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研究论文

N-皮考林酰肼及其双核钯配合物的晶体结构和荧光性质

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摘要 合成了配体*N*-皮考林酰肼(简写为Hphz)及其双核钯配合物[$Pd_2(phz)_2Cl_2$]. X射线衍射实验结果表明, 配体和配合物晶体均属于单斜晶系, 空间群分别为*C* 2/*c*和*P* $2_1/c$, 分子式分别为$C_6H_7N_3O$和$C_{12}H_{12}Cl_2N_6O_2Pd_2$. 晶体学参数, Hphz, a=1.9245(2) nm, b=0.38927(2) nm, c=1.8073(2) nm, b=107.255(2)°, V=1.2931(2) nm^3, Z=8, D_c=1.409 Mg/m^3, F(000)=576, μ(Mo Kα)=0.102 mm^{-1}, R=0.0541, wR=0.1762; [$Pd_2(phz)_2Cl_2$], a=1.48274(9) nm, b=1.44797(9) nm, c=0.73951(5) nm, b=92.719(3)°, V=1.5860(2) nm^3, Z=4, D_c=2.329 Mg/m^3, F(000)=1072, μ(Mo Kα)=2.62 mm^{-1}, R=0.0262, wR=0.0555. 在配合物[$Pd_2(phz)_2Cl_2$]分子内, 两个钯(II)原子, 均呈畸变的N_3Cl平面正方形配位构型, 晶体内通过分子间氢键N—H…Cl 作用形成一维链状结构, 分子间吡啶环存在相互作用. 量子化学从头算方法计算结果表明, 分子内及分子间的金属钯之间也存在相互作用. 红外光谱表明, 配体在形成配合物后, ν(C=O)和ν(C=N)红移, ν(C—N)蓝移, 荧光光谱表明, 配合物金属对配体n-π*激发(310 nm)引起的发射峰有较大的影响.

关键词 晶体结构 *N*-皮考林酰肼 双核钯配合物

分类号

Crystal Structure and Fluorescence of *N*-Picoloylhydrazide and Its Binuclear Palladium Complex

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Abstract *N*-Picoloylhydrazide (Hphz) and its binuclear palladium complex [$Pd_2(phz)_2Cl_2$] were synthesized and determined by single crystal X-ray diffraction. They belong to monoclinic system. Crystal data: Hphz($C_6H_7N_3O$), space group *C*2/*c*, a=1.9245(2) nm, b=0.38927(2) nm, c=1.8073(2) nm, b=107.255(2)°, V=1.2931(2) nm^3, Z=8, D_c=1.409 Mg/m^3, F(000)=576, m((Mo Kα)=0.102 mm^{-1}, 0.0541 for 1257 observed reflections [$I\geq\sigma(I)$], wR=0.1762, GOF=1.124; [$Pd_2(phz)_2Cl_2$]($C_{12}H_{12}Cl_2N_6O_2Pd_2$), space group $P2_1/c$, a=1.48274(9) nm, b=1.44797(9) nm, c=0.73951(5) nm, β=92.719(3)°, V=1.5860(2) nm^3, Z=4, D_c=2.329 Mg/m^3, F(000)=1072, μ(Mo Kα)=2.62 mm^{-1}, R=0.0262 for 2937 observed reflections [$I\geq\sigma(I)$], wR=0.0555, GOF=0.959. The palladium(II) ion of the complex [$Pd_2(phz)_2Cl_2$] is coordinated with two pyridine nitrogen atom and two diazine nitrogen atom, forming a distorted square geometry. Pd…Pd distance is 0.38111 nm in the complex. There is a one-dimensional chain structure through the intermolecular hydrogen bonds N—H…Cl in complex crystal. There are π-π interactions in the neighboring ligands. The *ab initio* calculation with Hartree-Fork method showed that there are interactions between Pd and Pd in the complex molecule and the neighboring molecule. ν(C=O) and ν(C=N) were shifted to lower frequencies and ν(C—N) was shifted to higher frequencies in IR spectra. The emission lines (l_{ex}=310 nm) were shifted to higher frequencies in fluorescence spectra.

Key words crystal structure *N*-picoloylhydrazide binuclear palladium complex

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