Initial use of 1-hydroxybenzotriazole in the chemistry of group 12 metals: An 1D zinc(II) coordination polymer and a mononuclear cadmium(II) complex containing the deprotonated ligand in a novel monodentate ligation mode

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The intense contemporary interest in molecular coordination polymers (also known as metal-organic coordination networks, metal-organic frameworks or organic–inorganic hybrid materials) reflects both the fundamental chemistry of complex materials and practical applications to fields and areas as diverse as catalysis, electrical conductivity, magnetism, optical materials, molecular electronics, medicine, membranes, sensing and zeolitic behaviour [1]. The ultimate goal is the transformation of a number of coordination polymers to materials. Such materials often combine the unique features of the organic and inorganic components giving rise to composite or novel physical properties and providing access to a domain of complex multifunctional materials. Coordination polymers are also significant from a structural chemistry viewpoint with new, intriguing molecular topologies being discovered, as well as providing examples of interesting structural phenomena, e.g. the interpenetration of the networks [2].

The process of building a coordination polymer is principally directed by the coordination bond. From the chemical composition viewpoint, the simplest coordination polymer consists of a metal ion and a deprotonated polyfunctional organic ligand. The use of new, unusual organic ligands towards the synthesis of metal-organic coordination networks is thus of great importance not only for the discovery of compounds with novel structures and interesting physical properties, but also as a means of building up families of related complexes so that structure–property relations can be developed. Recently, polyazaheteroaromatic compounds such as pyrazoles, imidazoles, triazoles and tetrazoles, in their neutral and anionic forms, have been exploited for the construction of complex inorganic–organic architectures [3]. Benzotriazole (btaH, Scheme 1), specifically, is an attractive ligand for the design of coordination polymers because of its ability to bridge multiple metal sites and its facile derivatization to provide bridging ligands with additional functionality. One of the latter ligands is 1-hydroxybenzotriazole (btaOH, Scheme 1). In particular, the 1-hydroxybenzotriazole(−1) ion (btaO−, Scheme 1) [4] is an ideal ligand for the construction of coordination polymers. As a structural building block, btaOH or btaO− may link metal centers through the N1 and N2 positions to provide one-dimensional (1D) and oligomeric secondary building units, which can then be linked through the O atom to expand the dimensionality of the materials. Thus, a rich structural chemistry may evolve from such connectivity. In earlier studies we used the btaO− ligand for the assembly of [CuII(btaO)2(MeOH)]₄ [5a], [MnII(btaO)2(NCS)₄]−...
(DMF)₆ [5b] and [Mn₂(btaO)₂(O₂CMe)₂(MeOH)]₂ [5c] which have 3D, 1D and 2D, respectively, polymeric structures. These complexes, all three reported by our group, are the only coordination polymers possessing the btaO⁻ ligand, the remaining known complexes being polynuclear species (clusters) [6] and one monomer [7]. Encouraged by the 3D structure of [Cu(I)(btaO)₂(MeOH)]₂ [5a], we decided to use btaO⁻ as the exclusive organic ligand in zinc and cadmium chemistry. The initial results of our investigation, which can be considered as continuation of our research efforts on the chemistry and properties of coordination polymers [5,8], are reported in this communication.

Reaction of an aqueous solution (15 ml) of Zn(ClO₄)₂·6H₂O (0.19 g. 0.5 mmol) with two equivalents of btaOK (0.17 g,1.0 mmol) [9] in DMF (20 ml) and storage of the obtained solution at room temperature for three days led to precipitation of colourless, needle-like crystals of [Zn(btaO)₂]ₙ (1; 0.15 g, yield ~80%) [10], see Eq. (1). Complex [Cd(btaO)₂(H₂O)₄]·3H₂O (2·3H₂O) was prepared by the addition of methanolic solution (15 ml) of btaOK·H₂O (0.11 g,0.8 mmol) to an aqueous solution (5 ml) of Cd(O₂CMe)₂·2H₂O (0.11 g,0.4 mmol). Slow evaporation of the resulting solution at room temperature afforded X-ray quality, colourless plates of the product (0.12 g, yield ~65%) [10] within one day, see Eq. (2).

\[
\begin{align*}
n\text{Zn(ClO}_4)_2 \cdot 6\text{H}_2\text{O} + 2\text{Na}_{\text{btaOK}} & \rightarrow [\text{Zn(btaO)}_2]_n + 2\text{NaClO}_4 + 6\text{H}_2\text{O} \\
\text{Cd(O}_2\text{CMe})_2 + 2\text{btaOK} \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} & \rightarrow [\text{Cd(btaO)}_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O} + 2\text{MeCO}_2\text{H}.
\end{align*}
\]

A perspective view of 1 is shown in Fig. 1. Complex 1 crystallizes in the monoclinic space group P2₁/n [11]. The Zn⁰ atoms and the btaO⁻ ligands have assembled to form an one-dimensional (1D) double-stranded chain running parallel to the b-axis. Each Zn⁰ atom is in a distorted tetrahedral coordination environment being surrounded by four btaO⁻ ligands, two of which act as O-donors and two as N-donors through the N3 atom (Scheme 1). In this orientation, the η²:η¹:μ btaO⁻ ligands (2.1100 using Harris notation [12]) in Scheme 2 bridge two Zn¹ atoms in a bend fashion rather than linearly and give rise to the double-stranded chain. The double-stranded chains pack in such a way that two C–H···O hydrogen bonds (and their symmetry related) form and hold the chains together. In this arrangement, each double-stranded chain is connected to four neighboring chains resulting in a pecu (primitive cubic) rod packing (Fig. S1).

Complex 2 crystallizes in the monoclinic space group P2₁/n [11]. An ORTEP drawing of the mononuclear complex [Cd(btaO)₂(H₂O)₄] is shown in Fig. 2. The Cd⁰ atom is in a distorted octahedral environment being surrounded by four H₂O molecules and two terminal btaO⁻ ligands. The btaO⁻ ligands coordinate through the N3 atom adopting the 1.0100 coordination mode (Scheme 2) that has not been observed so far in the coordination chemistry of btaO⁻.

The presence of the terminal H₂O molecules, and the uncoordinated and deprotonated hydroxyl O atom of the btaO⁻ ligands implies the existence of a number of hydrogen bonds around each [Cd(btaO)₂(H₂O)₄] unit. Indeed, each mononuclear complex is surrounded by four other [Cd(btaO)₂(H₂O)₄] complexes forming a total of 16 hydrogen bonds with them. Specifically, the hydrogen bonding involves all the H₂O hydrogen atoms, two H₂O oxygen atoms, the two deprotonated btaO⁻ oxygen atoms and the two uncoordinated btaO⁻ nitrogen atoms (N2 in Scheme 1). In this arrangement, each [Cd(btaO)₂(H₂O)₄] acts as both hydrogen bond donor and hydrogen bond acceptor, donating 8 hydrogen bonds and accepting eight hydrogen bonds from four neighboring mononuclear complexes creating an undulating 2D network running parallel to the bc plane (Fig. 3). The three lattice H₂O molecules are also hydrogen bonded to each other and to the 2D layers, thus connecting them and creating a 3D pattern. Although the lattice H₂O hydrogen atoms were not found from the difference map, it is evidenced by the O···O distances that they form hydrogen bonded zig-zag tapes comprising alternating 6- and 4-membered rings running down the c-axis (Figs. S2 and S3).

Compounds 1 and 2 are the tenth and eleventh, respectively, metal complexes (both Werner- and organometallic-type) containing btaO⁻ ligands, but the first with metals of group 12. Since most of these were reported relatively recently, we felt it timely to collect the metal/btaO⁻ complexes in Table 1, together with the ligand’s coordination modes; the latter are illustrated in Scheme 2. Four are coordination polymers, six are clusters, whereas only 2·3H₂O is a mononuclear complex. The most common coordination mode of bta⁻ is the 2.0110 one observed in five compounds.
The 1.0100 mode found in \( \text{2} / \text{C}1 \text{3H}_2 \text{O} \) is new. It should be mentioned at this point that complex \([\text{Fe(btaOH})_6]\text{(ClO}_4\text{)}_3\), which contains formally neutral btaOH ligands, has also been structurally characterized [7]; the ligands exist as zwitterions (N1 is protonated) exhibiting the 1.100 ligation mode (Scheme 2).

The presence of aqua ligands and lattice H \( \text{2O} \) molecules in \( \text{2} / \text{C}1 \text{3H}_2 \text{O} \) is manifested by a medium, and a strong and broad IR band at 3445 and \( \times 3385 \text{ cm}^{-1} \), respectively. The bands in the 1210–1100 cm\(^{-1}\) region are associated with the \( \nu_\text{as(NNN)} \), \( \nu_\text{s(NNN)} \) and \( \nu_\text{(N–O)} \) vibrational modes [5,6,13], but exact assignments seem impossible. In the spectrum of \( \text{1} \) the band at 1152 cm\(^{-1}\) is assigned to \( \nu_\text{(N–O)} \) [5]. This band has been shifted to a lower wavenumber, i.e. at 1156 cm\(^{-1}\), in the spectrum of \( \text{2} \cdot \text{3H}_2 \text{O} \) where the deprotonated oxygen atom of the btaO\(^-\) ligand is uncoordinated. This, at first glance unusual spectral feature, is attributed to the fact that the deprotonated oxygen atom is hydrogen bonded and it thus can be considered as pseudo coordinated.

Complex \( \text{1} \) is thermally stable under nitrogen up to 300 °C as evidenced by its TG/DTG pattern (Fig. S4) and it decomposes in three steps at about 310, 400 and 560 °C; the mass loss continues above 950 °C (the highest temperature limit of the instrument used). Complex \( \text{2} \cdot \text{3H}_2 \text{O} \) loses moisture and the three lattice H \( \text{2O} \) molecules between room temperature and \( \sim 105 °C \) (Fig. S5). A plateau is reached at about 110 °C up to \( \sim 280 °C \), suggesting that \([\text{Cd(btaO})_2\text{(H}_2\text{O})_3] \text{ (2)} \) is thermally stable. The intermediate \( \text{2} \)
decomposes between 290 and 340 °C, losing the four coordinated H2O molecules. A small plateau is observed between 345 and 360 °C, suggesting that the fully anhydrous species with the empirical formula "Cd(btaO)2" is relatively stable. The formation of the two intermediates is summarized in Eqs. (3a) and (3b).

The photoluminescence properties of solid 1 and 2·3H2O were also studied at room temperature [15]. The salt btaOK exhibits a very weak emission at ~24350 nm upon excitation at 300 nm, attributed to a π* → n transition [16]. Both complexes have almost the same photoluminescence behaviour. Upon maximum excitation at 330 nm, the complexes display photoluminescence with a maximum at 375 (1) and 373 (2·3H2O) nm; the excitation and emission spectra of 2·3H2O are presented in Fig. 4. The most probable origin of the emission is a ligand-to-metal charge transfer transition [15,16].

In summary, the use of btaOH in reactions with ZnII and CdII sources had led to two complexes with interesting structures and properties. An important chemical message of this work is that deprotonated 1-hydroxybenzotriazole can indeed support coordination polymer chemistry (see 1) without requiring the co-presence of ancillary groups. Binary complexes of metal ions, other than ZnII, are not known to date, and it is currently not evident whether such species could be capable of existence. We are studying this matter. Synthetic efforts are also in progress to “activate”

![Fig. 3. View of the intralayer hydrogen bonding pattern in 2. Most carbon atoms and all hydrogen atoms of the btaO ligands have been omitted for clarity.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Coordination modeb</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn3(btaO)2(NCS)2(DMF)2n</td>
<td>3.2100</td>
<td>[5b]</td>
</tr>
<tr>
<td>Mn3(btaO)2(OCMe)2(NeOH)2n</td>
<td>3.1110, 3.2100</td>
<td>[5c]</td>
</tr>
<tr>
<td>Ni3(btaO)2(NH3)n</td>
<td>2.0110</td>
<td>[6b]</td>
</tr>
<tr>
<td>Ni(OH)2(btaO)2(acac)(H2O)n</td>
<td>2.0110, 4.2110</td>
<td>[6c]</td>
</tr>
<tr>
<td>Ni(OH)2(btaO)2(OCMe)2(H2O)2</td>
<td>Py*OH</td>
<td>n</td>
</tr>
<tr>
<td>Cu(btaO)2(MeOH)n</td>
<td>2.1100</td>
<td>[5a]</td>
</tr>
<tr>
<td>Zn(btaO)2)n</td>
<td>2.1100</td>
<td>This work</td>
</tr>
<tr>
<td>Cd(btaO)2(H2O)4</td>
<td>3H2O (2·3H2O)</td>
<td>1.0100</td>
</tr>
<tr>
<td>Os3(CO)10(btaO)</td>
<td>2.0110</td>
<td>[6a]</td>
</tr>
<tr>
<td>Os3(C=NHP)(CO)10(btaO)</td>
<td>2.0110</td>
<td>[6a]</td>
</tr>
<tr>
<td>Os3(C(CH2Ph)(CO)10(btaO)</td>
<td>2.0110</td>
<td>[6a]</td>
</tr>
</tbody>
</table>

a Lattice solvate molecules have been omitted.

b Using Harris notation [12]; see also Scheme 2.

c 1D polymer.

d 2D polymer.

e 3D polymer.

Wavelength (nm)

Photoluminescence (a.u.)

**Fig. 4.** Excitation (emission at 373 nm) (A) and emission (excitation at 330 nm) (B) spectra of solid 2·3H2O at room temperature.
higher bridging capabilities, e.g. $\mu_4$ (the only complex known with a $\mu_4$ btaO$^-$ ligand is cluster $[\text{Ni}_3(\text{OH})_2(\text{btaO})_4(\text{acac})_3(\text{H}_2\text{O})_3]$$^6c$ or $\mu_5$, for btaO$^-$ as a means to get access to 3D coordination polymers.

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Appendix A. Supplementary material

CCDC 704559 and 704560 contain the supplementary crystallographic data for 1 and 2 · 3H$_2$O, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figs. S1–S3 illustrate the packing diagrams of 1 version, at doi:10.1016/j.inoche.2008.11.010.

References


[4] Since the –OH group of 1-hydroxybenzotriazolate is deprotonated, an alternative name for btaO$^-$ would be 1-oxidobenzotriazolate.


[9] Prepared from the reaction of equimolar amounts of btaOH·H$_2$O and KOH in H$_2$O/EtOH; the salt was characterized by elemental analyses, IR and $^1$H NMR spectra.

[10] Satisfactory C, H and N analyses were obtained for 1 and 2 · 3H$_2$O.

[11] Crystallographic data: $\text{C}_3\text{H}_8\text{N}_6\text{O}_2\text{Zn}$, $M = 333.63$, monoclinic, $P_{2}_1/n$, $a = 21.459(14) \AA$, $b = 6.033(4) \AA$, $c = 9.536(6) \AA$, $\beta = 91.60(2)^\circ$, $V = 1234.1(14) \text{Å}^3$, $Z = 4$, $D_c = 1.796 \text{ cm}^{-3}$, $\mu(\text{CuK} \alpha) = 2.924 \text{ mm}^{-1}$, $T = 298 \text{ K}$, 1860 reflections collected, 1747 unique ($R_{\text{int}} = 0.022$), $R_1 = 0.0349$ ($0.0943$) for 1719 observed ($>2\sigma(I)$) reflections. 2 $\text{C}_3\text{H}_8\text{N}_6\text{O}_2\text{Cd}$, $M = 506.74$, monoclinic, $P_{2}_1/n$, $a = 28.245(12) \AA$, $b = 9.901(4) \AA$, $c = 6.596(3) \text{ Å}$, $\beta = 94.893(15)^\circ$, $V = 1938.2(14) \text{ Å}^3$, $Z = 4$, $D_c = 1.716 \text{ cm}^{-3}$, $\mu(\text{MoK} \alpha) = 1.184 \text{ mm}^{-1}$, $T = 298 \text{ K}$, 3703 reflections collected, 3406 unique ($R_{\text{int}} = 0.021$), $R_1 = 0.0334$ ($0.0957$) for 2723 observed ($>2\sigma(I)$) reflections.


[15] The measurements were made by using a Cary Eclipse fluorescence spectrophotometer; the complete study will be presented in the full paper.