Synthesis，Crystal Structure and Thermal Behavior of 5-Nitroisophthalate Complex with Mn(Ⅱ)

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Abstract：The crystal of the title complex $Mn(nip)(H_2O)_5$ (nip = 5-nitroisophthalate) was synthesized，and cultured in the filtrate of the reaction mixture. The X-ray single crystal diffractometer with graphite monochromated MoK_α(λ = 0.71073 Å)，elemental microanalysis，FT-IR，DSC and TG-DTG techniques were used to characterize the structure and thermal behaviors of the title complex. The results show that the central Mn^{2+} cation coordinates to the ligands 5-nitroisophthalate and $5H_2O$ in a distorted octahedral pattern. And the title coordination compound loses its five water molecules at the first step and the 5-nitroisophthalate at the second step during heating based on the thermal analyses and FT-IR data.

Key words：analytical chemistry；$Mn(nip)(H_2O)_5$；complex；crystal structure；thermal decomposition

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1　Introduction

The coordination polymers with microporous structures have attracted researchers' attention in the past few decades. In these coordination polymers，the organic molecules play a very important role in their final crystal framework structures [1-3]，for example，carboxylate group，that has been widely exploited as ligand recently because of the carboxylate various coordination styles but also because the final materials using carboxylate as ligand perform novel structural properties [4-8]. Due to the polymers topological diversities，they have been used in many fields such as catalysis，gas and solution adsorption or separation [9-13]. Of the ligands with carboxylate groups，the isophthalic acid (IPA) is used as organic linkers and because of its structure characters the obtained coordination polymers also behave diverse novel structures [14-17]. Based on the finely selected ligand 5-nitroisophthalic acid (NIPA)，the crystal of the title complex was synthesized，cultured and characterized，and thermal analyses was performed on the crystal，and the thermodynamic mechanisms of the crystal were studied.

2　Experimental

2.1　Instruments

Elemental analysis was performed on Flash EA 1112 full-automatic microanalyser. The FT-IR analysis was performed on Bruker Equinox 55 infrared spectrometer using KBr pellet in the range of $4000 - 400$ cm^{-1} with the resolution of 4 cm^{-1}. Pyris 1 DSC curve was collected for differential scanning calorimetry analysis using high pure nitrogen as purge gas with a flowing rate of 20 ml·min^{-1}. The crystal sample was powdered and sealed in aluminum pan with the heat rate of 10 K·min^{-1}. Pyris 1 TGA was used for TG-DTG analysis using high pure nitrogen as purge gas with a flowing rate of 20 ml·min^{-1}. The crystal sample was powdered and put in the platinum sample pan with the heat rate of 10 K·min^{-1}.

2.2　Synthesis of $Mn(nip)(H_2O)_5$

$MnCO_3$(0.1150 g，1 mmol) was dissolved in 10 ml distilled water and 70% $HClO_4$ added to adjust the pH = 3 – 4. At the same time，NIPA (0.2113 g，1 mmol) was dissolved in 10 ml distilled water and the solution adjusted to pH = 6 – 7 using 15% NaOH. Accompanied by stirring，the NIPA solution was heated to about 353 K，and then added the above $MnCO_3$ solution slowly. The mixture solution was adjusted to pH = 6 – 7 and reacted at 353 K for about 30 min.

The reaction was stopped after 30 min，and solution

filtrated and cultured in the room atmosphere. The pink block-shaped crystal suitable for X-ray single crystal characterization formed after 7 days (about 65% yield based on Mn). The resulting crystal was collected by filtration, washed with water (2 ml × 3), and dried at room temperature.

The elemental analysis: theoretical (found) value (%): C 27.13(26.35), H 3.70(3.93), N 3.96(4.15).

FT-IR spectra (KBr pellet, cm^{-1}): 3333(s, O—H), 2924(w, =C—H), 1686(m, C=O), 1557(s, N=O), 1453(m, C=C), 1352(s, N=O), 794(w, $\delta_{=C-H}$), 718(m, $\delta_{=C-H}$).

2.3 Data collection, structure solution and refinement

A pink bock-shaped single crystal with dimensions of 0.38 mm × 0.38 mm × 0.10 mm was mounted on Siemens P4 X-ray single crystal diffractometer which uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and $\omega/2\theta$ scanning mode at 294(2) K. The collected reflections are 2689, the independent reflections are 2335 [R(int) = 0.0122]. Lp corrections and empirical adsorption corrections were performed on all data. The structure was solved by direct methods using SHELXS-97 program[18] and refined by full-matrix least squares on F^2 using SHELXL-97 program[19]. All non-hydrogen atoms were located anisotropically and all hydrogen atoms were located from the difference Fourier map and refined isotropically. Detailed information on crystal structure and data determination is listed in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.

3 Results and discussion

3.1 Synthesis

In the preparation of coordination polymers, some preparation conditions such as the reaction temperature, the type of the solvent and the pH value of the solution have great influence on the final materials[17, 20]. In the experiment, the NIPA has been fully deprotonated but the coordination polymers was not obtained. It is inferred that the type of the solvent affects the experiment results.

3.2 Crystal structures

The molecular structure, coordination octahedron and the packing of Mn(nip)(H$_2$O)$_5$ are illustrated in Fig. 1 – 3, and the selected bond lengths and bond angles in Table 3.

Table 1 Crystal data and structure refinement for Mn(nip)(H$_2$O)$_5$

empirical formula	C$_8$H$_{13}$MnNO$_{11}$
formula weight	354.13
temperature/K	294(2)
crystal system	triclinic
space group	P-1
cell parameters	a = 7.892(10) Å, α = 69.52(1)° b = 9.422(2) Å, β = 87.96(2)° c = 9.716(2) Å, γ = 76.68(1)°
$\theta/(°)$	2.24 – 25.25
limiting indices	0 ≤ h ≤ 9 −10 ≤ k ≤ 10 −11 ≤ l ≤ 11
D_c/g·cm^{-3}	1.788
Z	2
volume/Å^3	657.8(2)
F(000)	362
μ(Mo K$_\alpha$)/mm^{-1}	1.063
S	1.067
reflections collected	2689
independent reflections [R(int) = 0.0122]	2335
R indices (all data)	R_1 = 0.0427, wR_2 = 0.0810
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0327, wR_2 = 0.0784
largest difference peak and hole /e·Å^{-3}	0.263 and −0.210

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropicdisplacement parameters (Å^2 $\times 10^3$) for Mn(nip)(H$_2$O)$_5$

	x	y	z	U(eq)
Mn	8183(1)	−803(1)	7257(1)	25(1)
O1	7435(2)	1431(2)	5453(2)	34(1)
O2	4535(2)	2052(2)	5484(2)	37(1)
O3	2047(3)	5839(2)	349(2)	42(1)
O4	3086(2)	7956(2)	−572(2)	31(1)
O5	8347(3)	8177(3)	1822(2)	52(1)
O6	9961(3)	6055(3)	3283(3)	64(1)
O7	10950(2)	−839(2)	6964(2)	31(1)
O8	5481(3)	−745(3)	7600(3)	56(1)
O9	8854(3)	−3037(2)	8981(2)	40(1)
O10	8490(3)	−1925(3)	5573(3)	45(1)
O11	8572(3)	441(3)	8684(2)	43(1)
N	8604(3)	6795(3)	2558(2)	36(1)
C1	5950(3)	2326(3)	4993(3)	26(1)
C2	5933(3)	3846(3)	3756(3)	25(1)
C3	4577(3)	4535(3)	2696(3)	26(1)
C4	4560(3)	5925(3)	1550(3)	23(1)
C5	5884(3)	6685(3)	1519(3)	26(1)
C6	7218(3)	5979(3)	2578(3)	26(1)
C7	7303(3)	4565(3)	3683(3)	28(1)
C8	3121(3)	6609(3)	357(3)	24(1)

Note: U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

In the molecular structure of the title compound (Fig. 1), the central Mn^{2+} cation coordinates to one O atom from 5-nitroisophthalate and five O atoms from H_2O in an octahedral symmetry, and the Mn^{2+} center adopts sp^3d^2 or d^2sp^3 hybridization. From the references [21,22], the Mn^{2+} center always adopts sp^3d^2 fashion. So there will be five mono-electrons in the inner orbital of Mn(Ⅱ) coordination center which implies its potential uses in the magnetic or optical materials.
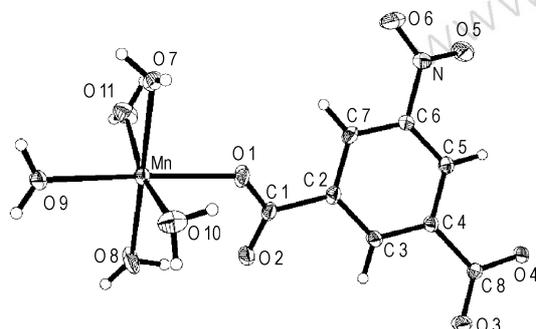

Fig. 2　Coordination octahedron of the title complex

Fig. 1　Molecular structure of
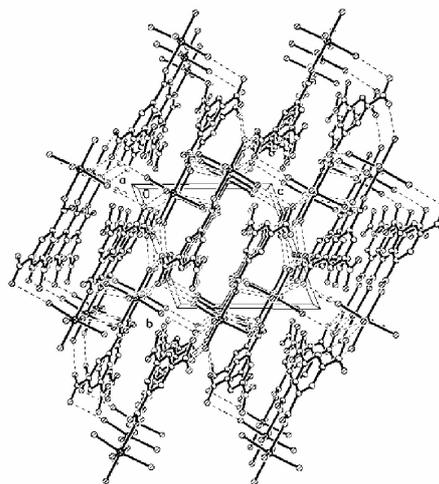the title complex (ellipsoid probability 50%)

Fig. 3　Packing of the title coordination compound along an axis

Table 3　Selected bond lengths and bond angles for Mn(nip)(H₂O)₅

bond	bond lengths/Å	bond	bond angles/(°)	bond	bond angles/(°)
Mn—O1	2.1847(18)	O1—Mn—O9	177.58(8)	O7—Mn—O8	178.20(10)
Mn—O7	2.186(2)	O10—MnO11	164.01(9)	O7—Mn—O10	84.20(9)
Mn—O8	2.138(2)	O1—Mn—O7	91.41(7)	O7—Mn—O11	80.38(9)
Mn—O9	2.144(2)	O1—Mn—O8	88.93(8)	O8—Mn—O10	97.59(11)
Mn—O10	2.216(2)	O1—Mn—O10	87.37(9)	O8—Mn—O11	97.86(11)
Mn—O11	2.174(2)	O1—Mn—O11	88.79(9)	O1—C1—O2	125.3(2)
O1—C1	1.266(3)	O9—Mn—O7	89.97(8)	O3—C8—O4	124.1(2)
O2—C1	1.245(3)	O9—Mn—O8	89.74(9)		
O3—C8	1.239(3)	O9—Mn—O10	90.80(10)		
O4—C8	1.269(3)	O9—Mn—O11	93.39(9)		

The coordination octahedron of title complex is illustrated in Fig. 2, in which the Mn(Ⅱ) center is coordinated by six O atoms into a distorted fashion. The bond lengths of Mn—O in Table 3 also indicate that the Mn(Ⅱ) center is in a slightly distorted symmetry. The Mn—O bond lengths are 2.1847(18) of Mn—O1, 2.186(2) of Mn—O7, 2.138(2) of Mn—O8, 2.144(2) of Mn—O9, 2.216(2) of Mn—O10, 2.174(2) Å of Mn—O11 respectively. The Mn—O bond lengths of the title complex fall in the range of the Mn—O bond lengths in the reported coordination polymers [Mn(ta)(phen)]$_n$ (2.105(10) – 2.150(8) Å) and [(m-phth)(Mn)(bpp)$_2$] · 0.5H$_2$O

(2.113(2) –2.288(2) Å)[23,24]. This further demonstrates the formation of the title complex. The bond angles existing in the octahedral [177.58(8) for O1—Mn—O9, 178.20(10) for O7—Mn—O8, 164.01(9)° for O10—Mn—O11] also demonstrate the distorted octahedron in the Mn coordination center. From the comparisons of bond lengths, bond angles between Mn(nip)(H$_2$O)$_5$, [Mn(ta)(phen)]$_n$ and [(m-phth)(Mn)(bpp)$_2$] · 0.5H$_2$O, the coordination style of Mn^{2+} in Mn(nip)(H$_2$O)$_5$ is nearer to perfect octahedron.

The bond lengths of O1—C1 and O2—C1, O3—C8 and O4—C8 are 1.266(3) and 1.245(3), 1.239(3) and

1.269(3) Å respectively. The bond angles of O1—C1—O2 and O3—C8—O4 are 125. 3 (2)° and 124. 1 (2)°. Compared with the data when the ligand has not been coordinated, the C—O bond lengths are all averaged and the O—C—O bond angles are expanded when the carboxylate group is coordinated to central cation or deprotonated.

There exist hydrogen bonds between neighboring molecules as illustrated in the packing of $Mn(nip)(H_2O)_5$ along a axis (Fig. 3). And these hydrogen bonds link the molecules together to form an infinite spatial framework.

3.3 Thermal analysis

In the curve of differential scanning calorimetry analysis, there are one endothermic peak at 365 K and one exothermic peak at 684 K for $Mn(nip)(H_2O)_5$ complex. The first peak can be assigned to the melting of the crystal and the loss of the coordinated water molecules. The second peak may be assigned to the decomposition of the complex. The enthalpy energy of the decomposition is calculated as about $2.0192 \text{ kJ} \cdot \text{mol}^{-1}$ from the DSC curve.

The TG-DTG results are illustrated in Fig. 5, in which there are two main mass loss stages. The first mass loss with 24.61% starts at 338 K, ends at 551 K and reaches its largest rate at about 355 K. The second is 60.98% that starts at 551 K, finishes at 741 K and reaches its largest rate at about 605 K. The total mass loss is 85.59%. The first step can be assigned to the loss of $5H_2O$ (calcd. 25.43%) that is demonstrated by missing of the water band at 3333 cm^{-1} in the FT-IR spectra of the residues at 551 K. The second step can be assigned to be the loss of 5-nitroisophthalate moiety (calcd. 59.05%) and formation of some kinds of polymer. The final residue is 14.41% of the total weight and assigned to be MnO (calcd. 20.03%). The existence of MnO in the final residue is demonstrated by the FT-IR spectra of the DSC final residue at 610 cm^{-1} and 489 cm^{-1}[25].

Combined the thermal analyses and the FT-IR results above, the thermal decomposition mechanisms of the Mn (nip)(H_2O)_5 complex are predicted as follows:
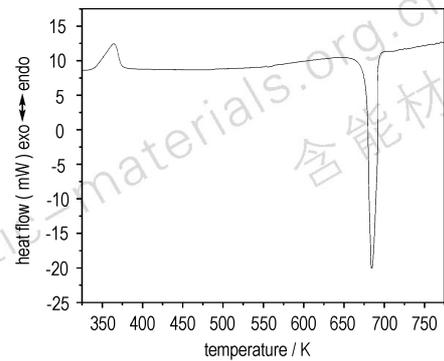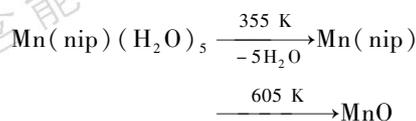
$$Mn(nip)(H_2O)_5 \xrightarrow[-5H_2O]{355 \text{ K}} Mn(nip)$$

$$\xrightarrow{605 \text{ K}} MnO$$

Fig. 4　DSC curve of $Mn(nip)(H_2O)_5$
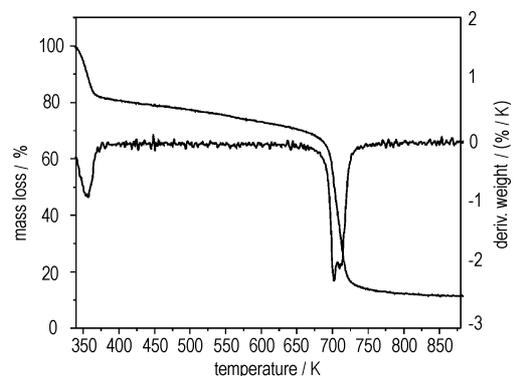
Fig. 5　TG-DTG curves of $Mn(nip)(H_2O)_5$

4　Conclusions

In the obtained complex $Mn(nip)(H_2O)_5$, $Mn(II)$ is coordinated to a slightly distorted octahedron. And in the packing diagrams, by means of hydrogen bonds, an infinite spatial framework is formed.

The thermal analyses of $Mn(nip)(H_2O)_5$ show that there are one endothermic peak and one exothermic peak in DSC curve, and there are two main mass loss stages in the TG-DTG curve. With the FT-IR spectra, the first stage is assigned to be the loss of five coordinated water molecules, the second stage to be the loss of the 5-nitroisophthalate moieties then formation of MnO and some kinds of polymers.

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5-硝基间苯二甲酸锰配合物的合成、晶体结构和热分解研究

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摘要：合成了 5-硝基间苯二甲酸锰的配合物——Mn(nip)(H$_2$O)$_5$，并用 X 射线单晶衍射、元素分析、DSC、TG 和 DTG 技术对其进行了表征。配合物的配位中心 Mn(Ⅱ)与 5-硝基间苯二甲酸和 5 个水分子配位形成配位八面体结构。根据热分析结果和 FT-IR 分析可推断，加热过程中该晶体先失去 5 个配位水，后失去配体 5-硝基间苯二甲酸，同时生成氧化锰和某种聚合物。

关键词：分析化学；Mn(nip)(H$_2$O)$_5$；配位化合物；晶体结构；热分解

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