Polymeric manganese(II) complex with isophthalate ion and 2,2'-dipyridylamine

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In the past decade the design and synthesis of metal-organic coordination polymers with anions of isophthalic (1,3-benzenedicarboxylic) acid, ipht, have become a growing field in crystal engineering due to their structural diversity and potential application as functional materials [1]. We have been continually interested in organic coordination polymers with anions of isophthalic (1,3-benzenedicarboxylic) acid, ipht, have become a growing field in crystal engineering due to their structural diversity and potential application as functional materials [1]. We have been continually interested in the title compound, C15H14MoN2O5. It crystallizes in the monoclinic space group P21/c with a=7.778(2)Å, b=30.0719(8)Å, c=10.5116(3)Å, α=90°, β=101.551(2)°, γ=90° and Z=8. The compound was hydrothermally synthesized in a Teflon-lined steel autoclave (T = 433 K, 5 days) starting from an aqueous solution containing Mn(NO3)2 and sodium isophthalate. The structure was refined using single-crystal X-ray diffraction data (Oxford diffractometer, CCD detector, T = 293 K).

Crystal data: C15H14MoN2O5, M = 390.25, monoclinic, space group C2/c, a = 14.8320(6) Å, b = 21.9325(6) Å, c = 11.9995(5) Å, β = 122.916(6)°, V = 3276.8(2) Å3, Z = 8, F(000) = 1592, µ(Mo Kα) = 0.836 mm−1. The refinement on F2 (287 parameters) yielded R1 = 0.037, wR2 = 0.067, S = 0.97 for all data, and R1 is 0.027 for 2478 observed reflections with I ≥ 2σ(I).

Keywords: complex, carboxylate ligand, crystal structure
The ability of cucurbit[e]uril, CB[6], to form host-guest complex with diammonium salts, in particular with linear aliphatic diammonium salts, has been widely used for the construction of pseudorotaxanes and rotaxanes that exhibited interesting dynamic, structural and functional properties. By contrast, the ability of CB[6] to host aromatic compounds has been less obvious. It has been shown that CB[6] and the dihydrochloride salt of bis-1,4-(allylaminomethyl)benzene, form only [3] pseudorotaxane. This mode of binding with two molecules of CB[6] hosting the allylic side chains of the guest was led to the interpretation that the aromatic moiety is too big to be encapsulated in the cavity of CB[6].[1] However, it has already been reported that CB[6] and p-xylylenediammonium salt, 1, form a stable inclusion complex, 1b.[2] Furthermore, 4-aminobipyridine, and 4-(2-pyridyl)aniline, form strong, 1:1 inclusion complexes with CB[6], whereas the bifunctional analog forms strong 1:2 complex with CB[6], exhibiting remarkably large enhancements of fluorescence intensity and quantum yields.[3] These led us to speculate that the encapsulation of aromatic guest molecules, within the inner cavity of CB[6] can be thermodynamically favored but their formation may involve unexpectedly high kinetic barriers.

Novel pseudorotaxane compounds based on CB[6] and p-xylylenediammonium salts derivatives, 1, 3–4, were obtained by crystallization from aqueous solutions that contain a mixture of each diammonium guest and CB[6] at room temperature. The X-ray diffraction analysis of their complexes, 1b, 3b and 4a was also supported by 1H NMR in solution. The 1:2 complex of guest 2, namely 2a, was evident by NMR, but suitable for X-ray analysis single crystal were not be able to obtain. Nevertheless, upon heating and crystallization, the 1:1 complex, 2b, was obtained.

Further support for these two different binding modes was obtained from ITC measurements at room temperature. Each 1:1 complex exhibits two types of hydrogen bonding between the portal oxygen atoms and the guest. The more obvious bonds are formed with the ammonium hydrogen atoms of the ammonium diammonium salts (NH2.O=C, 1,980(3)–2,420(3) Å). The less obvious, but quite visible from the solid state structure, are the hydrogen bonding between the carbonyl oxygens of CB[6] and the benzylidene methylene hydrogens of the guest: CH=O=C, 2,317(3)–2,508(2) Å Complex 4a exhibited two distinguished hydrogen bond interactions: one corresponds to donor water molecule that is bridged by carbonyl oxygen of each cucurbituril unit (C=O(10)..O=C(11A), 2.73–2.88 Å) could explain the asymmetric observed in the structure of 4a where the CB units are obviously attracted to one another, creating an angle of 42.56° between them.

Our results show that 2:1 host-guest complexes, 2a and 4a, kinetic compounds, which may be converted to the thermodynamic products upon prolonged heating.