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[Ho_2(phen)_4(H_2O)_4(OH)_2](phen)_2(NO_3)_4的合成、晶体结构及磁性

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摘要 在甲醇与水的混合溶剂中，经浓硝酸硝化的Ho_2O_3与1，10-邻菲啰啉反应形成氢氧根桥联的双核钬配合物[Ho_2(phen)_4(H_2O)_4(OH)_2] (phen)_2(NO_3)_4 （phen = 1,10-邻菲啰啉）。单晶X射线衍射晶体结构测定表明晶体属三斜晶系， P1-bar (no. 2)空间群，晶胞参数a = 1.1241(1) nm, b = 1.1439(1) nm, c = 1. 4058 (1) nm, α = 93.989(7)°, β = 98.173(7)°, γ = 108.19(1)°, V = 1.6874(4) nm~3, Z = 1, D_c = 1.737 g/cm~3, F(000) = 880，7752个独立衍射 点中，5702个可观测点满足F_o~2 ≥ 2σ (F_o~2)，R_1 = 0.0499, wR_2 = 0. 858。标题配合物由中心对称的双核[Ho_2(phen)_4(H_2O)_4-(OH)_2]~(4+)配阳离 子，邻菲啰啉phen分子及硝酸根NO_3~-阴离子组成。敏个稀土原子与2个邻菲啰啉 配体，2相水分子和2个氢氧根配位形成配位数为8的[HoN_4O_4]四方反棱柱。配位 多面体通过两氢氧根基团形成共棱的[Ho_2N_8O_6]双四方反棱柱[d(Ho-N) = 0. 2549～0.2565 nm, d(Ho-O_(H_2O) = 0.2356, 0.2366 nm, d(Ho-O_(OH)) = 0. 2223, 0.2240 nm]。通过氢键和芳环堆积作用，配阳离子和邻菲啰啉分子排列形成 平行于（10 1-bar）的两维层结构，NO_3~-阴离子位于层之间。标题配合物为顺磁 物质，在5 ～300K区间内遵循Curie-Weiss定律X_m (T + 4.43) = 14.72 cm~3·K ·mol~(-1)(X_m为每摩尔Ho~(3+)离子磁化率），其Ho~(3+)离子的室温有效磁矩为 10.76 B. M.，与Ho~(3+)自由离子的磁矩基本相同，表明稀土离子间不存在磁交换作用。

关键词 钬络合物 双核络合物 晶体结构 磁性 二氮杂菲 P

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Synthesis, Crystal Structure and Magnetic Property of [Ho_2(phen)_4 (H_2O)_4(OH)_2](phen)_2(NO_3)_4

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Abstract Reaction of nitrated Ho_2O_3 with 1,10-phenanthroline in CH_3OH/H_2O results in a novel hydroxo bridged dinuclear Ho(III) complex [Ho_2(phen)_4(H_2O)_4(OH)_2] (phen)_2(NO_3)_4. Single crystal X-ray diffraction study shows that the title compound crystallizes in the triclinic space group P 1-bar (no. 2) with the cell dimensions; a = 1.1241 (1) nm, b = 1.1439(1) nm, c = 1.4058 (1) nm, α = 93.989(7)°, β = 98.173(7)°, γ = 108.19(1)°, V = 1.6874(4) nm~3, Z = 1, D_c = 1. 737 g/cm~3, F(000) = 880, R_1 = 0.0499, wR_2 = 0.0858 for 5702 observed reflections [F_o~2 ≥ 2σ (F_o~2)] out of 7752 unique reflections. The compound consists of the centrosymmetric dinuclear [Ho_2(phen)_4(H_2O) _4(OH) _2]~(4+ complex cations, uncoordinated phen molecules and nitrate anions. The holmium atom coordinates to two phen ligands, two H_2O molecules and two hydroxo groups to form a [HoN_4O_4] square antiprism. An edge-shared bi-square-antiprism forms via the two bridging OH groups [d(Ho-N) = 0.2549～0.2565 nm, d(Ho-O_(H_2O) = 0.2356, 0.2366 nm, d(Ho-O_(OH)) = 0.2223, 0.2240 nm]. The complex cations and the uncoordinating phen molecules are assembled via hydrogen bonding and π -π stacking interactions into 2D layers parallel to (10 1-bar), between which the nitrate anions are sandwiched. The title compound behaves paramagnetically and obeys Curie-Weiss law X_m (T + 4.43) = 14. 72 cm~3·K·mol~(-1) between 5～300 K (X_m: magnetic susceptibility per mole Ho~(3+) ions). The effective magnetic moment at room temperature is 10.76 B. M., which is equal to the expected value for a free Ho~(3+) ion, suggesting no magnetic exchange within the dinuclear dinuclear cations.

Key words HOLMIUM COMPLEX DINUCLEAR COMPLEX CRYSTAL STRUCTURE MAGNETISM PHENANTHROLINE P

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