

以芳香族多羧酸为配体的 Ni(II)配位超分子的研制及 光诱导下的表面电子行为

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Preparation and Light-Induced Surface Electron Behavior of Ni(II) Based on Aromatic Polycarboxyl Acids

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1. 文献[22]中化合物(1)的合成方法: Synthesis of the Single Crystals of $\text{Ni}_3(\text{btc})_2(\text{H}_2\text{O})_{14}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}_3(\text{btc})_2(\text{H}_2\text{O})_{12}$. Agarose was purchased from Prolabo and used without further purification. Dilute aqueous solutions of hydrated nickel(II) chloride and sodium salt of 1,3,5-benzenetricarboxylic acid were allowed to slowly diffuse, in an U-shaped tube, through agar-agar gel media at room temperature. After a few weeks of diffusion, single crystals of both phases were obtained depending on the strength of the gel medium. Anal. Calc. for $\text{Ni}_3(\text{btc})_2(\text{H}_2\text{O})_{14}\cdot 4\text{H}_2\text{O}$ (found): Ni 19.3% (19.5); C 23.6% (23.5); O 52.5% (52.4); H 4.6% (4.4).

2. 文献[23]中化合物(2)的合成方法: A DMF (10 ml) solution of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol) and benzene-1,2,4,5-tetracarboxylic acid (0.13 g, 0.5 mmol) was mixed with a DMF solution (10 ml) of 2,20-bipyridine (0.08 g, 0.5 mmol). After one month, green crystals separated from the solution.

3. 结构图及结构数据

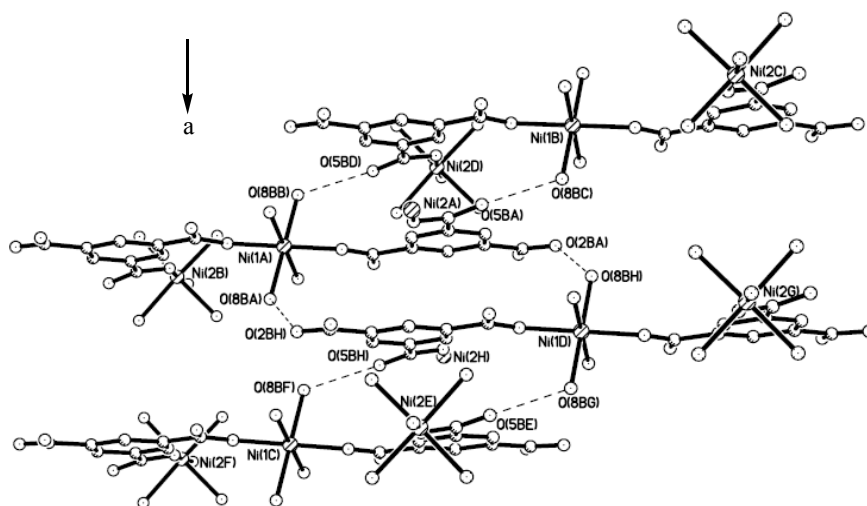


图 1s 化合物(1)在 a 方向的氢键链

在 a 方向上, 与对称中心 Ni(1)离子配位的水分子 O(8AB)和 O(8AA)分别与相邻两个分子中未配位的羧基 O 原子 O(5AD)和 O(2AH)形成氢键, O(8)-H...O(5)以及 O(8)-H...O(2)之间的距离分别为 0.2711 和 0.2841 nm. 这两条氢键使得化合物的分子被连接成沿 a 方向的一维链.

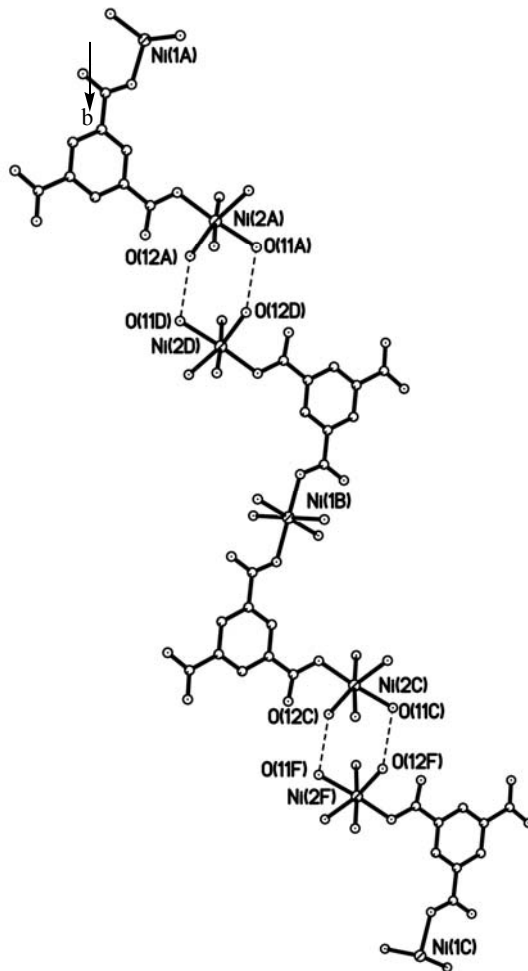


图 2s 化合物(1)沿 b 方向的氢键链

b 方向上, 配位水分子 O(11)和 O(12)原子分别与 O(12)和 O(11)原子之间形成分子间氢键, O(11)-H...O(12)之间的距离为 0.2805 nm. 该相互平行的两条氢键使相邻的分子被连接成沿 b 方向延伸的一维链.

在 293K 下, 选取化合物单晶体, 在 Smart APEX II CCD 单晶衍射仪上收集衍射数据. 以 $\text{MoK}\alpha$ 射线($\lambda=0.071073\text{nm}$)为辐射源, IP 面探测器采用 ω 扫描方式. 全部衍射数据都经 LP 因子和经验吸收校正. 晶体结构用直接法解出, 经全矩阵最小二乘程序修正. 全部结构计算和绘图采用 SHELXTL 程序系统. 化合物的主要晶体学数据和结构修正见表 1s.

表 1s 化合物的主要晶体学数据和结构修正

	(1)	(2)
Empirical formula	C ₁₈ H ₃₆ Ni ₃ O ₃₀	C ₁₅ H ₁₁ N ₂ NiO ₈
Formula weight	908.60	405.97
Temperature/K	293(2)	293(2)
Wavelength/ nm	0.071073	0.071073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/n
a (nm)	0.6738(2)	1.21919(10)
b (nm)	1.0763(3)	0.75708(7)
c (nm)	1.2400(4)	1.78781(15)
α (°)	98.613(4)	90
β (°)	102.811(4)	100.015(3)
γ (°)	107.489(4)	90
Volume(Å ³)	813.4(4)	1625.0(2)
Z	1	4
Theta range for data collection/(°)	1.73 to 29.00	1.88 to 27.48
Dc(g/cm ³)	1.855	1.659
<i>F</i> (000)	468	828
Data / restraints / parameters	3729 / 0 / 244	3700 / 0 / 274
Goodness-of-fit on F ²	1.052	0.970
Reflections collected / unique	5048 / 3729	3700 / 3700
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1971	R1 = 0.0443, wR2 = 0.1165
R indices (all data)	R1 = 0.0800, wR2 = 0.2140	R1 = 0.0652, wR2 = 0.1223
Largest diff. peak and hole/(e.nm ⁻³)	2147 and -783	637 and -679

表 2s 化合物的键长及键角 (Å) 和 (°)

Complex (1)					
Ni(1)-O(4)	2.040(3)	O(4)-Ni(1)-O(8)	90.35(14)	O(10)-Ni(2)-O(13)	176.79(13)
Ni(1)-O(8)	2.093(4)	O(4)#1-Ni(1)-O(8)	89.65(14)	O(6)-Ni(2)-O(9)	92.47(14)
Ni(1)-O(7)	2.148(4)	O(4)#1-Ni(1)-O(7)	87.59(13)	O(10)-Ni(2)-O(9)	92.51(15)
Ni(2)-O(6)	2.062(3)	O(4)-Ni(1)-O(7)	92.41(13)	O(6)-Ni(2)-O(11)	176.03(12)
Ni(2)-O(10)	2.082(3)	O(8)#1-Ni(1)-O(7)	89.98(15)	O(10)-Ni(2)-O(11)	88.38(14)
Ni(2)-O(13)	2.092(4)	O(8)-Ni(1)-O(7)	90.02(15)	O(6)-Ni(2)-O(12)	98.52(13)
Ni(2)-O(9)	2.122(3)	O(6)-Ni(2)-O(10)	89.91(13)	O(9)-Ni(2)-O(11)	84.03(15)
Ni(2)-O(11)	2.138(3)	O(6)-Ni(2)-O(13)	92.67(13)	O(13)-Ni(2)-O(11)	88.93(14)
Ni(2)-O(12)	2.156(4)	O(10)-Ni(2)-O(12)	86.66(16)	O(9)-Ni(2)-O(12)	168.97(15)
Complex (2)					
Ni(1)-O(2)	2.060(2)	O(2)-Ni(1)-N(1)	93.50(11)	O(1)-Ni(1)-O(3)	85.81(9)
Ni(1)-N(1)	2.071(3)	O(2)-Ni(1)-O(1)	91.67(10)	N(2)-Ni(1)-O(3)	93.49(10)
Ni(1)-O(1)	2.086(2)	N(1)-Ni(1)-O(1)	172.34(10)	O(2)-Ni(1)-O(4)	87.05(9)
Ni(1)-N(2)	2.088(3)	O(2)-Ni(1)-N(2)	86.27(10)	N(1)-Ni(1)-O(4)	93.18(10)
Ni(1)-O(3)	2.094(2)	N(1)-Ni(1)-N(2)	78.77(11)	O(1)-Ni(1)-O(4)	92.73(9)
Ni(1)-O(4)	2.104(2)	O(1)-Ni(1)-N(2)	95.94(10)	N(2)-Ni(1)-O(4)	169.20(10)
O(4)-C(5)	1.262(4)	O(2)-Ni(1)-O(3)	177.43(9)	O(3)-Ni(1)-O(4)	93.56(9)
O(5)-C(5)	1.254(4)	N(1)-Ni(1)-O(3)	88.96(11)	O(5)-C(5)-O(4)	125.4(3)

Symmetry transformations used for the generated atoms: #1 -x,-y, -z

表 3s 化合物(1)的氢键数据 (Å) 和 (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8A)...O(5)	0.850	2.61	2.914	112
O(8)-H(8A)...O(2)	0.850	2.287	2.841	122.99
O(10)-H(10B)...O(1)	0.850	2.376	3.197	162.47
O(11)-H(11A)...O(12)	0.850	2.169	2.805	131.44
O(12)-H(12A)...O(11)	0.850	2.344	2.344	114.49
O(12)-H(12A)...O(15)	0.850	2.389	2.886	117.89
O(15)-H(15A)...O(2)	1.196	1.661	2.847	170.47
O(15)-H(15B)...O(13)	0.694	2.496	2.960	126.29

表 4s 化合物(2)的氢键数据 (Å) 和 (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)#1	0.850	2.062	2.821	148.4
O(2)-H(2B)...O(7)#2	0.850	2.287	3.153	147.6
O(1)-H(1B)...O(5) #3	0.850	2.535	2.670	122.5
O(3)-H(3B)...O(7) #4	0.850	2.394	2.720	100.8

4. 表面光电压光谱仪的组成

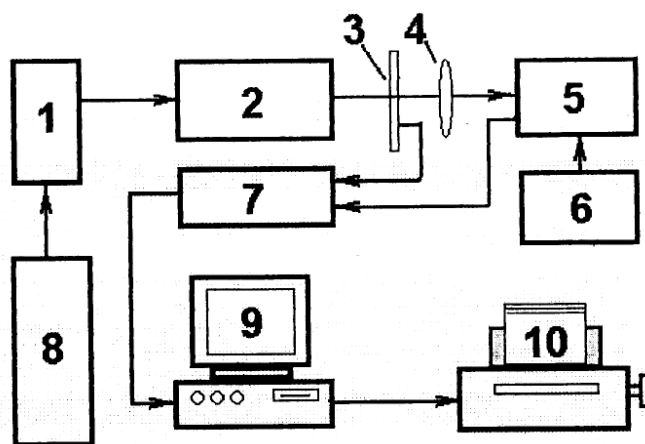


图 3s 光电压仪器组成^[a]

1 氙灯光源; 2 单色仪; 3 斩波器; 4 透镜 ; 5 光电电压池; 6 外电场 ; 7 锁相放大器; 8 电源 ; 9 计算机 ; 10 打印机

^[a]L. Kronik, Y. Shapira, Surf. Interface. Anal, 31 (2001) 954-965.

5. 表面光电压池的构造

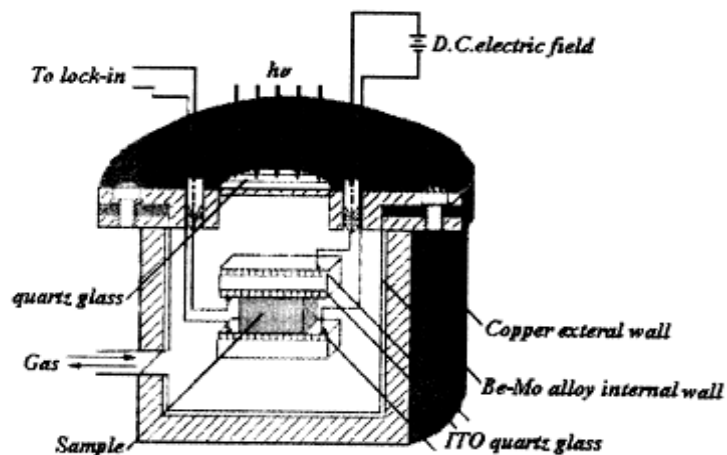


图 4s 表面光电压池的构造^[b]

^[b] S. Datta, S. Ghosh. Rev. Sci. Ins. 72 (2001) 171-182.

6. 化合物的红外光谱

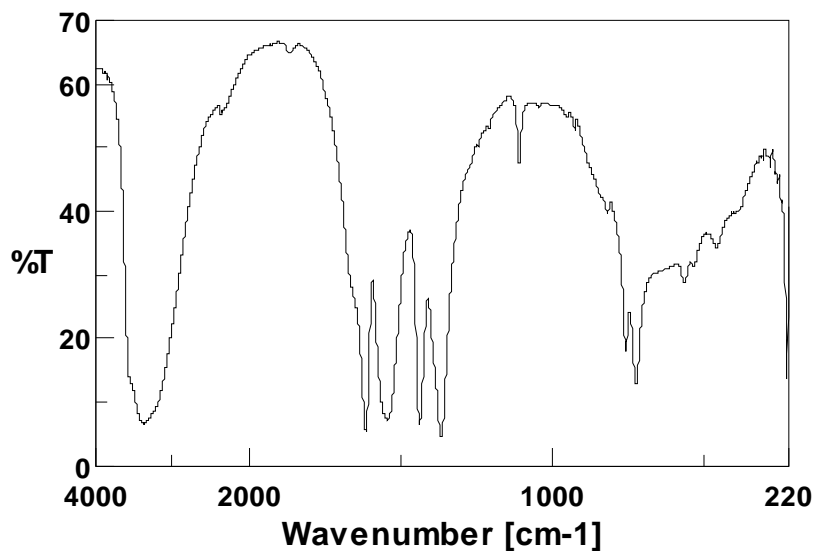


图 5s 化合物(1)的红外光谱图

Assignment : 3395 (ν_{OH}); 1613 ($\nu_{\text{asCOO-}}$); 1363 ($\nu_{\text{sCOO-}}$); 1541, 1476, 434 ($\nu_{\text{ArC=C}}$); 1205, 1108 ($\nu_{\text{C-C,C-O}}$);

754,721 ($\delta_{\text{C-H}}$); 563,456 ($\nu_{\text{Ni-O}}$).

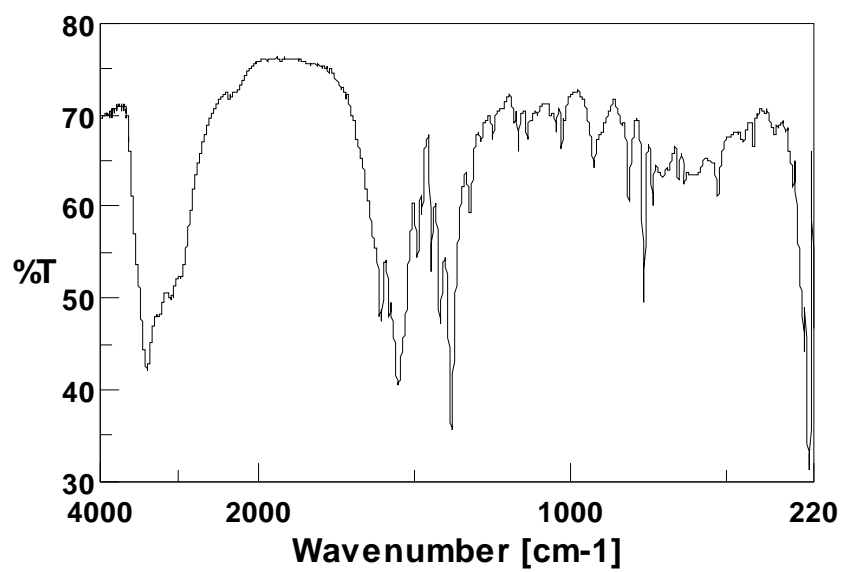


图 6s 化合物(2)的红外光谱图

Assignment: 3407, 3253 (ν_{OH}); 3078 ($\nu_{\text{Ar-C-H}}$); 1545($\nu_{\text{asCOO-}}$); 1378 ($\nu_{\text{sCOO-}}$); 1597, 1549, 1494, ($\nu_{\text{Ar-C-C}}$);

1164, 1140, 1025 ($\nu_{\text{C-C, C-O}}$); 810,763,735 ($\delta_{\text{C-H}}$); 647($\nu_{\text{Ni-N}}$); 521($\nu_{\text{Ni-O}}$).