

Inorganic Chemistry

Unexpected Side Products of Chemical Transformations in Cobalt(II) Pseudoclathrochelates: An X-Ray Diffraction Study

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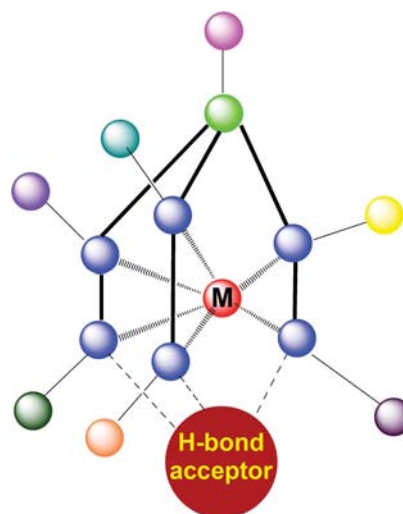
It is generally accepted that transition metal (pseudo)clathrochelates, a unique class of coordination compounds are easily obtained by a simple template condensation of appropriate oximes, boronic acids and metal salts. Our X-ray diffraction study of single crystals unexpectedly found in the reaction

mixtures of different pseudoclathrochelates, however, shows that other compounds are sometimes identified among the products of their synthesis or chemical transformations occurring in different media; those can interfere with their future practical applications.

1. Introduction

A popular synthetic strategy towards cage complexes of 3d-metals (clathrochelates)^[1] recently emerged as prospective single molecule magnets (SMM)^[2–4] and paramagnetic probes for magnetic resonance imaging (MRI)^[2,3] is the use of monocapped tripodal ligands^[2–5] pseudo-cross-linked *via* hydrogen bonding by a counterion or by a neutral H-bond acceptor (Scheme 1). The resulting decrease in the ligand field strength compared to macropolycyclic covalent analogues with a quasaromatic cage system (regular clathrochelates)^[1,6] produced high-spin cobalt(II) pseudoclathrochelates^[2–5] that featured a very large axial anisotropy of magnetic susceptibility tensor owing to their unusual trigonal-prismatic (TP, the distortion angle $\varphi = 0^\circ$) coordination geometry.^[7]

Chemical design of these cobalt(II) pseudoclathrochelates is, however, a huge synthetic challenge,^[4] as only a boron capping atom ensures^[1,2] a TP coordination geometry of such complexes; otherwise, they have a trigonal-antiprismatic (TAP, $\varphi = 60^\circ$) geometry^[1,6] unfavourable for their use as SMMs or paramagnetic probes for MRI.^[8] In addition, H-bonded boron-



Scheme 1. Monocapped complexes of the tripodal pseudo-cross-linked *via* hydrogen bonding.

capped 3d-metal pseudoclathrochelates (Scheme 1) are only relatively stable, unlike their macropolycyclic analogues formed by covalent and strong coordination bonds,^[1,6] and can readily exchange pseudocapping H-bonded species (Scheme 2)^[5] or undergo intramolecular cyclization reactions (Scheme 3).^[9] As a result, optimization of the synthetic approaches towards these trigonal-prismatic cobalt(II) complexes requires an insight into side products of their synthesis and their chemical transformations in different media.

Here we report a series of such products, including a binuclear complex (3), a pseudoclathrochelate with a new coordination mode (5) and even a coordination polymer (7) obtained from the same oximes and boronic acids in conventional synthetic procedures of clathrochelate chemistry (Schemes 4–6).

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Conflict of Interest

The authors declare no conflict of interest.

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