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论文

配合物$[Fe(CO)_x(Ph_2Ppy)_y(HgCl_2)_z]$($x$=3, 4; y=1, 2; z=0, 1, 2)的Fe—Hg相互作用及^{31}P化学位移的理论研究

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摘要：

用密度泛函理论PBE0法计算配合物$[Fe(CO)_x(Ph_2Ppy)_y(HgCl_2)_z]$(1: x=4, y=1, z=0; 2: x=3, y=2, z=0; 3: x=4, y=1, z=1; 4: x=3, y=2, z=1; 5: x=4, y=1, z=2; 6: x=3, y=2, z=2)的几何构型, 用PBE0-GIAO法计算配合物1~6的^{31}P化学位移. 计算结果表明, 含2个Ph_2Ppy的配合物5和6的Fe—Hg相互作用略大于含单个Ph_2Ppy的配合物3和4. 含2个$HgCl_2$的配合物4和6存在Fe—Hg σ键, 比含单个$HgCl_2$的配合物3和5的Fe—Hg相互作用强, 配合物3和5的Fe—Hg相互作用以Fe→Hg和Fe←Hg离域为主. 配合物3中Fe的负电荷比5的小, 故配合物5的Fe—Hg相互作用比配合物3的强且Fe→Hg离域比较显著, 而配合物3的Fe←Hg离域更显著. Fe—Hg相互作用增大了双核配合物中P核周围的电子密度, 其^{31}P化学位移比相应的单核配合物小, 且含2个$HgCl_2$的双核配合物的^{31}P化学位移更小. 含单个Ph_2Ppy的配合物的^{31}P化学位移小于含2个Ph_2Ppy的配合物.

关键词： 密度泛函理论; 自然键轨道; Fe—Hg相互作用; ^{31}P核磁共振

Theoretical Studies on the Fe—Hg Interactions and the ^{31}P NMR in $[Fe(CO)_x(Ph_2Ppy)_y(HgCl_2)_z]$($x$=3, 4; y=1, 2; z=0, 1, 2)

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Abstract:

To study the Fe—Hg interactions and their effects on ^{31}P NMR, $[Fe(CO)_x(Ph_2Ppy)_y(HgCl_2)_z]$(1: x=4, y=1, z=0; 2: x=3, y=2, z=0; 3: x=4, y=1, z=1; 4: x=3, y=2, z=1; 5: x=4, y=1, z=2; 6: x=3, y=2, z=2) were calculated by DFT PBE0 method. PBE0-GIAO method was employed to calculate the ^{31}P chemical shifts. The conclusions can be drawn: (1) The Fe—Hg interactions in complexes with two Ph_2Ppy are slightly stronger than those with one Ph_2Ppy, and which in complexes with two $HgCl_2$ are stronger than those with one $HgCl_2$. (2) There is a Fe—Hg σ bond in complexes with two $HgCl_2$. Fe—Hg interactions mainly exhibit the Fe→Hg and Fe←Hg indirect charge-transfer. Contrasted to complex 5, the CO→Fe σ-donation and CO←Fe π-back donation in complex 3 decrease the electron density of Fe. So the Fe—Hg interaction in complex 5 is stronger and acts as Fe→Hg charge-transfer, while that in complex 3 mainly acts as Fe←Hg. (3) Through Fe—Hg interaction, the charge-transfer from Ph and py towards the P, Fe and Hg atoms increases the electron density on P nucleus. So, compared with mononuclear complexes, the ^{31}P chemical shifts in binuclear complexes show some reduction. The ^{31}P chemical shifts in complexes with two $HgCl_2$ or one Ph_2Ppy are less than those with one $HgCl_2$ or two Ph_2Ppy.

Keywords: Density functional theory; Natural bond orbital; Fe—Hg Interaction; ^{31}P NMR

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