研究简报

希土胺羧酸配合物的研究

Ⅲ.吡啶-2，6-二甲酸钕配合物 $\{[Nd(HDPA)(DPA)(H_2O)_2]\cdot 4H_2O\}_n$ 合成及其晶体结构

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关键词: 希土　吡啶-2,6-二甲酸　晶体结构

关于吡啶-2,6-二甲酸希土配合物晶体结构有 $Na_3[Ln(DPA)_3]\cdot yNaClO_4\cdot xH_2O$ 类型的报道[1]。本文合成了 $\{[Nd(HDPA)(DPA)(H_2O)_2]\cdot 4H_2O\}_n$ 配合物单晶并测定了其结构。

配合物的合成

将硝酸希土溶液与吡啶-2,6-二甲酸以 1∶3 的摩尔比混合，加入适量蒸馏水和四甲基铵盐，加热搅拌并滴加四甲基铵碱至吡啶-2，6-二甲酸溶解。冷却后调溶液 pH 至 2，室温下放置数天得到单晶。

结果和讨论

元素分析结果表明配合物具有 $Ln(HDPA)(DPA)\cdot 6H_2O$ 组成(Ln 为 Nd, Gd; H_2DPA 为吡啶-2,6-二甲酸)。

用 X 射线衍射方法测定了 $\{[Nd(HDPA)(DPA)(H_2O)_2]\cdot 4H_2O\}_n$ 的晶体结构，共收集独立衍射点 3769 个，其中 1540 个可观察点 ($I>2.5\sigma(I)$)参加了修正。最终偏差因子 $R=0.059$，$R\omega=0.061$。晶体属单斜晶系，空间群 $P2(1)/a$，晶胞参数如下：$a=12.842(4)$ Å，$b=11.170(3)$ Å，$c=13.984(3)$ Å，$\beta=102.11(3)^\circ$，$Z=4$，$V=1961.1$ Å^3，$d_{calc.}=1.976 g\cdot cm^{-3}$。

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所有非氢原子坐标及热参数列于表1，键长和键角列于表2。

表1　非氢原子坐标($\times 10^3$)和热参数($\times 10^3$, $Å^2$)

Table 1 Non-hydrogen Atomic Coordinates($\times 10^3$) and Their Thermal Parameters($\times 10^3$, $Å^2$)

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
Nd	351.29(7)	294.9(1)	230.45(8)	10.8(1)	C(21)	85(1)	50(2)	325(1)	12(3)
O(1)	370(1)	102(1)	152(1)	20(3)	C(22)	152(1)	−41(2)	362(2)	18(4)
O(2)	374(1)	−24(1)	32(1)	31(4)	C(23)	105(1)	−143(2)	400(2)	29(5)
O(3)	365(1)	487(1)	144.4(9)	15(3)	C(24)	−000(2)	−139(2)	407(2)	21(4)
O(4)	371(1)	599(2)	18(1)	33(4)	C(25)	−59(1)	−38(2)	373(1	15(4)
O(5)	216.4(9)	168(1)	281.7(9)	15(3)	C(1)	372(2)	70(2)	73(2	36(6)
O(6)	47.1(9)	220(1)	227.1(9)	17(3)	C(2)	366(2)	504(2)	64(2)	28(5)
O(7)	−217(1)	72(1)	343(1)	22(3)	C(3)	120(1)	153(2)	274(1)	13(4)
O(8)	−218(1)	−105(2)	420(1)	34(3)	C(4)	−173(2)	−24(2)	379(2)	25(5)
N(11)	369(1)	295(2)	55(1)	19(3)	O(11)	436(1)	182(1)	377(1)	21(3)
N(21)	−20(1)	50(1)	331(1)	15(3)	O(22)	174(1)	347(1)	163(1)	24(3)
C(11)	367(3)	187(3)	13(3)	70(10)	O(33)	150.0(9)	308(1)	460(1)	21(3)
C(12)	365(2)	183(2)	−92(2)	29(5)	O(44)	100(1)	557(1)	471(1)	29(3)
C(13)	367(2)	284(3)	−142(2)	49(7)	O(55)	385(1)	775(2)	127(2)	55(5)
C(14)	362(2)	395(3)	−105(3)	60(7)	O(66)	412(2)	−93(2)	300(2)	80(8)
C(15)	362(1)	395(2)	−3(2)	19(4)					

这一吡啶-2,6-二甲酸钕配合物是长链分子,其基本重复单元为$[Nd(HDPA)(DPA)(H_2O)_2 \cdot 4H_2O$，配合物单元之间通过羧基桥将相邻的钕原子联结起来（图1）。

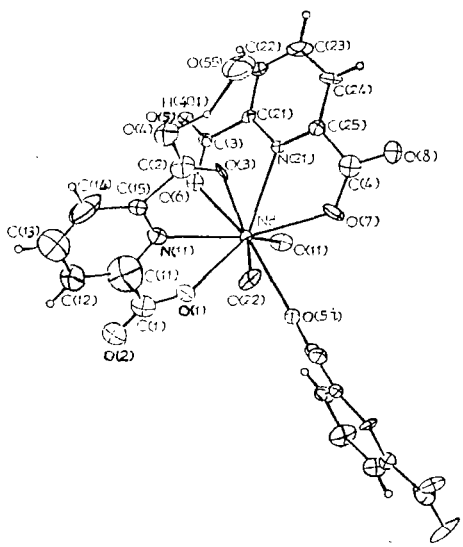

图1　$\{[Nd(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$ 的晶体结构

Fig.1　Crystal structure of $\{[Nd(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$

在$\{[Nd(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$配合物中钕原子与来自同一配合物单元的两个吡

啶-2,6-二甲酸的 2 个氮原子(N(11), (N(21))配位; 4 个羧基的 4 个氧原子(O(1), O(3), O(6), O(7))配位; 来自 2 个水分子的氧原子 (O(11), O(22))配位; 再与来自另一配合物单元的羧基的 1 个氧原子(O(5i))配位. 所以钕的配位数为 9.

在配合物单元中有 1 个吡啶-2,6-二甲酸的羧基氢未解离, 此未解离的氢原子 (H(401))与 1 个水分子的氧原子 (O (55)) 形成氢键.

表 2 部分键长和键角

Table 2 Selected Chemical Bond Lengths and Angles

bond length (Å)

Nd-O(1)	2.457(9)	Nd-O(6)	2.531(5)	Nd-O(22)	2.466(6)
Nd-O(3)	2.488(7)	Nd-O(7)	2.458(7)	Nd-N(11)	2.508(8)
Nd-O(5)	2.458(5)	Nd-O(11)	2.455(6)	Nd-N(21)	2.591(7)

bond angle(°)

O(1)-Nd-O(3)	121.3(2)	O(3)-Nd-N(21)	65.5(2)	O(6)-Nd-O(11)	73.3(2)
O(1)-Nd-O(5)	76.5(2)	O(3)-Nd-O(11)	121.4(2)	O(6)-Nd-O(22)	144.2(2)
O(1)-N(d)-O(6)	75.0(2)	O(3)-Nd-O(22)	71.3(2)	O(7)-Nd-N(11)	137.9(3)
O(1)-Nd-O(7)	154.1(2)	O(5)-Nd-O(6)	136.9(2)	O(7)-Nd-N(21)	61.4(2)
O(1)-Nd-N(11)	61.8(3)	O(5)-Nd-O(7)	78.0(2)	O(7)-Nd-O(11)	86.1(2)
O(1)-Nd-N(21)	135.8(2)	O(5)-Nd-C(13)	119.8(2)	O(7)-Nd-O(22)	78.4(2)
O(1)-Nd-O(11)	81.6(2)	O(5)-Nd-N(21)	129.3(2)	N(11)-Nd-N(21)	110.8(3)
O(1)-Nd-O(22)	97.2(2)	O(5)-Nd-O(11)	71.2(2)	N(11)-Nd-O(11)	134.6(3)
O(3)-Nd-O(5)	139.9(2)	O(5)-Nd-O(22)	70.8(2)	N(11)-Nd-O(22)	73.5(2)
O(3)-Nd-O(6)	83.0(2)	O(6)-Nd-O(7)	122.9(2)	N(21)-Nd-O(11)	76.5(2)
O(3)-Nd-O(7)	81.8(2)	O(6)-Nd-N(11)	72.1(2)	N(21)-Nd-O(22)	123.5(2)
O(3)-Nd-N(11)	59.8(3)	O(6)-Nd-N(21)	62.2(2)	O(11)-Nd-O(22)	141.2(2)

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STUDIES ON RARE EARTH COMPLEXES OF AMINOPOLYCARBOXYLIC ACID

Ⅲ. SYNTHESIS AND CRYSTAL STRUCTURE OF $\{[Nd(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$ COMPLEX

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The complexes of $\{[Ln(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$ have been synthesized (Ln = Nd, Gd; H_2DPA = dipicolinic acid)and studied by thermoanalysis and infrared spectroscopy.

The crystal structure of $\{[Nd(HDPA)(DPA)(H_2O)_2] \cdot 4H_2O\}_n$ has been determined by single crystal diffraction. 3767 independent reflections were collected, of which 1540 were used for structure refining. The final deviation factors of R and R_ω equal to 0.059 and 0.067 respectively. Four formula units crystallize in a monoclinic cell with the dimensions $a = 12.842$ Å, $b = 11.170$ Å, $c = 13.984$ Å, $\beta = 102.11°$. The space group is $P2(1)/a$. The result turns out that the complex is a one dimensional polymer in which the Nd atoms are connected by the bridging carboxyl groups.

In the complex, every neodymium ion is coordinated by five carboxylate oxygen ,four of which are from the four carboxylate groups of the two dipicolinic acid molecules and the other is the bridging carboxylate oxygen of dipicolinic ion in the pyr neighboring formula unit; the two nitrogen from the pyridine rings and the two oxygen from two water molecules ,so that coordination number of the neodymium is 9. The hydrogen on the undissociated carboxylic acid in the HDPA forms a hydrogen bond with the water molecule.

Keywords: rare earth dipicolinic acid crystal structure