.057 5, wR_2=0.125 9

that complex $[Ce(dipic)_3]\cdot(H_2bipy)\cdot 4H_2O$ crystallizes in the $P\bar{1}$ space group and consists of a zero-dimensional network structure. The asymmetric unit of complex **1** consists of one $[Ce(dipic)_3]^{2-}$ coordination anion, one protonated 4,4′-bipyridine cation $(H_2bipy)^{2+}$ and four lattice water molecules. The molecular structure of **1** is shown in Fig.1. The nine-coordinate Ce(Ⅳ) ion is surrounded by three dipicolinate groups in the usual tridentate mode: terminal ligand, chelate tridentate to the Ce(Ⅳ) ion with each carboxyl group attached to one uncoordinated oxygen atom. The coordination polyhedron of anion $[Ce(dipic)_3]^{2-}$ is a distorted tricapped trigonal prism. The cap positions are occupied by the nitrogen atoms which are more distant from the metal center than oxygen atoms (Table 2). Recently, such a coordination anion had been the object of three cerium-dipicolinate frameworks $(C_4N_2H_{12})_{1.5}[Ce(C_7H_3NO_4)_3]\cdot 7H_2O$ [14], $[Ca(H_2dipic)(OH_2)_3][Ce(dipic)_3]\cdot 5H_2O$ [21] and $[Sr(H_2dipic)(H_2O)_3][Ce(dipic)_3]\cdot 6H_2O$ [22]. The Ce^{4+}-N bond and Ce^{4+}-O bond distances in complex **1** are from 0.250 2 to 0.250 8 nm and from 0.232 1 to 0.239 9 nm, respectively.



Thermal ellipsoids at 30% probability

Fig.1　A portion view of complex **1** with atom labeling of the asymmetric unit

Table 2 Selected bond distances (nm) and angles (°) for complexes 1 and 2

Complex **1**					
Ce1-O1	0.232 1(2)	Ce1-O7	0.233 0(5)	Ce1-O11	0.234 1(4)
Ce1-O5	0.235 1(4)	Ce1-O3	0.235 4(5)	Ce1-O9	0.239 8(4)
Ce1-N3	0.250 2(5)	Ce1-N2	0.250 2(6)	Ce1-N1	0.250 8(6)
O1-Ce1-O7	80.29(17)	O1-Ce1-O11	81.23(17)	O7-Ce1-O11	75.98(17)
O1-Ce1-O5	85.74(17)	O7-Ce1-O5	128.05(18)	O11-Ce1-O5	150.15(17)
O1-Ce1-O3	128.01(17)	O7-Ce1-O3	144.27(17)	O11-Ce1-O3	86.53(16)
O5-Ce1-O3	80.56(17)	O1-Ce1-O9	147.21(17)	O7-Ce1-O9	91.261(60)
O11-Ce1-O9	127.58(15)	O5-Ce1-O9	74.68(15)	O3-Ce1-O9	74.96(16)
O1-Ce1-N3	139.05(16)	O7-Ce1-N3	71.40(17)	O11-Ce1-N3	63.83(15)
O5-Ce1-N3	135.09(16)	O3-Ce1-N3	72.94(16)	O9-Ce1-N3	63.90(15)
O1-Ce1-N2	73.80(18)	O7-Ce1-N2	64.04(18)	O11-Ce1-N2	135.49(18)
O5-Ce1-N2	64.01(18)	O3-Ce1-N2	137.72(17)	O9-Ce1-N2	74.03(16)
N3-Ce1-N2	116.47(17)	O1-Ce1-N1	64.12(19)	O7-Ce1-N1	136.95(17)
O11-Ce1-N1	75.40(17)	O5-Ce1-N1	74.76(17)	O3-Ce1-N1	63.90(17)
O9-Ce1-N1	131.76(17)	N3-Ce1-N1	121.32(18)	N2-Ce1-N1	122.21(18)
Complex **2**					
Ce1-O11	0.232 3(4)	Ce1-O12	0.234 0(3)	Ce1-O3	0.234 9(3)
Ce1-O7	0.235 3(4)	Ce1-O4	0.238 4(3)	Ce1-O8	0.239 3(3)
Ce1-N3	0.249 4(4)	Ce1-N1	0.251 3(4)	Ce1-N2	0.252 7(4)
O11-Ce1-O12	128.31(13)	O11-Ce1-O3	80.87(13)	O12-Ce1-O3	145.55(13)
O11-Ce1-O7	148.38(13)	O12-Ce1-O7	78.10(13)	O3-Ce1-O7	82.42(14)
O11-Ce1-O4	87.26(13)	O12-Ce1-O4	77.37(13)	O3-Ce1-O4	127.66(12)
O7-Ce1-O4	82.00(13)	O11-Ce1-O8	76.42(13)	O12-Ce1-O8	88.67(13)
O3-Ce1-O8	80.55(13)	O7-Ce1-O8	126.72(13)	O4-Ce1-O8	144.97(13)
O11-Ce1-N3	63.87(13)	O12-Ce1-N3	64.45(13)	O3-Ce1-N3	139.93(14)
O7-Ce1-N3	137.65(14)	O4-Ce1-N3	71.53(13)	O8-Ce1-N3	73.46(13)
O11-Ce1-N1	72.57(13)	O12-Ce1-N1	135.75(13)	O3-Ce1-N1	63.76(13)
O7-Ce1-N1	75.99(13)	O4-Ce1-N1	64.03(12)	O8-Ce1-N1	135.48(13)
N3-Ce1-N1	117.83(13)	O11-Ce1-N2	135.07(13)	O12-Ce1-N2	71.47(13)
O3-Ce1-N2	74.49(13)	O7-Ce1-N2	63.84(13)	O4-Ce1-N2	137.36(14)
O8-Ce1-N2	63.01(13)	N3-Ce1-N2	117.31(13)	N1-Ce1-N2	124.86(13)

All are similar to those found in the related Ce^{4+}-N donor and Ce^{4+}-O donor complexes[21-24]. Additionally, the distortion of the Ce(Ⅳ) ion coordination sphere is clearly reflected by the internal (N, O)-Ce-(N, O) bond angles. The O-Ce-O angles are in the range of 74.68(15)° ~150.15 (17)°, whereas the O-Ce-N angles can be found in the range of 63.90(15)°~139.05(16)° and the N-Ce-N angles in the range of 116.47(17)°~122.21(18)°. The selected bond distances and angles are listed in Table 2.

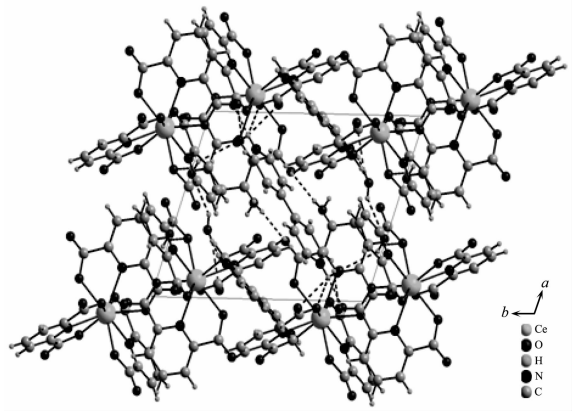
Each dipicolinic group is totally unprotonated, in agreement with the IR analysis results. Hence, such entity is doubly negatively charged. As show in Fig.2, in the complex, protonated 4,4′-H_2bipy cation acts as a counter-ion that does not participate in the coordination. They are bound to the molecular entities through N–H···O hydrogen bonds (Table 3) or van der Waals interaction. Some free water molecules, either ordered or disordered, occur within the structure, and they are fixed inside the lattice (molecular entity or

Table 3　Hydrogen bonds for complex 1

D–H···A	*d*(D-H) / nm	*d*(H···A)/ nm	*d*(D···A) / nm	∠D–H···A / (°)
O13–H13A···O11	0.085 9	0.232 8	0.308 6	147.33
O13–H13B···O16	0.086 0	0.243 8	0.300 5	124.03
O14–H14A···O6	0.086 1	0.204 1	0.280 7	147.88
O15–H15A···O13^{i}	0.084 7	0.249 6	0.305 6	124.41
O15–H15B···O2^{ii}	0.084 2	0.265 6	0.342 7	152.97
O16–H16A···O8	0.088 2	0.249 6	0.309 3	125.51
O16–H16B···O2^{iii}	0.085 2	0.235 7	0.304 0	137.51
O16–H16B···O1^{iii}	0.085 2	0.244 4	0.320 0	148.17
N4–H4B···O10^{iv}	0.086 0	0.182 4	0.267 8	171.92
N5–H5A···O15	0.086 0	0.188 3	0.271 5	162.26

Symmetry codes: ^{i} x, y+1, z; ^{ii} $-x$+1, $-y$+1, $-z$+1; ^{iii} $-x$+2, $-y$, $-z$+1; ^{iv} $-x$+2, $-y$+1, $-z$.

counter-ion) by hydrogen bonding but the O ··· O distances are usual or rather long[14]. These strong N–H ··· O and O–H ··· O hydrogen bonds interaction to further strengthen the stability of molecular framework.

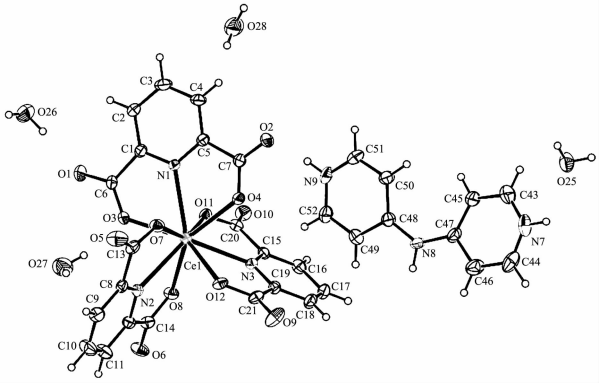


Dashed lines indicate hydrogen bonds

Fig.2　Molecular packing diagram of complex **1**

2.2.2　$[Ce(dipic)_3]\cdot(H_2bpa)\cdot 3.5H_2O$ (**2**)

Single-crystal XRD analysis reveals that complex $[Ce(dipic)_3]\cdot(H_2bpa)\cdot 3.5H_2O$ crystallizes in the $P\bar{1}$ space group and consists of a zero-dimensional network structure. As shown in Fig.3, the title complex **2** consists one $[Ce(dipic)_3]^{2-}$ coordination anion, one protonated Bis (4-pyridyl)amine cation $(H_2bpa)^{2+}$ and three and a half lattice water molecules. The two complexes have similar molecular structures and coordination modes and differ only in terms of the counter-ion. Therefore, complex **2** will not be discussed in detail.



Thermal ellipsoids at 30% probability

Fig.3　Molecular structure of the complex **2**

2.3　IR spectra

The IR spectra of complexes **1** and **2** are show that the strong bands at 3 432 and 3 437 cm^{-1}, respectively, are attributed to the stretching vibrations of water molecules, indicating the existence of water molecules. The characteristic absorptions near 1 649 and 1 647 cm^{-1}, respectively, are attributed to the asymmetric stretching vibration of the carboxylate groups ($\nu_{as}(COO^-)$) and 1 425 and 1 426 cm^{-1} for symmetric stretching vibration ($\nu_s(COO^-)$). The $\Delta\nu(\nu_{as}(COO^-)-\nu_s(COO^-))$ are 224 and 221 cm^{-1} between the two bands of the coordinated carboxyl, respectively. They are all larger than 200 cm^{-1}, indicating that the coordinated carboxyl in the complexes is monodentated[26]. Moreover, the strong bands at 3 090 and 3 072 cm^{-1}, respectively, are attributed to the protonated N atoms[27], indicating the existence of protonated 4,4′-bipyridine and bis (4-pyridyl)amine cations. These assignments are consistent with the structure analysis results.

2.4　Thermal analysis

The thermogravimetric analysis of the two complexes was done between room temperature and

848 ℃ at a heating rate of 7 ℃·min^{-1} in nitrogen atmosphere, and their behaviors were different, as indicated in Fig.4. For **1**, the loss of lattice water molecules occurs from 64 to 170 ℃ (Weight loss: 8.10%, Calcd. 8.32%). The loss of organic ligands starts from about 280 ℃, when the complex was not yet decomposed, and does not end at the temperature limit. This result confirms the existence of different binding affinities of 2,6-H_2dipic ligands and protonated 4,4′-H_2bipy, some of which are very strong. For **2**, the loss of lattice water molecules occurs from 50 to 150 ℃, (Weight loss: 7.13%, Calcd. 7.23%). In the following, two continuous steps to about 710 ℃ correspond to the loss of organic ligand (Weight loss: 70%, Calcd. 71.16%). Beyond 710 and 848 ℃, no weight loss was observed, indicating the complete decomposition of **2**. The residual weight 23.163% (Calcd. 21.60%) corresponds to CeO_2.

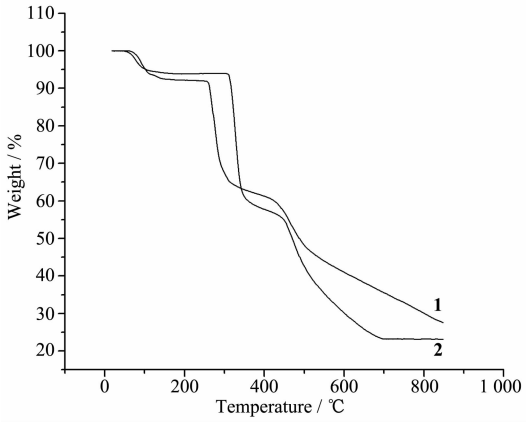


Fig.4 Thermogravimetric analysis curves of complexes **1** and **2**

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