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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ABSTRACT

The chemistry of 1-hydroxybenzotriazole (btaOH) with the group 12 metal ions Zn(II) and Cd(II) resulted in the 1D coordination polymer $[Zn(btaO)_2]_n$ (1) and the mononuclear complex $[Cd(btaO)_2(H_2O)_4] \cdot 3H_2O$ ($2 \cdot 3H_2O$), respectively. Polymer 1 forms double-stranded chains which are further supported by weak C–H···O hydrogen bonds resulting in a **pcu** (primitive cubic) rod packing. The mononuclear complexes of 2 form undulating hydrogen bonded layers while the lattice water molecules form 1D hydrogen bonded tapes, comprising 4- and 6-membered rings, within the layers and bridge them to the third dimension. The thermal and optical properties of both compounds are presented. IR data are discussed in terms of the chemical composition of the compounds and the coordination mode of btaO⁻.

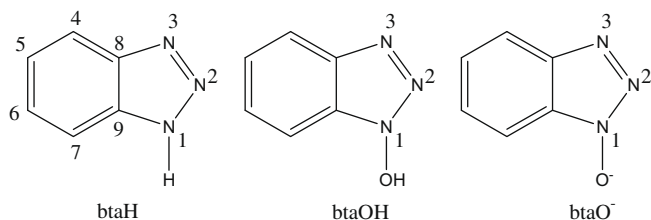© 2008 Elsevier B.V. All rights reserved.

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 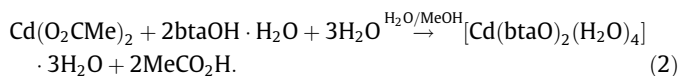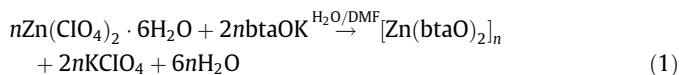simplest coordination polymer consists of a metal ion and a deprotonated polyfunctional organic ligand. The use of new, unusual organic ligands towards the synthesis of metal-organic coordination networks is thus of great importance not only for the discovery of compounds with novel structures and interesting 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 $[Cu^{II}(btaO)_2(MeOH)]_n$ [5a], $[Mn_3^{II}(btaO)_2(NCS)_4$-

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Scheme 1. Structural formulae and abbreviations of the ligands discussed in the text.

$(DMF)_8]_n$ [5b] and $[Mn_3^{II}(btaO)_4(O_2CMe)_2(MeOH)_2]_n$ [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 $[Cu^{II}(btaO)_2(MeOH)]_n$ [5a], we decided to use btaO$^-$ as the *exclusive* organic ligand in zinc and cadimium 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 $Zn(ClO_4)_2 \cdot 6H_2O$ (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 $[Cd(btaO)_2(H_2O)_4] \cdot 3H_2O$ (**2** $\cdot 3H_2O$) was prepared by the addition of methanolic solution (15 ml) of btaOH $\cdot H_2O$ (0.11 g, 0.8 mmol) to an aqueous solution (5 ml) of $Cd(O_2CMe)_2 \cdot 2H_2O$ (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)

$$nZn(ClO_4)_2 \cdot 6H_2O + 2nbtaOK \xrightarrow{H_2O/DMF} [Zn(btaO)_2]_n$$
$$+ 2nKClO_4 + 6nH_2O \tag{1}$$

$$Cd(O_2CMe)_2 + 2btaOH \cdot H_2O + 3H_2O \xrightarrow{H_2O/MeOH} [Cd(btaO)_2(H_2O)_4]$$
$$\cdot 3H_2O + 2MeCO_2H. \tag{2}$$

A perspective view of **1** is shown in Fig. 1. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ [11]. The Zn^{II} atoms and the btaO$^-$ ligands have assembled to form an one-dimensional (1D) double-stranded chain running parallel to the *b*-axis. Each Zn^{II} 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 $\eta^1:\eta^1:\mu$ btaO$^-$ ligands (2.1100 using Harris notation [12] in Scheme 2) bridge two Zn^{II} 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 **pcu** (primitive cubic) rod packing (Fig. S1).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ [11]. An ORTEP drawing of the mononuclear complex $[Cd(btaO)_2(H_2O)_4]$ is shown in Fig. 2. The Cd^{II} atom is in a distorted octahedral environment being surrounded by four H_2O 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 H_2O molecules, and the uncoordinated and deprotonated hydroxyl O atom of the btaO$^-$ ligands implies the existence of a number of hydrogen bonds around each $[Cd(btaO)_2(H_2O)_4]$ unit. Indeed, each mononuclear complex is surrounded by four other $[Cd(btaO)_2(H_2O)_4]$ complexes forming a total of 16 hydrogen bonds with them. Specifically, the hydrogen bonding involves all the H_2O hydrogen atoms, two H_2O oxygen atoms, the two deprotonated btaO$^-$ oxygen atoms and the two uncoordinated btaO$^-$ nitrogen atoms (N2 in Scheme 1). In this arrangement, each $[Cd(btaO)_2(H_2O)_4]$ 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 H_2O molecules are also hydrogen bonded to each other and to the 2D layers, thus connecting them and creating a 3D pattern. Although the lattice H_2O 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** $\cdot 3H_2O$ is a mononuclear complex. The most common coordination mode of bta$^-$ is the 2.0110 one observed in five compounds.
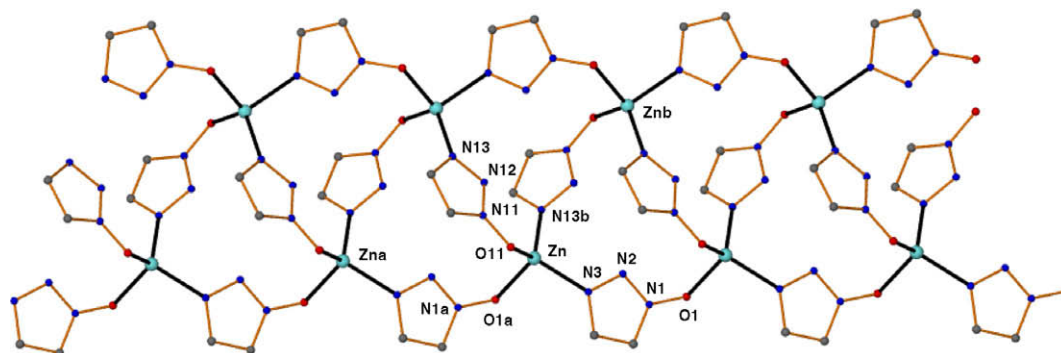

Fig. 1. Perspective view of the double stranded chain of **1**. Most carbon and all hydrogen atoms of the btaO$^-$ ligands have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Zn···Zna 6.033(1), Zn···Znb 5.634(1), Zn–N3 2.006(3), Zn–N13b 1.980(2), Zn–O1a 1.984(2), Zn–O11 1.945(3), O11–Zn–N3 114.77(10), O1a–Zn–O11 106.25(9), O11–Zn–N13b 118.57(9), O1a–Zn–N13b 99.61(9), N3–Zn–N13b 108.01(11), O1a–Zn–N3 99.61(9), O1a–Zn–N13b 107.69(9), Zn–O1a–N1a 118.60(16), Zn–O11–N11 117.21(15). Symmetry code operators *a*: *x*, *y* − 1, *z*; *b*: 3/2 − *x*, 1/2 + *y*, 3/2 − *z*.
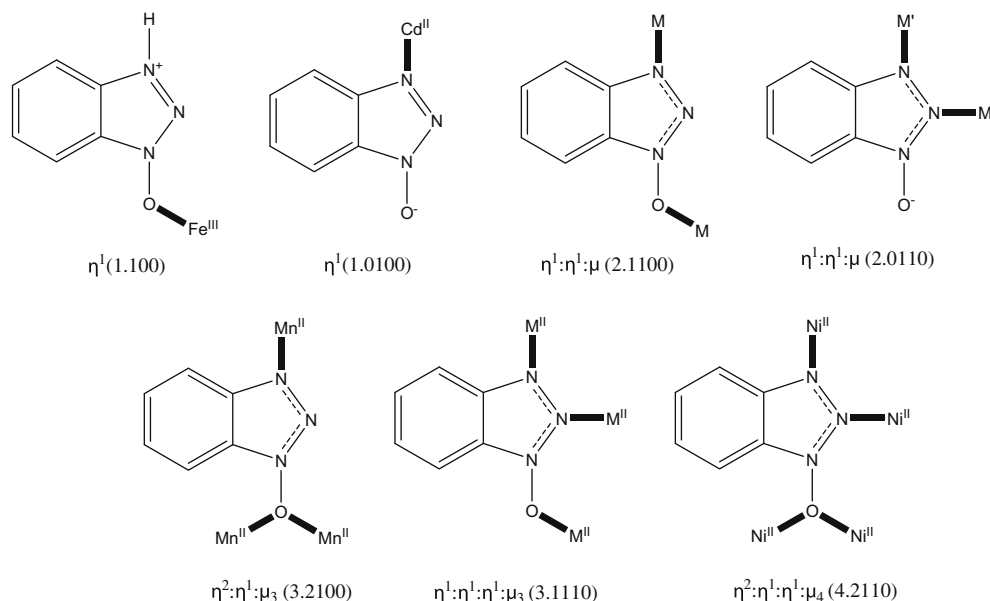
Scheme 2. The up-to-date crystallographically established ligation modes of btaOH (top left) and btaO$^-$ in metal (both Werner-type and organometallic) complexes. M = Cu^{II}, Zn^{II}; M' = Ni^{II}, Os; M'' = Mn^{II}, Ni^{II}. The 1.0100 mode observed in **2** · 3H$_2$O has not been previously reported. The Harris notation [12] for the description of the modes is given in parentheses.

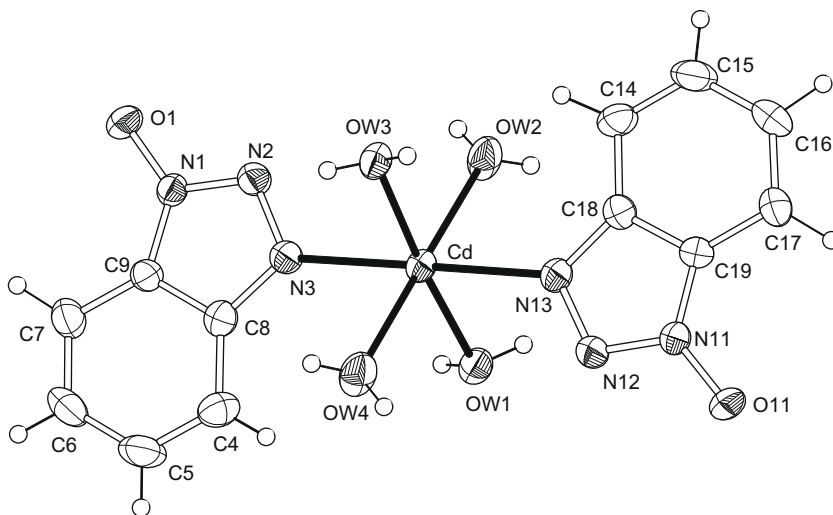**Fig. 2.** ORTEP drawing (50% probability) of **2** showing the coordination environment around the Cd^{II} atom. Selected interatomic distances (Å) and angles (°): Cd–OW1 2.331(3), Cd–OW2 2.285(3), Cd–OW3 2.325(3), Cd–OW4 2.285(3), Cd–N3 2.321(3), Cd–N13 2.325(3), N3–Cd–N13 179.72(11), OW1–Cd–OW3 176.14(10), OW2–Cd–OW4 179.55(14).

The 1.0100 mode found in **2** · 3H$_2$O is new. It should be mentioned at this point that complex [Fe(btaOH)$_6$](ClO$_4$)$_3$, 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$_2$O molecules in **2** · 3H$_2$O is manifested by a medium, and a strong and broad IR band at 3445 and ~3385 cm^{-1}, respectively. The bands in the 1210–1100 cm^{-1} region are associated with the ν_{as}(NNN), ν_s(NNN) and ν(N–O) vibrational modes [5,6,13], but exact assignments seem impossible. In the spectrum of **1** the band at 1152 cm^{-1} is assigned to ν(N–O) [5]. This band has been shifted to a lower wavenumber in the complex compared with its frequency (1192 cm^{-1}) in the IR spectrum of potassium 1-hydroxybenzotriazolate, btaOK; such a shift is normally observed [5] in the complexes where the

deprotonated oxygen is a donor atom, and it is consistent with the literature data [14]. Surprisingly, this mode appears also at a low wavenumber, i.e. at 1156 cm^{-1}, in the spectrum of **2** · 3H$_2$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 **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 **2** · 3H$_2$O loses moisture and the three lattice H$_2$O molecules between room temperature and ~105 °C (Fig. S5). A plateau is reached at about 110 °C up to ~280 °C, suggesting that [Cd(btaO)$_2$(H$_2$O)$_4$] (**2**) is thermally stable. The intermediate **2**
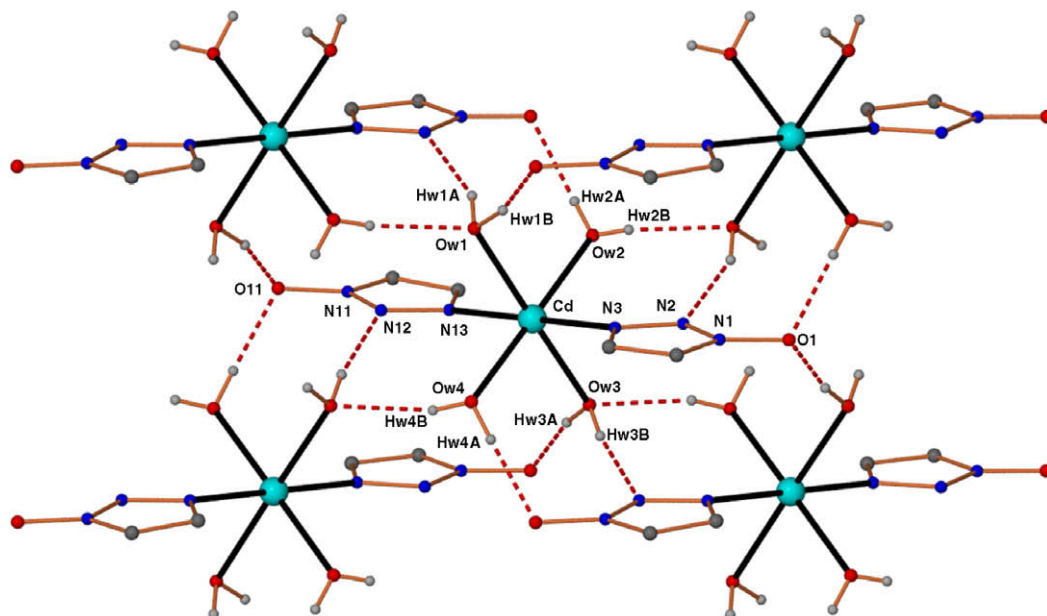
Fig. 3. View of the intralayer hydrogen bonding pattern in **2**. Most carbon atoms and all hydrogen atoms of the btaO⁻ ligands have been omitted for clarity.

Table 1
Formulae and btaO⁻ coordination modes of the structurally characterized metal/1-hydroxybenzotriazole complexes.

Complex[a]	Coordination mode[b]	Ref.
$[Mn_3^{II}(btaO)_2(NCS)_4(DMF)_8]_n$ [c]	3.2100	[5b]
$[Mn_3^{II}(btaO)_4(O_2CMe)_2(MeOH)_2]_n$ [d]	3.1110, 3.2100	[5c]
$[Ni_3(btaO)_6(NH_3)_6]$	2.0110	[6b]
$[Ni_7(OH)_2(btaO)_4(acac)_8(H_2O)_2]$	2.0110, 4.2110	[6c]
$[Ni_{13}(OH)_6(btaO)_{12}(O_2CMe)_8(H_2O)_6(Pr^nOH)_4]$	3.1110	[6d]
$[Cu(btaO)_2(MeOH)]_n$ [e]	2.1100	[5a]
$[Zn(btaO)_2]_n$ [f] (**1**)	2.1100	This work
$[Cd(btaO)_2(H_2O)_4]\cdot 3H_2O$ (**2** · 3H₂O)	1.0100	This work
$[Os_3H(CO)_{10}(btaO)]$	2.0110	[6a]
$[Os_3(C=NHPr^n)(CO)_{10}(btaO)]$	2.0110	[6a]
$[Os_3(C=NCH_2Ph)(CO)_{10}(btaO)]$	2.0110	[6a]

[a] Lattice solvate molecules have been omitted.
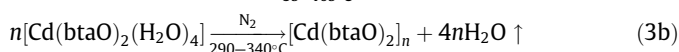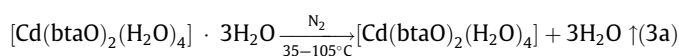[b] Using Harris notation [12]; see also Scheme 2.
[c] 1D polymer.
[d] 2D polymer.
[e] 3D polymer.
[f] 1D polymer.

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 IR spectrum of the completely anhydrous intermediate (obtained after a TG experiment up to 345 °C by keeping the heating rate very low, i.e. 1 °C min⁻¹) is different in the btaO⁻ bands' regions compared with the spectrum of **1**. This may indicate formation of an anhydrous coordination polymer through bridging btaO⁻ ligands with higher (than in **1**) denticity levels. Attempts for the preparation (and subsequent crystallization) of compound "Cd(btaO)₂" from solution have been unsuccessful.

$$[Cd(btaO)_2(H_2O)_4] \cdot 3H_2O \xrightarrow[\text{35–105°C}]{N_2} [Cd(btaO)_2(H_2O)_4] + 3H_2O \uparrow \quad (3a)$$

$$n[Cd(btaO)_2(H_2O)_4] \xrightarrow[\text{290–340°C}]{N_2} [Cd(btaO)_2]_n + 4nH_2O \uparrow \quad (3b)$$

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 ∼350 nm upon excitation at 300 nm, attrib-

uted to a $\pi^* \rightarrow n$ 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 Zn^II and Cd^II 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 Zn^II, 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"
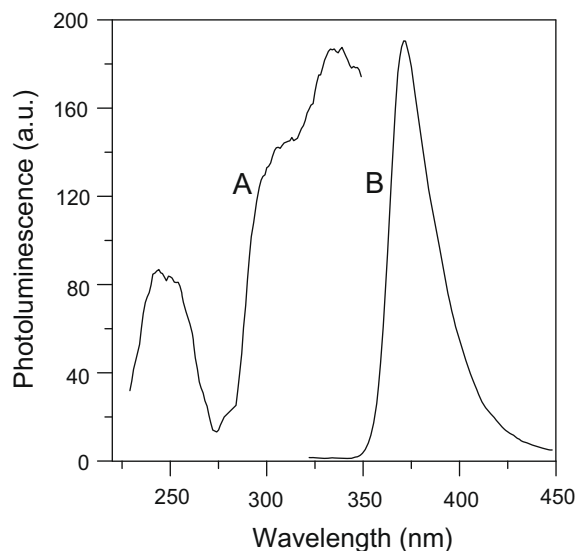

Fig. 4. Excitation (emission at 373 nm) (A) and emission (excitation at 330 nm) (B) spectra of solid **2** · 3H₂O at room temperature.

higher bridging capabilities, e.g. μ_4 (the only complex known with a μ_4 btaO$^-$ ligand is cluster [Ni$_7$(OH)$_2$(btaO)$_4$(acac)$_8$(H$_2$O)$_2$] [6c]) or μ_5, for btaO$^-$ as a means to get access to 3D coordination polymers.

Acknowledgements

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** and **2** · 3H$_2$O, while Figs. S4 and S5 the TG/DTG patterns of **1** and **2** · 3H$_2$O, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.11.010.

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[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: **1**: C$_{12}$H$_8$N$_6$O$_2$Zn, M = 333.63, monoclinic, $P2_1/n$, a = 21.459(14) Å, b = 6.033(4) Å, c = 9.536(6) Å, β = 91.60(2)°, V = 1234.1(14) Å^3, Z = 4, D_c = 1.796 g cm^3, μ(Cu Kα) = 2.924 mm^{-1}, T = 298 K, 1860 reflections collected, 1747 unique (R_{int} = 0.022), R_1 on F (wR_2 on F^2) = 0.0349 (0.0943) for 1719 observed ($I > 2\sigma(I)$) reflections. **2** · 3H$_2$O: C$_{12}$H$_{22}$N$_6$O$_9$Cd, M = 506.74, monoclinic, $P2_1/n$, a = 28.245(12) Å, b = 9.901(4) Å, c = 6.956(3) Å, β = 94.893(15)°, V = 1938.2(14) Å^3, Z = 4, D_c = 1.716 g cm^3, μ(Mo Kα) = 1.184 mm^{-1}, T = 298 K, 3703 reflections collected, 3406 unique (R_{int} = 0.021), R_1 on F (wR_2 on F^2) = 0.0334 (0.0927) for 2723 observed ($I > 2\sigma(I)$) reflections.
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