# Homo- and Heteropentanuclear Coordination Compounds with $T_\mathrm{d}$ Symmetry − the Solid State Structures of [MZn$_4$(L)$_4$(L$'$)$_6$] (M = Co$^\mathrm{II}$ or Zn; L = chloride or acac; L$'$ = 1,2,3-benzotriazolate)

**Shyam Biswas, Markus Tonigold, and Dirk Volkmer***

Ulm/Germany, Ulm University, Institute of Inorganic Chemistry II, Materials and Catalysis

*Dedicated to Professor Gerald Henkel on the Occasion of his 60$^{th}$ Birthday*

**Abstract.** The syntheses of homo- and heteropentanuclear coordination compounds with the molecular formulae [MZn$_4$(L)$_4$(L$'$)$_6$] (M = Co$^\mathrm{II}$ or Zn; L = chloride or acac; L$'$ = 1,2,3-benzotriazolate) are reported. These compounds display a highly symmetric coordination unit consisting of a central metal ion (M = Co$^\mathrm{II}$ or Zn) which is octahedrally coordinated by 6 tridentate benzotriazolate-type ligands via their N(2) donor atom. The benzotriazolate ligands span the edges of an imaginary tetrahedron thus providing four coordination sites at the corners of the tetrahedron, which are then filled by four zinc ions. The coordination shell of the latter are completed by bidentate acetylacetonate (acac) ligands or by chloride anions, respectively.

The solid state structures of two homopentanuclear metal complexes, namely [Zn$_5$(acac)$_4$(bta)$_6$]·4C$_6$H$_{12}$ (**1**) (acacH = acetylacetone; btaH = 1,2,3-benzotriazole), and [Zn$_5$Cl$_4$(Me$_2$bta)$_6$]·2DMF (**2**) (Me$_2$btaH = 5,6-dimethyl-1,2,3-benzotriazole) were determined by single crystal X-ray structure analysis. The heteropentanuclear metal complex [Co$^\mathrm{II}$Zn$_4$Cl$_4$(Me$_2$bta)$_6$]·2DMF (**3**) is isostructural with compound **2**. Compound **1** was synthesized from stoichiometric amounts of Zn(acac)$_2$ and btaH employing dichloromethane as solvent. The synthesis of compound **2** requires addition of an auxiliary base to the DMF solution of anhydrous ZnCl$_2$ and Me$_2$btaH. For compound **3** a stoichiometric ratio of Co(NO$_3$)$_2$·6H$_2$O, anhydrous ZnCl$_2$ and Me$_2$btaH was employed during synthesis. Phase purity of all compounds was proved by X-ray powder diffraction (XRPD) analysis, IR spectroscopy, and elemental analysis. Crystal data: for **1** (C$_{80}$H$_{100}$N$_{18}$O$_8$Zn$_5$): monoclinic, space group $P2_1/c$ with $a = 23.781(5)$ Å, $b = 16.000(3)$ Å, $c = 25.170(5)$ Å, $\beta = 115.29(3)°$, $V = 8659(3)$ Å$^3$, $Z = 4$, $\rho = 1.357$ g cm$^{-3}$. For **2** (C$_{54}$H$_{62}$Cl$_4$N$_{20}$O$_2$Zn$_5$): cubic, space group $Fd\bar{3}m$ with $a = 23.367(3)$ Å, $V = 12759(3)$ Å$^3$, $Z = 8$, $\rho = 1.553$ g cm$^{-3}$. For **3** (C$_{54}$H$_{62}$Cl$_4$CoN$_{20}$O$_2$Zn$_4$): cubic, space group $Fd\bar{3}m$ with $a = 23.443(3)$ Å, $V = 12884(3)$ Å$^3$, $Z = 8$, $\rho = 1.532$ g cm$^{-3}$.

## Introduction

Benzotriazole and its derivatives (Scheme 1) are well-studied corrosion inhibitors for certain metals, particularly copper [1] and its alloys [2]. They are also important tridentate ligands in the field of polynuclear metal complexes and clusters compounds as they can bind to metal ions in a variety of different coordination modes [3]. Focussing our summary on coordination compounds of benzotriazoles with divalent metal ions, a range of pentanuclear metal complexes of the formula [M$_5$(L)$_{4-x}$(OH)$_x$(L$'$)$_6$ (H$_2$O)$_{4x}$] where M = Cu, Ni; L$'$ = bta or Me$_2$bta; L = β-diketonate, $x = 0, 1$] [4] were described in literature. Moreover, a mixed-valent pentanuclear copper [5] and a nonanuclear nickel [6] complex have been reported. Most of these complexes are prepared from solution, employing metal(II) β-diketonates as precursor, thus taking advantage of the proton transfer reaction between metal(II) β-diketonates and benzotriazoles ligands, which leads to a partial replacement of β-diketonato by deprotonated benzotriazole ligands. Our interest in homo- and heteronuclear coordination compounds of the type [MZn$_4$(L)$_4$(L$'$)$_6$] (M = Co$^\mathrm{II}$ or Zn$^\mathrm{II}$; L = chloride or acac; L$'$ = 1,2,3-benzotriazolate) originates from the high molecular symmetry ($T_d$) of the central pentanuclear coordination unit, which, however, constitutes two different coordination sites (Scheme 2): A central, octahedral site and four symmetry equivalent coordination sites, which typically have low coordination numbers (4 or 5). Due to the different coordination motifs of both sites the directed synthesis of heteronuclear metal complexes seems feasible, starting from a stoichiometric ratio of metal salts and btaH ligand. We are especially interested in heteropentanuclear metal complexes where the central, octahedrally coordinated metal ion constitutes a redox-active open-shell d-transition metal ion and the four peripheral coordination sites are filled with Lewis acidic metal ions such as Zn$^\mathrm{II}$.

* Professor Dr. Dirk Volkmer
Ulm University, Institute of Inorganic Chemistry II, Materials and Catalysis
Albert-Einstein-Allee 11
D-89081, Ulm/Germany
Fax: (+)49 (0)731 50-23039
E-mail: dirk.volkmer@uni-ulm.de

These compounds might show interesting bifunctional reactivity, e.g. the combination of (fast) electron transfer coupled to a strong polarisation of coordinated ligands. In this work we show that the synthesis of heteronuclear metal complexes is straight-forward, which are isostructural with the homonuclear counterparts containing zinc ions only. Moreover, by comparative structure analysis we demonstrate that access to the coordination environment of the peripheral zinc ions is relatively free, such that either monodentate or bidentate ligands L can easily bind to the metal ions without distorting the structure of the central $[MZn_4(bta)_6]^{4+}$ moiety.



1H-benzo[d][1,2,3]triazole (btaH)



5,6-dimethyl-1H-benzo[d][1,2,3]triazole (Me₂-btaH)
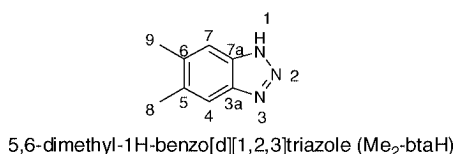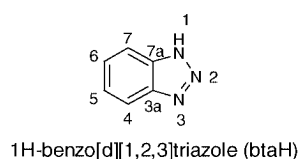
**Scheme 1**  Structures of 1,2,3-triazole ligands used in this work
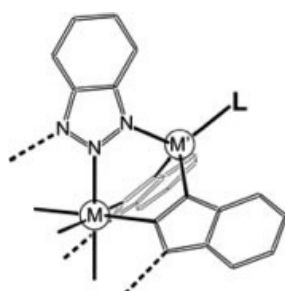


**Scheme 2**  Different coordination sites in pentanuclear coordination units of type $[MZn_4(L)_4(L')_6]$
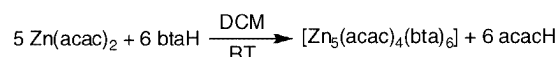
## Results and Discussion

### Syntheses

All metal complexes described here are crystalline and stable in air at ambient conditions. Compound **1** is soluble in chloroform, dichloromethane, DMF, DMSO and even in non-polar solvents such as diethyl ether or benzene. Compounds **2** and **3** are sparingly soluble in solvents such as 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, bromobenzene, xylene, mesitylene or 1-methyl-2-pyrrolidone (NMP).
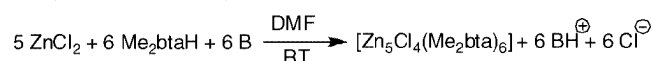
A previously developed synthetic method [4] was employed to synthesize compound **1** whereas a completely different strategy was adopted to prepare compounds **2** and **3**. For the preparation of compound **2**, we employed a stoichiometric ratio of $ZnCl_2$ and Me₂batH (5:6) in DMF in

the presence of a weakly coordinating base (2,6-lutidine) in order to deprotonate the NH group of the benzotriazole ligand. Compound **3** was prepared by the same method except that $Co(NO_3)_2 \cdot 6\ H_2O$ : $ZnCl_2$ : Me₂btaH were used at a stoichiometric ratio of 1:4:6. Compound **2** can also be prepared by a solvothermal approach using an excess of Me₂btaH ligand which can accept the protons liberated from coordinated bta ligands. However, the solvothermal approach was unsuccessful for preparing the heteronuclear complex **3**. All the preparations are summarized in Scheme **3** (B represents the base 2,6-lutidine):
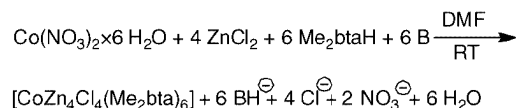
Compound **1**:

$$5\ Zn(acac)_2 + 6\ btaH \xrightarrow[\text{RT}]{\text{DCM}} [Zn_5(acac)_4(bta)_6] + 6\ acacH$$

Compound **2** (method B):

$$5\ ZnCl_2 + 6\ Me_2btaH + 6\ B \xrightarrow[\text{RT}]{\text{DMF}} [Zn_5Cl_4(Me_2bta)_6] + 6\ BH^{\oplus} + 6\ Cl^{\ominus}$$

Compound **3**:

$$Co(NO_3)_2 \times 6\ H_2O + 4\ ZnCl_2 + 6\ Me_2btaH + 6\ B \xrightarrow[\text{RT}]{\text{DMF}}$$

$$[CoZn_4Cl_4(Me_2bta)_6] + 6\ BH^{\oplus} + 4\ Cl^{\ominus} + 2\ NO_3^{\ominus} + 6\ H_2O$$

**Scheme 3**  Chemical equations for the preparation of compounds **1−3**.

### Characterization

Phase purity of all three metal complexes was confirmed by elemental analysis and by X-ray powder diffraction (XRPD). The experimental XRPD patterns are consistent with the simulated ones as gleaned from the single crystal X-ray diffraction data, confirming the phase purity of **1−3**. The FT-IR spectrum of compound **1** is dominated by strong absorption attributable to the bidentate oxygen chelate and contains strong absorption bands between ca. 1500 to 1600 cm$^{-1}$ attributable to C=C and C=O stretching modes [7]. The coordinated bta ligand in compound **1** shows absorption bands at ca. 991 and 1195 cm$^{-1}$ which are assigned to C−H out-of-plane bending vibrations and vibrations involving both triazole ring breathing and C−H in-plane bending, respectively [8]. Similar values are found for compounds **2** and **3** at ca. 1001 and 1202 cm$^{-1}$ due to the coordinated Me₂bta. The IR spectra of the isostructural compound **2** and **3** are almost similar as expected.

TGA/IR analysis reveals that compounds **2** and **3** contain 2 DMF molecules per formula unit. A weight loss of 12 % in the range of 190 − 320 °C for **2** is due to the loss of two DMF molecules per cluster (expected: 10 %), and no further weight loss occurs below 490 °C. Compound **2** decomposes in the temperature range of 490 − 590 °C. Cluster **3** shows the same thermal behaviour as found for **2**.

An EDX measurement performed on compound **3** shows that the relative ratio of Co:Zn is 1:4.1, which closely matches the theoretical ratio (1:4.0).

The UV/Vis spectra of **2** and **3** display absorption bands in the UV region at around 26316 (380 nm) and 28248 (354 nm) cm$^{-1}$, which correspond to the intraligand n→π* and π→π* transitions, respectively [9]. In addition, compound **3** also exhibits well-developed bands in the range of 9000−25000 cm$^{-1}$ (Fig. 1) owing to the d−d transitions of Co$^{II}$ [10].
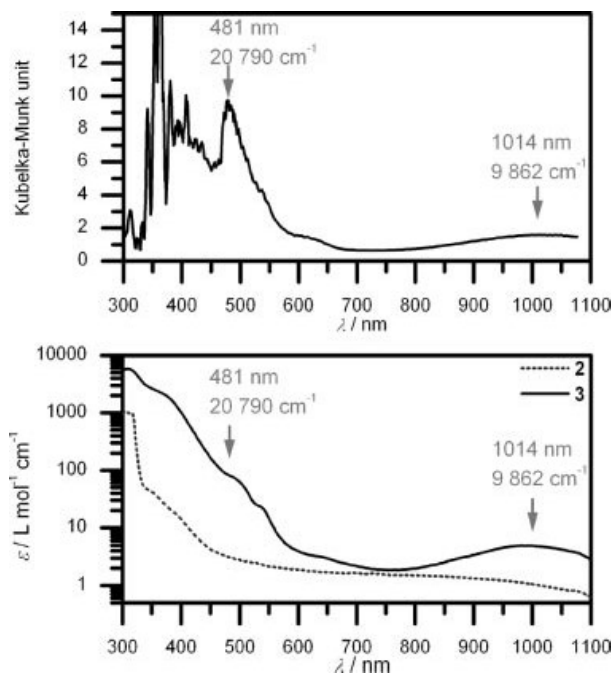


**Figure 1** Top: UV/Vis diffuse reflectance spectrum (DRS) (calculated via the Kubelka-Munk function) for **3**. Bottom: UV/Vis spectra for solutions of **2** and **3** in NMP.

Compound **3**, which contains an octahedrally coordinated Co$^{II}$ ion, shows one main absorption band in the visible region (at 20790 cm$^{-1}$, 481 nm), as well as one weak and broad absorption in the red end of the visible region (at 9862 cm$^{-1}$, 1014 nm), which can be attributed to the spin allowed transitions from $^4T_{1g}(F)$ to $^4T_{1g}(P)$ ($\nu_3$) and to $^4T_{2g}(F)$ ($\nu_1$), respectively. The $\nu_3$ transition of **3** is observable only as a small shoulder of the aromatic region in 1-methyl-2-pyrrolidone (NMP) solution (Figure 1, bottom). The assignment of this shoulder to the $\nu_3$ transition is verified by comparision with the spectrum of **2** as well as with the UV/Vis diffuse reflectance spectrum (DRS) of **3** (Figure 1, top). The values of $Dq$ (1080 cm$^{-1}$) and $B$ (800 cm$^{-1}$) which have been estimated from these transitions are typical for six-coordinate octahedral Co$^{II}$ complexes [10]. All the spectral data mentioned above provide substantial evidence for the fact that the Co$^{II}$ atom is octahedrally coordinated in the present cluster structure. Based on UV/Vis spectroscopic data, even a partial replacement of the four tetrahedrally coordinated Zn ions by Co ions might be ruled out, since tetrahedrally coordinated Co$^{II}$ atoms would become immediately apparent in the UV/Vis spectra, due to their much more intense („Laporte allowed") absorption bands (typically by a factor between 10 and 50 for similar sets of ligands). Thus, in the X-ray structure analysis of compound **3**, the tetrahedral coordination sites are exclusively occupied by zinc ions.

## Crystal Structures

X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$, whereas **2** and **3** both crystallize in the cubic space group $Fd\bar{3}m$. In the pentanuclear zinc complexes **1** and **2**, six benzotriazole ligands are coordinated monodentately to the central Zn ion. The six benzotriazole ligands span a Cartesian coordinate system (Scheme 2) with the Cartesian axes running through the octahedral metal ion at the origin and the N(2) atoms of the coordinated ligands. The bta ligands are twisted around their coordinative bond to the central metal ion such that the nitrogen atoms are placed on the edges of an imaginary tetrahedron. At the corners of this tetrahedron are placed four additional Zn ions which are coordinated to the N(1) and N(3) donor atoms of the bta ligands (Fig. 2).
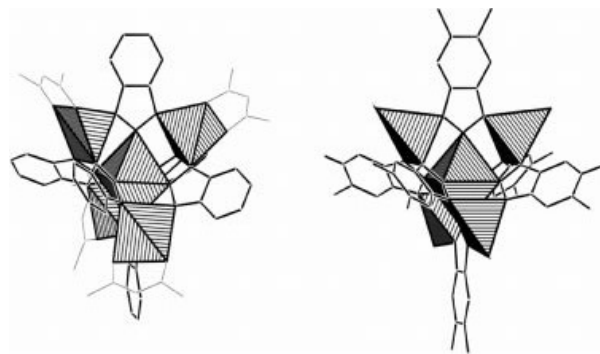


**Figure 2** Wire models of the pentanuclear coordination compounds **1** (left) as well as **2** or **3** (right). Coordination spheres of the metal ions are represented as polyhedrons. Hydrogen atoms are omitted for clarity.

The coordination of the peripheral zinc ions is quite flexible: Fivefold coordination due to the bidentate acetylacetonate ligand in **1**, fourfold coordination leading to a distorted tetrahedral coordination environment, due to the monodentate chloride ligand, such as in the crystal structures of **2** and **3**.

In **1**, the acetylacetonate ligand bound to the peripheral Zn ions leads to a reduction of molecular symmetry ($C_1$ instead of $T_d$) since the local five-fold coordination motif of the peripheral zinc ions is incompatible with the high local symmetry of the [Zn$_5$(bta)$_6$]$^{4+}$ coordination unit. Using monodentate chloride ligands, the pentanuclear coordination units in compounds **2** or **3** assume $T_d$ point group symmetry. Noteworthy, within the crystal lattice the atoms of **2** (and **3**, respectively) occupy special positions, such that the asymmetric unit in the cubic space group $Fd\bar{3}m$ contains only the minimum subset (= 9) of atoms required for a complete representation of a pentanuclear metal complex containing six Me$_2$bta ligands (75 atoms for each compound, excluding hydrogen atoms).

**Table 1** Single-crystal data and refinement summary for complexes **1**−**3**.

| Complex | 1 | 2 | 3 |
|---|---|---|---|
| Formula | $C_{80}H_{100}N_{18}O_8Zn_5$ | $C_{54}H_{62}Cl_4N_{20}O_2Zn_5$ | $C_{54}H_{62}Cl_4Co$ $N_{20}O_2Zn_4$ |
| Formula mass | 1768.63 | 1491.89 | 1485.45 |
| $T/K$ | 190(2) | 193(2) | 293(2) |
| $\lambda/\text{Å}$ | 0.71073 | 0.71073 | 0.71073 |
| Crystal dimensions/mm | 0.37x0.37x0.37 | 0.23x0.23x0.31 | 0.23x0.31x0.38 |
| Crystal system | monoclinic | cubic | cubic |
| Space group | $P2_1/c$ | $Fd\bar{3}m$ | $Fd\bar{3}m$ |
| $a/\text{Å}$ | 23.781(5) | 23.367(3) | 23.443(3) |
| $b/\text{Å}$ | 16.000(3) | | |
| $c/\text{Å}$ | 25.170(5) | | |
| $\beta/°$ | 115.29(3) | | |
| $V/\text{Å}^3$ | 8659(3) | 12759(3) | 12884(3) |
| $Z$ | 4 | 8 | 8 |
| $D_c/\text{g cm}^{-3}$ | 1.357 | 1.553 | 1.532 |
| $M/\text{mm}^{-1}$ | 1.427 | 2.077 | 1.942 |
| $F(000)$ | 3680 | 6080 | 6056 |
| $\theta$ Range/° | 2.01−25.99 | 2.47−25.93 | 2.46−25.93 |
| Measured reflections | 67610 | 22859 | 24619 |
| Independent reflections | 16887 | 645 | 647 |
| Data/restraints/parameters | 16887 / 42 / 985 | 645 / 0 / 43 | 647 / 0 / 43 |
| $R_1$ $(I > 2\sigma(I))$ [a] | 0.0462 | 0.0567 | 0.0659 |
| $wR_2$ (all data) [b] | 0.1111 | 0.2090 | 0.2274 |
| Goodness-of-fit on $F^2$ | 0.828 | 1.181 | 1.274 |
| $\Delta\rho_{max, min}/\text{e Å}^{-3}$ | 0.486, −0.340 | 2.639, −0.714 | 2.852, −0.427 |

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. [b] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{1/2}$.

**Table 2** Selected bond lengths/Å and angles/° of **2**.

| | | | |
|---|---|---|---|
| Zn(1)−N(2) | 2.183(7) | N(2)−Zn(1)−N(2)#2 | 180.000(1) |
| Zn(2)−N(1) | 2.024(5) | N(1)−Zn(2)−N(1)#3 | 99.56(18) |

**Table 3** Selected bond lengths/Å and angles/° of **1**.

| | | | |
|---|---|---|---|
| Zn(1)−N(14) | 2.159(3) | Zn(2)−N(1) | 2.074(4) |
| Zn(1)−N(8) | 2.177(3) | Zn(2)−N(9) | 2.022(3) |
| Zn(1)−N(11) | 2.187(3) | Zn(2)−N(15) | 2.100(3) |
| Zn(1)−N(17) | 2.203(3) | N(14)−Zn(1)−N(11) | 173.33(12) |
| Zn(1)−N(5) | 2.210(3) | N(8)−Zn(1)−N(17) | 174.53(12) |
| Zn(1)−N(2) | 2.221(3) | N(5)−Zn(1)−N(2) | 176.34(13) |

In **2** the octahedrally coordinated Zn atom, Zn(1), shows a Zn−N distance of 2.18 Å, and the tetrahedrally coordinated Zn atom shows a Zn−N distance of 2.02 Å. (Table 2 and Figure 3). These values are in good agreement to other Zn triazolate complexes (1.98−2.05 Å for tetrahedral coordination, 2.14−2.22 Å for octahedral coordination) [11]. In compound **1**, the binding of the bidentate acetylacetonate ligand leads to slightly larger Zn−N bond distances for the four exterior Zn ions (Zn(2)−N distances ranging from 2.16 − 2.22 Å) if compared with **2**. Furthermore, varying bond distances for the central, octahedrally coordinated Zn ion and a distortion from ideal octahedral coordination symmetry occurs in compound **1** (Table 3 and Figure 4).

The packing of **2** and **3** in the highly symmetric space group $Fd\bar{3}m$ is shown in Fig. 5.

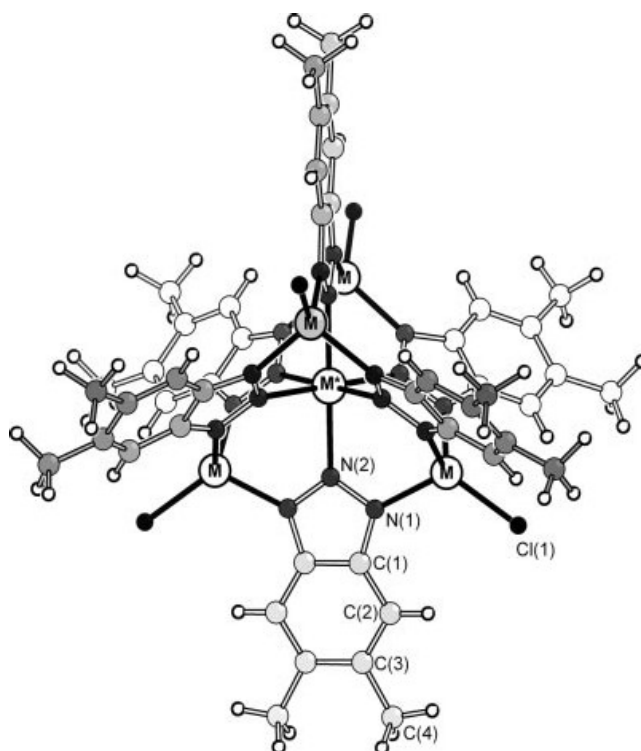No change in atom distances and bond angles occurs when the octahedral coordinated Zn ion in **2** is replaced by



**Figure 3** Ball-and-stick model of the pentanuclear metal complexes **2** and **3**. M* = M = Zn$^{II}$ for **2**, M* = Co$^{II}$, M = Zn$^{II}$ for **3**.
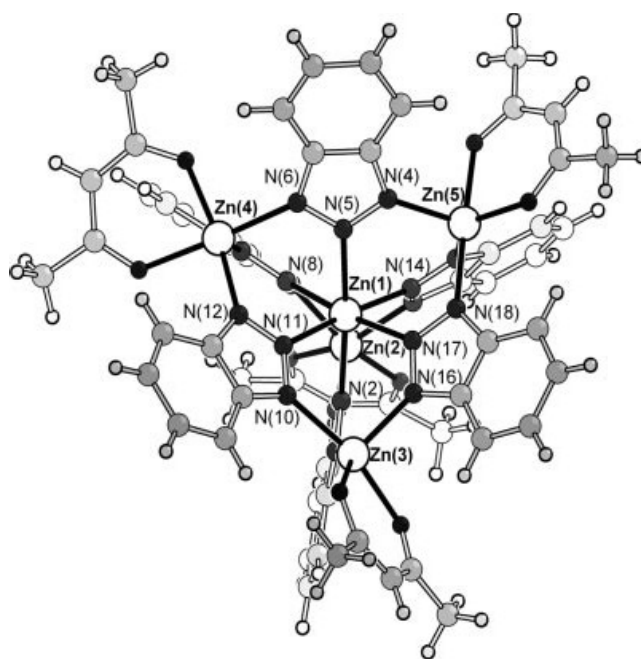


**Figure 4** Ball-and-stick model of the pentanuclear metal complex **1**.

a Co$^{II}$ ion, as found in the crystal structure of **3** (Table 4 and Figure 3).

The observed $\mu_3$-bridging coordination of deprotonated benzotriazoles was previously documented for copper
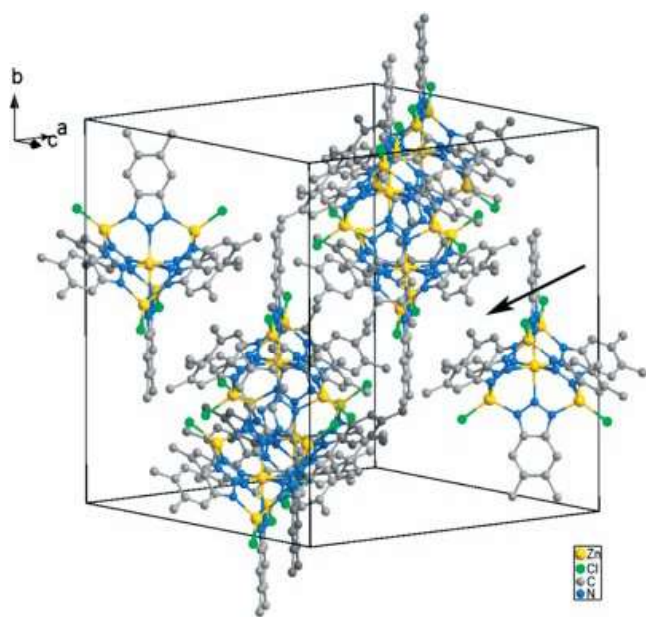
**Figure 5** Packing diagram of **2**. The metal complexes are closely packed in a way such that interdigitation of benzene moities between adjacent coordination units occurs. The black arrow points to a void region in the crystal lattice which contains a DMF molecule (Hydrogen atoms are omitted for clarity).

**Table 4** Selected bond lengths/Å and angles/° of **3**.

| | | | |
|---|---|---|---|
| Co(1)−N(2) | 2.177(8) | N(2)−Co(1)−N(2)#2 | 180.000(1) |
| Zn(1)−N(1) | 2.022(5) | N(1)−Zn(1)−N(1)#3 | 99.69(19) |

[4a−d, 5], thallium(I) [12], nickel [4e−f, 6] and $M^{III}$ (M = Fe, Cr, V) [3] complexes. Pentanuclear cluster built by six triazole ligands (as present in **1-3**) are known to literature only for copper complexes [4a−d, 5]. Compounds **1** and **2** are the first examples of this coordination mode in zinc chemistry.

## Experimental Section

### Materials and Methods

All starting materials were of reagent grade and used as received from the commercial supplier. Fourier transform infrared (FTIR) spectra were recorded from KBr pellets in the range $4000-400$ cm$^{-1}$ on a Bruker IFS FT-IR spectrometer. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br). UV/Vis diffuse reflectance spectra (DRS) were recorded on an Analytik Jena Specord 50 UV/Vis spectrometer in the range of $190-1100$ nm and converted into normal absorption spectra with the Kubelka−Munk function [13]. The lamps change at 320 nm and the mirrors change at 370, 400, 700 and 900 nm. UV/Vis spectra of solutions were measured in the range of $300-1100$ nm using $2.0 \times 10^{-3}$ (M) solutions of compound **2** and **3** in 1-methyl-2-pyrrolidone (NMP). Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed with a TGA/

SDTA851 Mettler Toledo analyzer in a temperature range of $25-800$ °C in flowing nitrogen at a heating rate of 10 °C min$^{-1}$. X-Ray powder diffraction (XRPD) patterns were measured using a Panalytical X'Pert Pro powder diffractometer operated at 40 kV, 40 mA for Cu target ($\lambda = 1.5406$ Å) with a scan speed of 30 s step$^{-1}$ and a step size of 0.008°. The simulated powder patterns were calculated using single-crystal X-ray diffraction data. Energy dispersive X-ray analysis (EDX) was performed on an EDAX (Phönix) X-ray detection system with 30 mm$^2$ SUTW window.

**Safety Note!** *Benzotriazoles and benzotriazolate complexes are potentially explosive, and caution should be exercised when dealing with such derivatives.* However, the small quantities used in this study were not found to present a hazard.

### Synthesis of [Hexakis(μ₃-Benzotriazolato)-tetrakis(2,4-pentanedionato)-penta-zink(II) cyclohexane solvate (1)

To a suspension of Zn(acac)$_2$ (0.264 g, 1.00 mmol) in 70 mL dichloromethane was added a solution of btaH (0.143 g, 1.20 mmol) in 10 mL dichloromethane. The mixture becomes clear within 5 minutes of stirring at room temperature. Stirring was continued for 1 h and the solution was kept at room temperature in an open vial. After evaporation of the solvent, the residue (0.283 g) was dissolved in cyclohexane (25 mL) and the solution was left to evaporate slowly at room temperature. Having reduced the volume of the solution by 50 %, colorless brick-like crystals of **1** were obtained within a week. They were filtered off and dried in vacuum to yield 0.102 g (0.057 mmol, 29 %). No melting point. Elemental analysis calcd. for $Zn_5C_{80}H_{100}N_{18}O_8$ (%): C, 54.53; H, 5.72; N, 14.31; Found: C, 54.09; H, 5.60; N, 14.35.

**¹H NMR** (400 MHz, CDCl$_3$, 25 °C, ppm): δ 8.08 (dd, 12H, PhH, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 3.03 Hz), 7.29 (dd, 12H, PhH, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 3.03 Hz), 5.82 (s, 4H, C=O−CH), 2.11 (s, 24H, CH$_3$−C=O), 1.45 (s, 41H, CH$_2$). **IR** (KBr, cm$^{-1}$): 3446 (br), 3071 (m), 3053 (sh), 2959 (w), 2919 (s), 2357 (br), 1947 (w), 1825 (w), 1600 (vs), 1515 (vs), 1393 (vs), 1261 (s), 1195 (vs), 1147 (w), 1015 (m), 991 (w), 922 (s), 850 (w), 784 (s), 748 (vs), 693 (w), 642 (m), 554 (s), 430 (w).

### Synthesis of Hexakis(μ₃-5,6-Dimethyl-benzotriazolato)-tetrachloro-penta-zinc(II) dimethylformamide solvate (2)

**Method A:** A mixture of anhydrous ZnCl$_2$ (0.028 g, 0.20 mmol) and Me$_2$btaH (0.123 g, 0.83 mmol) was dissolved in 4 mL of DMF and the solution was placed in a heating tube (10 mL). The tube was sealed and heated at 120 °C for 20 h, then cooled to room temperature. The supernatant was removed and the remaining crystals were washed with DMF (3 × 1 mL) and dried in air to yield 25 mg **2** (0.018 mmol, 46 %) as colorless octahedral crystals.

**Method B:** A mixture of anhydrous ZnCl$_2$ (0.050 g, 0.37 mmol) and Me$_2$btaH (0.065 g, 0.44 mmol) was placed in a small vial (5 mL) and dissolved in 3 mL DMF. The vial was then placed in a larger vial (30 mL) containing 6 mL DMF and 78 µL 2,6-lutidine. The larger vial was sealed and left undisturbed for 3 days. The resulting colorless octahedral crystals were collected by filtration, washed with DMF (3 × 1 mL), and dried in air to yield 37 mg **2** (0.027 mmol, 38 %). No melting point, decomposition at 490 °C. Elemental analysis calcd. for $C_{54}H_{62}Cl_4N_{20}O_2Zn_5$ (%): C, 43.72; H, 4.21; N, 18.89; Found: C, 43.35; H, 4.22; N, 18.74.

**¹H NMR** (400 MHz, bromobenzene-$d_5$, 25 °C, ppm): δ 8.73 (s, 12H, PhH), 8.08 (s, 2H, CHO), 2.84 (s, 12H, CH₃), 2.64 (s, 12H, CH₃), 2.43 (s, 36H, CH₃). **IR** (KBr, cm⁻¹): 3055 (w), 2984 (s), 2958 (sh), 2923 (m), 2862 (m), 2376 (w), 1683 (vs), 1573 (m), 1492 (w), 1455 (vs), 1378 (m), 1295 (w), 1257 (w), 1202 (vs), 1168 (s), 1083 (m), 1061 (w), 1028 (w), 1001 (s), 850 (vs), 830 (sh), 723 (w), 656 (w), 576 (w), 498 (s), 468 (s), 434 (m), 412 (w).

## Synthesis of Hexakis(μ₃-5,6-Dimethyl-benzotriazolato)-tetrakis(chloro-zinc(II))-cobalt(II)dimethylformamide solvate (3)

A mixture of Co(NO₃)₂×6 H₂O (0.032 g, 0.10 mmol), anhydrous ZnCl₂ (0.060 g, 0.44 mmol) and Me₂btaH (0.097 g, 0.65 mmol) was placed in a small vial and dissolved in 4 mL DMF. The vial was placed in a larger vial (30 mL) containing 8 mL DMF and 115 µL 2,6-lutidine. The larger vial was sealed and left undisturbed for 4 days. The resulting orange octahedral crystals were collected by filtration, washed 3 times with 1 mL DMF and dried in air to yield 39 mg **3** (0.029 mmol, 34 %). No melting point, decomposition at 490 °C. Elemental analysis calcd. for C₅₄H₆₂Cl₄CoN₂₀O₂Zn₄ (%): C, 43.87; H, 4.23; N, 18.96; Found: C, 43.94; H, 4.37; N, 18.97.

**IR** (KBr, cm⁻¹): 3437 (br), 3055 (w), 2982 (s), 2947 (sh), 2924 (m), 2857 (m), 2375 (w), 1683 (vs), 1573 (m), 1491 (w), 1456 (vs), 1379 (m), 1296 (w), 1258 (w), 1202 (vs), 1169 (s), 1085 (m), 1062 (w), 1027 (w), 1001 (s), 852 (vs), 831 (sh), 723 (w), 658 (w), 577 (w), 499 (s), 470 (s), 437 (w).

## X-ray crystallography

Single-crystal X-ray diffraction data were collected on a STOE IPDS diffractometer employing monochromated Mo-Kα radiation (λ = 0.71073). Initial structures were solved by direct methods and refined by full-matrix least-squares techniques based on $F^2$ using the SHELXL-97 program [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined using a riding model. For **2** and **3**, the residual electron density (< 2.9 e⁻ Å³) could not be refined, due to the strong disorder of occluded solvent molecules. Any attempts to localize the positions of solvent molecules in space groups of lower symmetry were unsuccessful. Using the program PLATON/SQUEEZE [15], we found 16 voids in the unit cell with a volume of 145 Å³ each, which might each contain a single DMF molecule (129 Å³ calculated from the density of DMF at room temperature (0.94 g cm⁻³, and molecular mass of 73.1 g/mol)). This number is equivalent to 2 DMF molecules per formula unit, in accordance to the TGA/IR and elemental analysis. Details of data collection and refinement of the compounds are summarized in Table 1. Selected bond lengths and angles are given in Table 2−4.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre with CCDC-695902 (compound **1**), CCDC-695903 (compound **2**) and CCDC-695904 (compound **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (Fax:(+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

## Conclusions

The work here clearly illustrates that the use of benzotriazoles is a versatile synthetic strategy for the formation of heteropolynuclear metal complexes. We demonstrate the existence of μ₃-bridging mode of binding of benzotriazol-

ates in Zn coordination chemistry. The synthetic strategy used to prepare complex **2** shows that the preparation of polynuclear coordination compounds of benzotriazoles with divalent metal ions is not restricted to the use of metal(II) β-diketonates as starting materials; pentanuclear metal complexes can likewise easily be prepared from metal(II) halides, provided that auxiliary base is added to the reaction mixture. Moreover, we have successfully prepared the heteropentanuclear metal complex (**3**) in which an open shell d⁷ metal ion (= Co^II) replaces the central octahedrally coordinated zinc ion in the structure of compound **2**. We could not find any indication for a mixed distribution of metal ions at the two different coordination sites in compound **3**, which can be rationalized in terms of the huge differences of ligand-field stabilisation energy if Co^II ions are placed in octahedral or tetrahedral coordination sites, respectively. Based on these findings it can be assumed that a huge variety of heteronuclear metal complexes isostructural with compound **3** could be prepared. Such compounds might display interesting combinations of useful properties such as luminescence *and* fast ligand exchange (useful in photocatalysis), or reversible electron transfer *and* Lewis acid activation of coordinated substrates (useful in bifunctional catalysis). Investigations in these directions are currently performed in our group and will be reported in due course.

## References

[1] I. Dugdale, J. B. Cotton, *Corros. Sci.* **1963**, *3*, 69−74.

[2] D. Chadwick, T. Hashemi, *Corros. Sci.* **1978**, *18*, 39−51.

[3] a) D. Collison, E. J. L. McInnes, E. K. Brechin, *Eur. J. Inorg. Chem.* **2006**, 2725−2733; b) J. Tabernor, L. F. Jones, S. L. Heath, C. Muryn, G. Aromí, J. Ribas, E. K. Brechin, D. Collison, *Dalton Trans.* **2004**, 975−976; c) R. H. Laye, Q. Wei, P. V. Mason, M. Shanmugam, S. J. Teat, E. K. Brechin, D. Collison, E. J. L. McInnes, *J. Am. Chem. Soc.* **2006**, *128*, 9020−9021; d) L. F. Jones, E. K. Brechin, D. Collison, A. Harrison, S. J. Teat, W. Wernsdorfer, *Chem. Commun.* **2002**, 2974−2975; e) L. F. Jones, G. Rajaraman, J. Brockman, M. Murugesu, J. Raftery, S. J. Teat, W. Wernsdorfer, G. Christou, E. K. Brechin, D. Collison, *Chem. Eur. J.* **2004**, *10*, 5180−5194; f) L. F. Jones, E. K. Brechin, D. Collison, J. Raftery, S. J. Teat, *Inorg. Chem.* **2003**, *42*, 6971−6973; g) L. F. Jones, J. Raftery, S. J. Teat, D. Collison, E. K. Brechin, *Polyhedron* **2005**, *24*, 2443−2449; h) R. Shaw, R. H. Laye, L. F. Jones, D. M. Low, C. Talbot-Eeckelaers, Q. Wei, C. J. Milios, S. Teat, M. Helliwell, J. Raftery, M. Evangelisti, M. Affronte, D. Collison, E. K. Brechin, E. J. L. McInnes, *Inorg. Chem.* **2007**, *46*, 4968−4978; i) D. M. Low, L. F. Jones, A. Bell, E. K. Brechin, T. Mallah, E. Riviére, S. J. Teat, E. J. L. McInnes, *Angew. Chem., Int. Ed.* **2003**, *42*, 3781−3784.

[4] a) M. Murrie, D. Collison, C. D. Garner, M. Helliwell, P. A. Tasker, S. S. Turner, *Polyhedron* **1998**, *17*, 3031−3043; b) J. H. Marshall, *Inorg. Chem.* **1978**, *17*, 3711−3713; c) J. Handley, D. Collison, C. D. Garner, M. Helliwell, R. Docherty, J. R. Lawson, P. A. Tasker, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1036−1038; d) W. Jinling, Y. Ming, Y. Yun, Z. Shuming, M. Fangming, *Chinese Science Bulletin* **2002**, *47*, 890−893;

e) E. G. Bakalbassis, E. Diamontopoulou, S. P. Perlepes, C. P. Raptopoulou, V. Tangoulis, A. Terzis, T. F. Zafiropoulos, *J. Chem. Soc., Chem. Commun.* **1995**, 1347−1348; f) V. Tangoulis, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassis, E. Diamontopoulou, S. P. Perlepes, *Inorg. Chem.* **1998**, *37*, 3142−3153.

[5] a) V. L. Himes, A. D. Mighell, A. R. Siedle, *J. Am. Chem. Soc.* **1981**, *103*, 211−212; b) G. F. Kokoszka, J. Baranowski, C. Goldstein, J. Orsini, A. D. Mighell, V. L. Himes, A. R. Siedle, *J. Am. Chem. Soc.* **1983**, *105*, 5627−5633.

[6] V. Tangoulis, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassis, E. Diamontopoulou, S. P. Perlepes, *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 463−472.

[7] K. Nakamoto in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 2nd ed., Wiley Interscience, New York, 1970, pp. 249.

[8] J. Rubim, I. G. R. Gutz, O. Sala, W. J. Orville-Thomas, *J. Mol. Struct.* **1983**, *100*, 571−583.

[9] A. Gilbert and J. Baggott, in *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, FL, 1991, pp. 87−89.

[10] a) A. B. P. Lever, in *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company, Amsterdam, 1968, ch. 9, pp. 317−349; b) The *Dq* and *B* values were estimated by using the transition energy ratio diagrams on pp. 393−400 of the same book as in ref. 10*a*.

[11] a) I. Sotofte, K. Nielsen, *Acta Chem. Scand. A* **1981**, *35*, 739−745; b) R.-F. Hu, J. Zhang, Y. Kang, Y.-G. Yao, *Inorg. Chem. Commun.* **2005**, *8*, 828−830; c) W. S. Sheldrick, P. Bell, *Z. Naturforsch.* **1986**, *41b*, 1117−1122; d) X. Meng, Y. Song, H. Hou, Y. Fan, G. Li, Y. Zhu, *Inorg. Chem.* **2003**, *42*, 1306−1315; e) F. Jian, H. Xiao, P. Sun, *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2004**, *60*, m38−m39; f) Z. An, H. Sun, R.-S. Wang, *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2005**, *61*, m-2157−2159; g) A.-H. Yuan, H. Zhou, *Acta Crystallogr, Sect. E: Struct. Rep. Online* **2004**, *60*, m1565−1567; h) Y.-C. Shen, Z.-J. Li, J.-K. Cheng, Y.-Y. Qin, Y.-G. Yao, *Inorg. Chem. Commun.* **2007**, *10*, 888−890.

[12] J. Reedijk, G. Roelofsen, A. R. Siedle, A. L. Spek, *Inorg. Chem.* **1979**, *18*, 1947−1951.

[13] W. W. Wendlandt, H. G. Hecht, in *Reflectance Spectroscopy*, Interscience Publishers/John Wiley & Sons, New York, 1966.

[14] G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

[15] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7−13.