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钼簇合物反应性能的研究-**SbCl3**和具有松散配位三核钼簇合物的加合反应及其产物的晶体结构

卢绍芳,黄建全,林五辉,黄金陵

中国科学院福建物质结构研究所

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摘要 报道具有松散配位的三核钼簇合物{Mo3(μ3-S)(μ-S)3[S2P(OEt)2]4.L(L'=H2O,C3H3ON,和SbCl3在HCl-EtOH中加合反应及其产物{Mo3(μ3-S)[(μ-S)3.SbCl3].[S2P(OEt)2]4(C2H5OH)}(C2H5OH)和{Mo3(μ3-S)[(μ-S)3.SbCl3][S2P(OEt)2]3[SXP(OEt)2].(C3H3ON)}(X=S,O)的晶体结构。结构测定结果表明,这两个加合物的分子由{Mo3(μ3-S)(μ-S)3[S2P(OEt)2]4.L(L=C2H5OH,C3H3ON)通过三个(μ-S)联结SbCl3而成,从而获得了{Mo3SbS4}的类立方烷簇胳构型,Sb一S之间存在较弱的配位键, 由此推断,若加合的金属原子的轨道和电子组态适宜,有可能通过这种[3+1]的成簇模式获得四核的同核或异核簇合物。

关键词 晶体结构测定 氯化物 X射线衍射分析 钼络合物 簇状化合物 加成反应 多核络合物 构型 锑化合物 恶唑 P

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Studies on reactivities of molybdenum clusters - the additive of SbCl3 to trimolybdenum clusters with loose coordination sites and crystal structure of the reaction products

LU SHAOFANG,HUANG JIANQUAN,LIN YUJUI,HUANG JINLING

Abstract The addition reaction of SbCl3 to Mo3(m3-S)(m-S)3[S2P(OEt)2]4L (L = H2O, oxazole (Q)) in a EtOH/EtOH-HCl medium yields {Mo3(m3-S)[(m-S)3SbCl3][S2P(OEt)2]4(EtOH)}(EtOH) (I) and {Mo3(m3-S)[(m-S)3SbCl3][S2P(OEt)2]3[SXP(OEt)2]Q} (X = S, O) (II) resp. I belongs to the monoclinic system, P21/n, with a 13.250(3), b 17.296(4), c 23.223(9) ? b 92.41(3)? Z = 4, R = 0.078. II belongs to the triclinic system, P1, with a 10.342(3), b 11.994(3), c 21.352(4) ? a 76.27(2), b 88.55(2), g 73.26(2)? Z = 2, R = 0.068. The 2 mol. structures are practically formed by connecting a Mo3 cluster with loose coordination sites, {Mo3(m3-S)(m-S)3[S2P(OEt)2]4L} with a SbCl3 mol. through 3 m-S atoms to form the {Mo3SbS4} core of a cubane-like type. There are relatively weak coordination bonds between the Sb and the 3 m-S atoms while no bonding interaction between the Sb and the 3 Mo atoms is found. In the addition compounds the structural character of the Mo3 clusters with loose coordination sites has not significantly changed. I crystals still have the reactivity for the loosely coordinated EtOH to be replaced by an oxazole ring to form II crystals. However, as a result of the addition, the 3 m-S atoms may be regarded as triple bridging S atoms each connecting 2 Mo atoms and a Sb atom. The information obtained in the structural anal. serves as evidence that the tetranuclear clusters might be formed by a [3 + 1] reaction mode.

Key words CRYSTAL STRUCTURE DETERMINATION CHLORIDE X-RAY DIFFRACTION ANALYSIS MOLYBDENUM COMPLEX CLUSTER COMPOUND ADDITION REACTION POLYNUCLEAR COMPLEX CONFIGURATION ANTIMONY COMPOUNDS

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通讯作者