配合物 $Ru(bpy)_2(dppx)(BF_4)_2$ 的快原子轰击质谱研究

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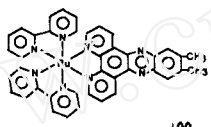
研究表明[1,2],钌的某些配合物在水溶液中不发光,但在嵌入 DNA 后,能够发光.这一特性使这些配合物有可能作为 DNA 的发光探针用于诊断和治疗某些疾病[3,4].因此,对于这类配合物的合成及其光致发光性质研究引起了人们的广泛关注.但对于这类配合物的质谱系统研究尚未见文献报道.本文探讨了新合成的钌配合物 $Ru(bpy)_2$ $dppx)(BF_4)_2$ bpy=2,2'bipyridine,dppx=dipyrido [3,2,-a-2',3'-c] phenaxylene 在不同底物中的快原子轰击质谱(FAB-MS),根据质量碎片和有关质谱知识表征了该化合物的结构特征.为该类化合物的合成及其分子结构表征提供了一些有价值的参考和借鉴.$Ru(bpy)_2(dppx)$ 的结构如下:



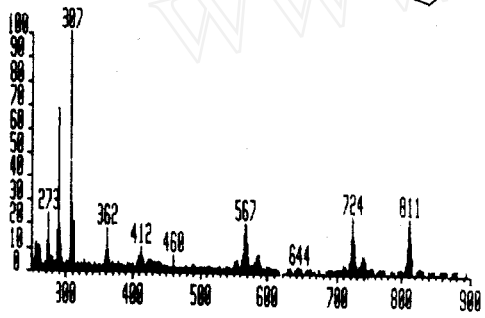


Figure 1. FAB mass spectrum of $Ru(bpy)_2(dppx)(BF_4)_2$, matrix is m-nitrobenzyi alcohol(m-NBA)$Ru(bpy)_2(dppx)(BF_4)_2$, (m/z273,289,307,460 are signals of m-NBA)

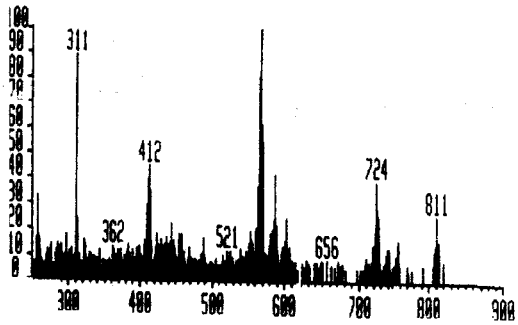


Figure 2. FAB mass spectrum of matrix i s nomothioglycerol (m/z257 is signal of matrix.

以 Ar 为轰击气体,快原子枪的工作条件为:1mA,8kv.我们试验了甘油,间硝基苄醇,硫代甘油三种不同的基质对 $Ru(bpy)_2(dppx)(BF_4)_2$ 的质谱的影响.实验结果表明,以甘油为基质时,得不到样品的信号,可能因为甘油极性太强.以硫代甘油,间硝基苄醇为基质时，得到的质谱图见图 1,2.

从这二张质谱图上,我们可以得出如下信息:

(1).以硫代甘油,间硝基苄醇为基质时,得到的样品信号基本一致,均出现了 m/z311, 362, 412, 568, 587, 724, 741, 811 的峰.

(2).钌有一组同位素,从钌的同位素峰可判断 m/z 311 为不含钌的碎片离子,可能为配体 $(dppx+H)^+$.其它峰信号均含金属钌

(3)从谱图上可以断定 m/z 362 为 $[Ru(bpy)_2(dppx)]^{2+}$的双电荷离子.

(4)根据质量碎片和有关质谱知识可推出 m/z412$[Ru(dppx)_2]^+$m/z568:$[Ru(bpy)(dppx)]^+$ m/z587:$[Ru(bpy)(dppx)F]^+$,m/z724:$[Ru(bpy)_2(dppx)]^+$,m/z741:$[Ru(bpy)_2(dppx)F+2H]^+$,

m/z811:$[Ru(bpy)_2(dppx)(BF_4)]^+$.

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THE MASS SPECTOMETRIC STUDY OF COMPLEX $RU(BPY)_2(DPPX)(BF_4)_2$

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It is reported ruthenium complexes show no photoluminescence in aqueous solution at ambient temperature , but display intense photoluminescence in the presence of double-helical DNA ,to which the complex bind avoidly . These characteristics may become particularly useful in developing new diagnostic reagent based upon luminescent DNA probes. So, there has been increasing attention given to the design of ruthenium complexes and their photoluminescence characteristics. But there is no report on mass spectrometric study of these complexes . In this paper, the fast atom bombardment mass spectra of newly synthesized ruthenium complex $Ru(bpy)_2(dppx)(BF_4)_2$ (bpy=2, 2'bipyridine, dppx=dipyrido<3,2,-a:2',3'-c>phenaxylene)was discussed. According to the fragment ions and related knowledge , the molecule structure is characterized. These will provide some valuable references to synthesize these complexes and characterize their molecule structures.