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研究论文

双帽Keggin型杂多阴离子$[H_4As_3Mo_{12}O_{40}]^-$和Keggin型杂多酸$H_3PM_{12}O_{40}$ (M＝Mo, W)质子化的DFT研究

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摘要 选用B3LYP方法在LanL2MB水平下, 对双帽α-Keggin型杂多阴离子$[H_4As_3Mo_{12}O_{40}]^-$的电子结构和质子的定位进行了密度泛函理论(DFT)研究. 结果表明, 双帽的形成大大影响了杂多阴离子$[As_3Mo_{12}O_{40}]^{5-}$的电子结构和性质, NBO分析显示参与成帽的三桥氧上的电子密度比双桥氧上的要大, 简单地从电荷密度来看, 质子将首先在三桥氧上定域成键, 但通过比较质子定域在几种桥氧上质子化稳定化能的大小, 发现$[H_4As_3Mo_{12}O_{40}]^-$中的四个质子将在八个双桥氧中的其中四个氧原子上定位, 而不是如文献中报道的在四个三桥氧上定域成键. 对杂多酸$H_3PM_{12}O_{40}$ (M＝Mo, W)中质子的定位也进行了理论计算并与文献进行了比较, 结果显示, $H_3PMo_{12}O_{40}$中质子是定位在双桥氧上; 而$H_3PW_{12}O_{40}$中质子将优先在双桥氧上定位, 但也可在端氧上定位; 这一结果与文献报道的相一致.

关键词 杂多化合物 双帽Keggin结构 质子化 DFT $[H_4As_3Mo_{12}O_{40}]^-$ $H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$

分类号

DFT Studies on the Protonation of Bicapped-Keggin-type Heteropolyanion $[H_4As_3Mo_{12}O_{40}]^-$ and Keggin-type Heteropoly Acids $H_3PM_{12}O_{40}$ (M＝Mo, W)

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Abstract DFT (density functional theory) calculations on the structure and the protonation sites of the bicapped-Keggin-type heteropoly anion $[H_4As_3Mo_{12}O_{40}]^-$ were performed using B3LYP method with LanL2MB basis sets. The calculation showed that, the formation of the two caps on the opposite Mo_4O_4 faces greatly influenced the electronic structure, thereafter the properties of this anion. The NBO analysis indicated that the negative charge density of the triply bridged oxygen atoms, participating in the formation of the caps, was greater than the density of the doubly bridged ones, thus protons might be preferably located on the triply bridged oxygen atoms as speculated by considering simply the electronic density. But detailed investigations through comparison of the stabilization energy after the cluster protonation predicted that, the most energetically favorable sites for the protonation of $[H_4As_3Mo_{12}O_{40}]^-$ were located on four of eight edge-sharing doubly bridged oxygen atoms, rather than the triply bridged ones as indicated in the literature. The protonation of the Keggin-type heteropoly acids $H_3PM_{12}O_{40}$ (M＝Mo and W) was also investigated and compared with the results reported in literature. The acidic protons of $H_3PM_{12}O_{40}$ are bound to the bridged oxygen atoms for $H_3PMo_{12}O_{40}$, while for $H_3PW_{12}O_{40}$, they may be located on bridged oxygen atoms preferably, though they can also be located on terminal ones, and this conclusion is consistent with the literature.

Key words heteropoly compound bicapped α-Keggin structure protonation DFT $[H_4As_3Mo_{12}O_{40}]^-$ $H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$

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