Influence of Matrix Surroundings on the Fluorescence Properties of Amino-Benzoic Acid Doped Silica Gel Materials

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Two kinds of organic-inorganic composite luminescent material were prepared through sol-gel route, by doping *o*-amino-benzoic acid (ABA) or N-phenylanthranilic acid (N-PA) into SiO_2 xerogels. Fluorescence properties and thermal properties of ABA and N-PA in SiO_2 xerogels were studied. The relationship between the fluorescence properties and the preparative condition was also studied. The results showed that the ABA was easy to form dimer of non-luminescence among the molecules. The quenching concentration of the ABA was obviously increased owing to the shield of silica network. The fluorescence intensity of the composite material prepared at the acid condition was decreased, and a red shift for the fluorescence peak appeared. With the increasing of the pH value, the fluorescence peak blue shifted and the intensity was increased. However, the fluorescent intensity of N-PA/SiO_2 was increasing due to the concentration of N-PA was increased. The thermal stability of ABA and N-PA in the composite material was also improved. But, when the temperature continued to increase, the collapse of the silica network made the organic molecules escape from the pore of the silica network, the decomposition of escaping molecules decreased the intensity of emission spectrum.

Keywords: **SiO_2 gel** ***o*-amino-benzoic acid** **N-phenylanthranilic acid** **fluorescence property**

研究简报

两个 β- 二酮 Co(Ⅱ)配合物[Co(β-diketonate)$_2$(py)$_2$]的合成和晶体结构

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关键词: Co(Ⅱ)配合物 苯甲酰丙酮 2- 噻吩甲酰三氟丙酮 晶体结构
分类号: O614.81+2

钴是生物学上重要的微量元素，它能在一些酶中代替锌，而不改变原来酶的活性[1]，钴的光谱和磁性是酶活性部位的有效探针[2]。钴催化剂是单活性中心催化剂[3]，同时又是很好的乙烯齐聚催化剂[4,5]。β- 二酮是重要的催化剂原料，徐德民等[6]报道了含有 β- 二酮金属配合物催化剂制备间规聚苯乙烯与聚丙烯共混复合物。宓霞等[7]报道了含 β- 二酮钛非茂催化剂催化降冰片烯聚合。近年来，已报道了一些 β- 二酮的 Co(Ⅲ)配合物[8-10]的晶体结构，本文报道两个 β- 二酮的 Co(Ⅱ)配合物的合成和晶体结构。

1 实验部分

1.1 配合物的制备

2.0mmol 苯甲酰丙酮 (bzacH) 溶于 10mL 的无水乙醇，1.0mmol $CoCl_2 \cdot 6H_2O$ 溶于 10mL 无水乙醇，将上述两溶液混合，然后加 0.4mL 吡啶，室温条件下搅拌 4h，红色溶液缓慢挥发得到配合物 [Co(bzac)$_2$(py)$_2$](**1**)晶体，产率 73%。

用 2- 噻吩甲酰三氟丙酮 (ttaH) 代替苯甲酰丙酮，与合成配合物 **1** 相同的方法，制得配合物 [Co(tta)$_2$(py)$_2$](**2**)晶体，产率 68%。

1.2 晶体结构解析

选取适当大小的配合物单晶，置于 Rigaku R-AXIS-CS3 单晶衍射仪上，用石墨单色器单色化的 Mo $K\alpha$ (λ = 0.071069nm) 辐射，收集衍射数据。晶体结构用直接法解出，非氢原子坐标及各向异性热参数经最小二乘法修正。氢原子由差 Fourier 合成和理论计算得到，它们的坐标和各向同性温度因子参加结构计算，但不参加修正。所有计算均在 PC 机上用 Siemens SHELXTL-97 程序包完成。配合物的主要晶体学参数列于表 1，主要的键长和键角列于表 2。

CCDC: 176343; 176344。

2 晶体结构描述

两个标题化合物均存在对称中心，Co(Ⅱ)位于对称中心(0, 0, 0)上。化合物的分子结构分别如图 1 和图 2 所示，图中标有“A”的原子与相应的原子存在对称中心关系(symmetry code: $-x$, $-y$, $-z$)。在赤道平面上，β- 二酮的两个氧原子与 Co(Ⅱ)配位形成反式的平面正方形结构，轴向位置分别由两个吡啶分子的两个氮原子占据，形成了畸变的八面体配位构型。在配合物 **1** 中，Co-O 键的键长分别为 0.2029(1)nm 和 0.2054(1)nm；在配合物 **2** 中，上述对应的

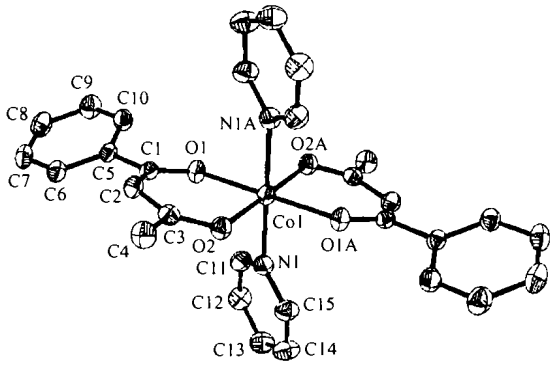

图 1 [Co(bzac)$_2$(py)$_2$]的分子结构

Fig. 1 Molecular structure of [Co(bzac)$_2$(py)$_2$]

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表 1 主要晶体学参数

Table 1 Crystallographic Data

	1	2
formula	$C_{30}H_{28}CoN_2O_4$	$C_{26}H_{18}CoF_6N_2O_4S_2$
formula weight	539.47	659.47
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/nm	0.7409(2)	0.9634(2)
b/nm	1.7430(4)	0.9678(2)
c/nm	1.0527(2)	0.9713(2)
α/(°)	90	111.18(3)
β/(°)	102.23(3)	114.61(3)
γ/(°)	90	99.05(3)
V/nm^3	1.3285(5)	0.7154(2)
Z	2	1
F(000)	562	333
D_c/(Mg · m^{-3})	1.349	1.531
μ/mm^{-1}	0.684	0.819
crystal dimensions/nm	0.43 × 0.37 × 0.30	0.38 × 0.30 × 0.23
independent reflections	3037	3154
observed reflections ($I > 2\sigma(I)$)	2437	2708
variables	169	187
residual electron density/(e · nm^{-3})	189, −319	709, −623
R, wR	0.0307, 0.0827	0.0595, 0.1769
GOF	1.042	1.054

表 2 主要的键长和键角

Table 2 Selected Bond Lengths(nm) and Selected Bond Angles(°)

complex 1					
Co(1)-O(1)	0.2029(1)	Co(1)-O(2)	0.2054(1)	Co(1)-N(1)	0.2201(1)
O(1)-C(1)	0.1274(2)	O(2)-C(3)	0.1265(2)	C(1)-C(2)	0.1393(2)
C(1)-C(5)	0.1499(2)	C(2)-C(3)	0.1403(2)	C(3)-C(4)	0.1504(2)
O(1)-Co(1)-O(2)	88.71(4)	O(1)-Co(1)-N(1)	89.56(5)	O(2)-Co(1)-N(1)	94.25(5)
C(1)-O(1)-Co(1)	126.56(9)	C(3)-O(2)-Co(1)	125.2(1)	C(15)-N(1)-Co(1)	124.3(1)
C(11)-N(1)-Co(1)	118.7(1)	O(1)-C(1)-C(2)	125.3(1)	O(1)-C(1)-C(5)	114.7(1)
C(2)-C(1)-C(5)	120.0(1)	C(1)-C(2)-C(3)	125.7(1)	O(2)-C(3)-C(2)	125.0(1)
O(2)-C(3)-C(4)	116.3(1)	C(2)-C(3)-C(4)	118.6(1)		
complex 2					
Co(1)-O(1)	0.2040(2)	Co(1)-O(2)	0.2043(2)	Co(1)-N(1)	0.2162(3)
O(1)-C(1)	0.1257(3)	O(2)-C(3)	0.1270(4)	C(1)-C(2)	0.1415(4)
C(1)-C(5)	0.1464(4)	C(2)-C(3)	0.1373(4)	C(3)-C(4)	0.1516(4)
O(1)-Co(1)-O(2)	88.79(8)	O(1)-Co(1)-N(1)	89.2(1)	O(2)-Co(1)-N(1)	88.7(1)
C(1)-O(1)-Co(1)	126.3(2)	C(3)-O(2)-Co(1)	122.3(2)	C(9)-N(1)-Co(1)	120.4(2)
C(13)-N(1)-Co(1)	122.3(2)	O(1)-C(1)-C(2)	125.3(2)	O(1)-C(1)-C(5)	116.6(2)
C(2)-C(1)-C(5)	118.1(2)	C(1)-C(2)-C(3)	123.1(3)	O(2)-C(3)-C(2)	130.0(3)
O(2)-C(3)-C(4)	112.4(2)	C(2)-C(3)-C(4)	117.6(3)		

键长分别为 0.2040(2)nm 和 0.2043(2)nm。

在配合物 **1** 中，C(1)-C(5)的键长为 0.1499(2) nm，比单键 C(sp^2)-C(sp^2)的平均键长 0.1482nm[11] 稍长。O(1)、C(1)、C(2)、C(3)和 O(2)五个原子组成一个平面，面上原子的平均偏差为 0.0039nm，该平面与苯环平面二面角为 37.74(8)°，即配体 bzac$^-$的非氢原子不在同一平面上。在配合物 **2** 中，除了氟原子外配体 tta$^-$的非氢原子在同一平面上，面上原子的平均偏差为 0.0032nm。C(1)-C(5)的键长为 0.1464(4) nm，比单键 C(sp^2)-C(sp^2)的平均键长稍

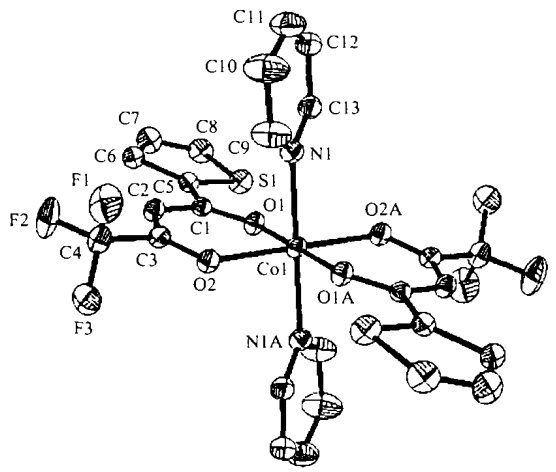

图 2　[Co(tta)$_2$(py)$_2$]的分子结构

Fig. 2　Molecular structure of [Co(tta)$_2$(py)$_2$]

短, 表明 C(1)与 C(5)原子间有一定的双键性, 即赤道平面上的原子形成一个大的共轭体系。

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Syntheses and Crystal Structures of Two β-Diketonate Co (Ⅱ) Complexes, [Co(β-Diketonate)$_2$(py)$_2$]

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Two Co (Ⅱ) complexes [Co(β-diketonate)$_2$(py)$_2$], [Co(bzac)$_2$(py)$_2$](**1**) and [Co(tta)$_2$(py)$_2$](**2**) (bzacH = benzoylacetone, ttaH = 2-thenoyltrifluoroacetone, py = pyridine) were synthesized and characterized by X-ray diffraction. Complex **1** crystallizes in monoclinic system, space group $P2_1/n$ with $a = 0.7409(2)$, $b = 1.7430(4)$, $c = 1.0527(2)$nm, $\beta = 102.23(3)°$, $V = 1.3285(5)$nm^3, $Z = 2$, $F(000) = 562$, $D_c = 1.349$g · cm^{-3}, μ(Mo$K\alpha$) = 0.684mm^{-1}. The structure was refined to $R = 0.0307$ and w$R = 0.0827$ for observed 2437 reflections with $I \geqslant 2\sigma(I)$. Complex **2** crystallizes in triclinic system, space group $P\bar{1}$ with $a = 0.9634(2)$, $b = 0.9678(2)$, $c = 0.9713(2)$nm, $\alpha = 111.18(3)$, $\beta = 114.61(3)$, $\gamma = 99.05(3)°$, $V = 0.7154(2)$nm^3, $Z = 1$, $F(000) = 333$, $D_c = 1.531$g · cm^{-3}, μ(Mo$K\alpha$) = 0.819mm^{-1}. The structure was refined to $R = 0.0595$ and w$R = 0.1769$ for observed 2708 reflections with $I \geqslant 2\sigma(I)$. In both structures the Co (Ⅱ) ions are six-coordinated to form distorted octahedron.

Keywords:　**Co (Ⅱ) complex**　**benzoylacetone**　**2-thenoyltrifluoroacetone**　**crystal structure**