Linkage Isomerism in Bis[hydrotris(1,2,4-triazolyl)borato]zinc from a Molecular Chelate Complex to a Three-dimensional Co-ordination Polymer†

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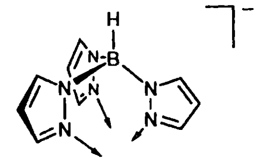
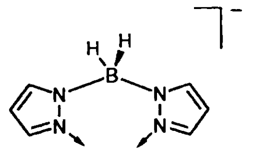
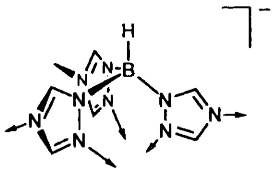
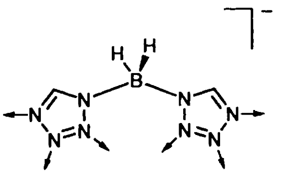
The reaction of zinc salts with $K[HB(C_2H_2N_3)_3]$ in water gave two crystalline polymorphic forms. A single-crystal X-ray study revealed that the fast crystallizing cubic platelets have the formula $[Zn\{HB(C_2H_2N_3)_3\}_2]\cdot 6H_2O$ with the orthorhombic space group *Pmcn* and $a = 20.98(1)$, $b = 10.734(6)$, $c = 11.747(3)$ Å and $Z = 4$. The borate acts as a tridentate chelate through the endodentate nitrogens to form zinc co-ordination octahedra embedded in layers of water molecules. The slowly crystallizing parallelepipeds as the second modification present a three-dimensional lattice built up by the borate bridging three zinc centres *via* the exodentate nitrogen donor atoms. The co-ordination polymer of the analytical formula $[Zn\{HB(C_2H_2N_3)_3\}_2]\cdot$ *ca.* $1.5H_2O$ crystallizes in the monoclinic space group *C2/c* with $a = 15.975(13)$, $b = 8.900(6)$, $c = 17.930(15)$ Å, $\beta = 121.36(5)°$ and $Z = 4$.

The prototypical poly(pyrazolyl)borates $[HB(pz)_3]^-$ and $[H_2B(pz)_2]^-$, which were introduced into co-ordination chemistry by Trofimenko more than 20 years ago,[1,2] have developed into one of the most versatile auxiliary ligands in modern (bio-)inorganic co-ordination chemistry.[3,4] Modifications of these ions, where the pyrazolyl rings are replaced by *e.g.* (1,2,4)-triazolyl or tetrazolyl, have been mentioned only briefly, however, [1,5,6] or not at all.[7] The ambidentate polytriazolyl- and tetrazolyl-borate anions, $[HB(C_2H_2N_3)_3]^-$, and $[H_2B(CHN_4)_2]^-$, with their multiple bonding centres would be expected to have an interesting co-ordination chemistry. Recently, the structural chemistry of the former has been studied in more detail and it was found to function as a tridentate chelate through the endodentate nitrogens with the formation of octahedral ML_2 complexes for M = Fe, Co[8] or Cu.[9] The additional exodentate nitrogen donors co-ordinate to solvent molecules of crystallization through hydrogen bonding, yet so far they have not been utilized for metal co-ordination,‡ although an AM1 theoretical calculation assigned a higher negative charge to these nucleophiles (Fig. 1).









Results and Discussion

Synthesis and Chemical Characterization.—The hydrotris(1,2,4-triazolyl)borate anion reacts with zinc(II) chloride or acetate in water at a 1:2 ratio to form bis[hydrotris(1,2,4-triazolyl)borato]zinc(II) **1** [equation (1) (X = Cl or O_2CMe)]

$$ZnX_2 + 2[HB(C_2H_2N_3)_3]^- \longrightarrow \underset{\mathbf{1}}{[Zn\{HB(C_2H_2N_3)_3\}_2]} + 2X^- \quad (1)$$

in two crystalline forms. Upon diffusion of the solutions cubic colourless platelets (**1a**) are first formed. This modification is somewhat soluble in water and upon standing over a period of months redissolves to give parallelepipedal crystals (**1b**) of the apparently more thermodynamically stable modification. Once formed the parallelepipeds cannot be dissolved without decomposition in water or organic solvents. A 1:1 ratio of ZnX_2 and $[HB(C_2H_2N_3)_3]^-$ gave no monofunctional, tetrahedral zinc complex [ZnX(L)], but only the bis complex, in agreement with observations with other tridentate ligands where the octahedral environment around zinc is strongly preferred in the absence of bulky substituents α to the co-ordinated nitrogen atom.[11]

The results of X-ray structural investigations (see below) show that the crystals of compound **1a** contain six molecules of water per formula unit which are quickly released when the crystal is taken out of the water phase. In the case of modification **1b** about 1.5 water molecules of crystallization per formula unit are detected which are not lost upon drying at room temperature. Owing to heavy disorder problems of the water molecules in the latter, room-temperature structure the exact number of the solvent molecules could not, however, be determined. Aside from the loss of solvent, both modifications are thermally stable, decomposing at around 305 °C. The infrared spectra (Fig. 2) of the two polymorphic forms are quite similar, yet exhibit distinct differences which must be ascribed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ A hint of a possible exodentate N co-ordination could, only be obtained from the structure of the salt $K[HB(C_2H_2N_3)_3]$. The tris(triazolyl)borate is chelated to potassium by two endodentate N atoms *and* participates in the formation of a one-dimensional co-ordination polymer with an exodentate N··· K contact.[9]

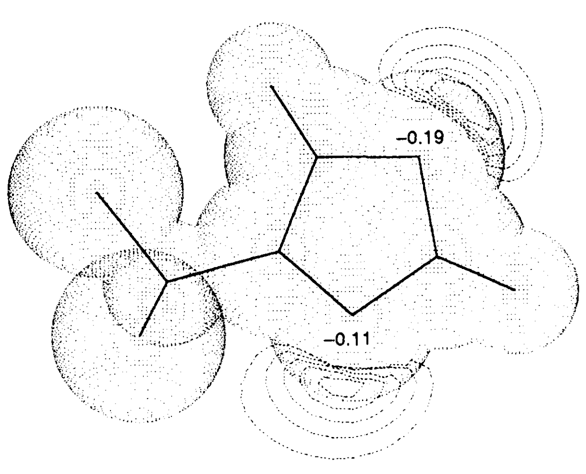

Fig. 1 Charge distribution (for the potential nitrogen donor atoms) and electrostatic potential in a triazolyl ring of $[HB(C_2H_2N_3)_3]^-$ according to an AM1 calculation.[10] For clarity only one ring is fully shown. Contour lines: −0.30 (minimum), −0.27, −0.24, −0.21, −0.18 (inside out)

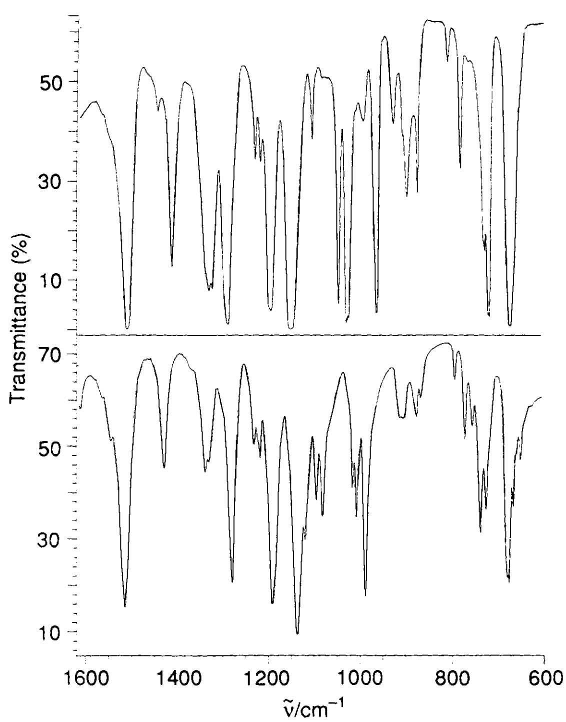

Fig. 2 Infrared spectra (fingerprint region, CsI pellet) of the modifications **1a** (top) and **1b** (bottom)

to a change in linkage mode (see below). The fingerprint region in the IR spectrum of **1a** is essentially superimposable with those of the molecular, octahedral bis[hydrotris(triazolyl)borato]-iron and -cobalt complexes.[9] The differences in the mass-spectral features are also attributed to the linkage isomerism, which is described in detail below. For **1a** the molecular ion and other metal-containing fragments are of high abundance, often similar to that of the triazolyl fragment peak at $m/z = 69$ (actually surpassing it when the isotopic distribution is summed), whereas for the (polymeric) modification **1b** the relative abundances of the metal-containing fragments are less than 10% of that of the triazolyl base peak.

Structures of Complexes **1a** *and* **1b**.—The polymorphic form **1a** consists of molecular, octahedral bis[hydrotris(1,2,4-triazolyl)borato]zinc complexes with the borate functioning as a tridentate chelate, through the endodentate nitrogen donors (Fig. 3). The zinc octahedra are arranged in layers separated by layers of water molecules. The facile loss of the water when the crystal is removed from solution indicates, however, rather weak solvent–solute interactions. A stereoview of the crystal structure (Fig. 4) illustrates the formation of this intercalate or layer clathrate. Aside from a lower crystal symmetry,* the structure of **1a** is isomorphous to that of the analogous iron and cobalt complexes $[M\{HB(C_2H_2N_3)_3\}_2]\cdot 6H_2O$ (M = Fe or Co).[8] Selected bond distances and angles are compiled in Table 1.

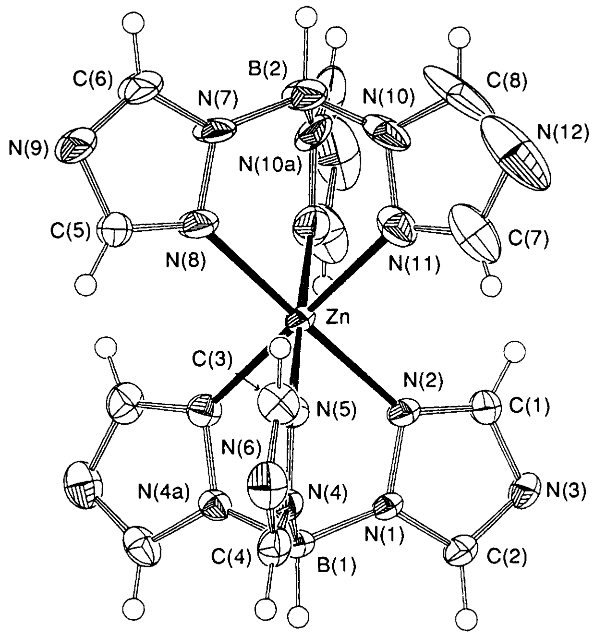

Fig. 3 Molecular structure of $[Zn\{HB(C_2H_2N_3)_3\}_2]$ in **1a** (PLATON-TME plot)[13]

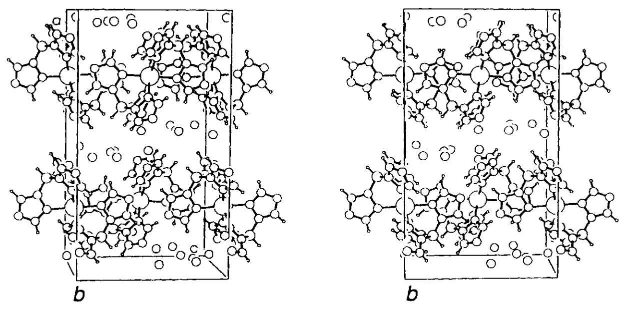

Fig. 4 Stereoview of the crystal structure of **1a** illustrating the intercalation of a two-dimensional water layer between metal complex layers (PLUTON plot)[12]

The quality of the data set allowed the determination of the hydrogen-bonding network around the water molecules. The hydrogen atoms of the latter were found and their positions refined. The potential hydrogen-bond lengths and angles of the short intermolecular contacts are given in Table 2. Fig. 5 shows a view of the water layer from above, including the hydrogen-bonded nitrogen atoms of the triazolyl rings (crossed circles). Note the positional disorder of the hydrogens on O(2) and O(3),

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* The iron and cobalt complexes crystallize in the space group *Cmca* at room temperature. We rationalize the different space group *Pmcn* for the zinc complex, measured at −100 °C, by a temperature-induced phase transition/ordering in the water layer.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1a** and **1b**

Complex **1a**[a]			
Zn–N(2)	2.130(4)	Zn–N(5)	2.148(4)
Zn–N(8)	2.132(4)	Zn–N(11)	2.159(4)
N(1)–N(2)	1.373(6)	N(1)–C(2)	1.335(5)
N(1)–B(1)	1.542(7)	N(2)–C(1)	1.315(6)
N(3)–C(1)	1.349(6)	N(3)–C(2)	1.336(6)
N(4)–N(5)	1.374(4)	N(4)–C(4)	1.328(5)
N(4)–B(1)	1.541(4)	N(5)–C(3)	1.316(5)
N(6)–C(3)	1.348(5)	N(6)–C(4)	1.330(5)
N(7)–N(8)	1.375(6)	N(7)–C(6)	1.321(6)
N(7)–B(2)	1.534(7)	N(8)–C(5)	1.311(6)
N(9)–C(5)	1.354(6)	N(9)–C(6)	1.316(8)
N(10)–N(11)	1.369(5)	N(10)–C(8)	1.347(6)
N(10)–B(2)	1.529(5)	N(11)–C(7)	1.323(6)
N(12)–C(7)	1.326(6)	N(12)–C(8)	1.274(7)
trans N–Zn–N	179.1(1)		
cis N–Zn–N	84.8(1)–95.4(1)		
N(1)–B(1)–N(4)	108.5(3)	N(4)–B(1)–N(4a)	107.9(3)
N(7)–B(2)–N(10)	108.9(3)	N(10)–B(2)–N(10a)	107.4(3)

Complex **1b**[b]			
Zn–N(3g)/N(3h)	2.171(3)	Zn–N(6a)/N(6b)	2.192(3)
Zn–N(9)/N(9f)	2.194(3)	N(1)–N(2)	1.380(4)
N(1)–C(2)	1.325(3)	N(1)–B	1.542(4)
N(2)–C(1)	1.311(3)	N(3)–C(1)	1.359(4)
N(3)–C(2)	1.328(4)	N(4)–N(5)	1.365(3)
N(4)–C(4)	1.326(4)	N(4)–B	1.556(4)
N(5)–C(3)	1.307(4)	N(6)–C(3)	1.339(4)
N(6)–C(4)	1.350(4)	N(7)–N(8)	1.370(3)
N(7)–C(6)	1.329(3)	N(7)–B	1.543(4)
N(8)–C(5)	1.313(3)	N(9)–C(5)	1.356(3)
N(9)–C(5)	1.356(3)	N(9)–C(6)	1.329(3)
trans N–Zn–N	180		
cis N–Zn–N	87.93(9)–92.07(9)		
N(1)–B–N(4)	108.7(2)		
N(4)–B–N(7)	108.8(2)	N(1)–B–N(7)	108.3(2)

[a] Symmetry operation: a $x, \frac{1}{2} - y, z$. [b] Symmetry operations: a $-x, y, \frac{1}{2} - z$; b $x, -y, \frac{1}{2} + z$; f $-x, -y, 1 - z$; g $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; h $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 2 Hydrogen-bonding scheme in compound **1a**

D–H ··· A	D ··· A/Å	D–H/Å	H ··· A/Å	D–H ··· A/°
O(1)–H(11) ··· N(6d)	2.854(5)	0.853(9)	2.003(9)	174.8(7)
O(2o)–H(21p) ··· O(4p)	2.740(5)	0.940(8)	1.842(8)	159(1)
O(2o)–H(22o) ··· O(1)	2.886(6)	0.97(1)	1.92(1)	178(1)
O(3j)–H(31j) ··· N(12q)	2.860(6)	0.86(1)	2.26(1)	126.8(7)
O(3j)–H(32j) ··· N(12q)	2.860(6)	0.92(1)	2.00(1)	156.5(7)
O(4d)–H(42d) ··· O(5)	2.553(7)	0.84(9)	1.724(8)	171(1)
O(5)–H(51) ··· O(3j)	2.867(7)	1.088(8)	2.01(1)	133.4(6)
O(5)–H(52) ··· O(1)	2.927(6)	0.970(7)	2.205(8)	130.3(4)

D = Donor, A = acceptor. All other O ··· O and O ··· N contacts are above 325 pm. Symmetry transformations: d $\frac{1}{2} - x, -y, -\frac{1}{2} + z$; j $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; o $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; p $\frac{1}{2} + x, y, \frac{1}{2} - z$; q $1 - x, -y, 1 - z$.

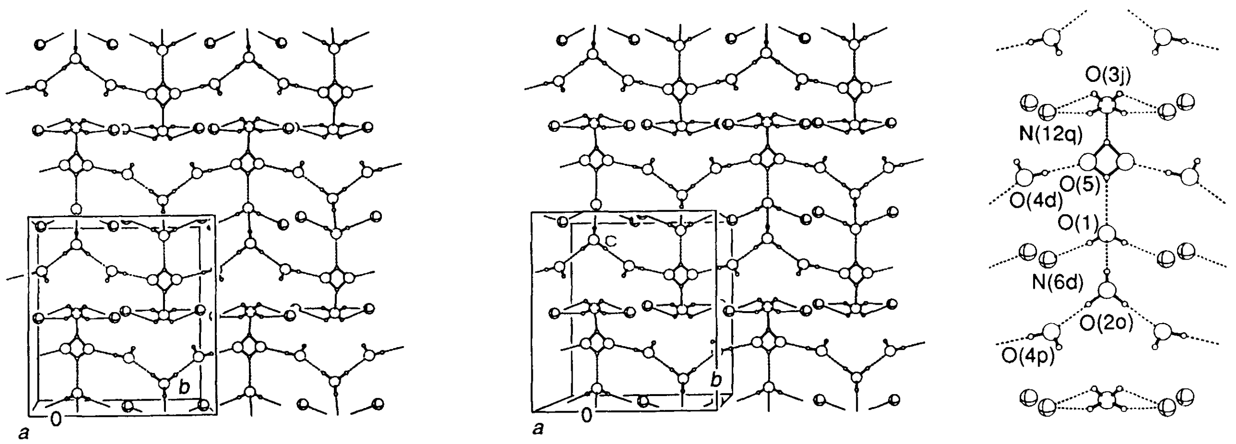

Fig. 5 Stereoscopic view from above of a water layer in compound **1a** with the hydrogen-bonding network (dashed lines) and including the hydrogen-bonded nitrogen atoms of the triazolyl rings (crossed circles, PLUTON[12]). The atomic numbering scheme is illustrated at the right. Atoms O(3), O(1) and O(2) lie on a mirror plane (symmetry operation $x, \frac{1}{2} - y, z$); for the symmetry labels see Table 2

and the two-site position of O(5). It is evident that two out of the six H_2O molecules embedded in the crystal lattice in **1a** are involved in hydrogen bonds to four exodentate nitrogen atoms. It is noteworthy that the water layer in **1a** is not built up from edge-sharing O_6 rings (analogously to the structure of ice) which have been observed in structures with stronger host–guest interactions such as in $Cd(H_2O)_2Ni(CN)_4{\cdot}4H_2O$.[13] Rather the hydrogen-bonding framework appears to form kinked strands of O_8 rings, which run parallel to the *b* axis. However, when the two-site position of the O(5) atoms and of the hydrogens on O(2) is taken into account the strands are interrupted and the water structure is better described as being comprised of individual rings or chain segments. Thereby, the structure of the water layer resembles more that of a frozen liquid with an assumed temperature-dependent formation of small H_2O clusters,[14] especially in comparison to the room-

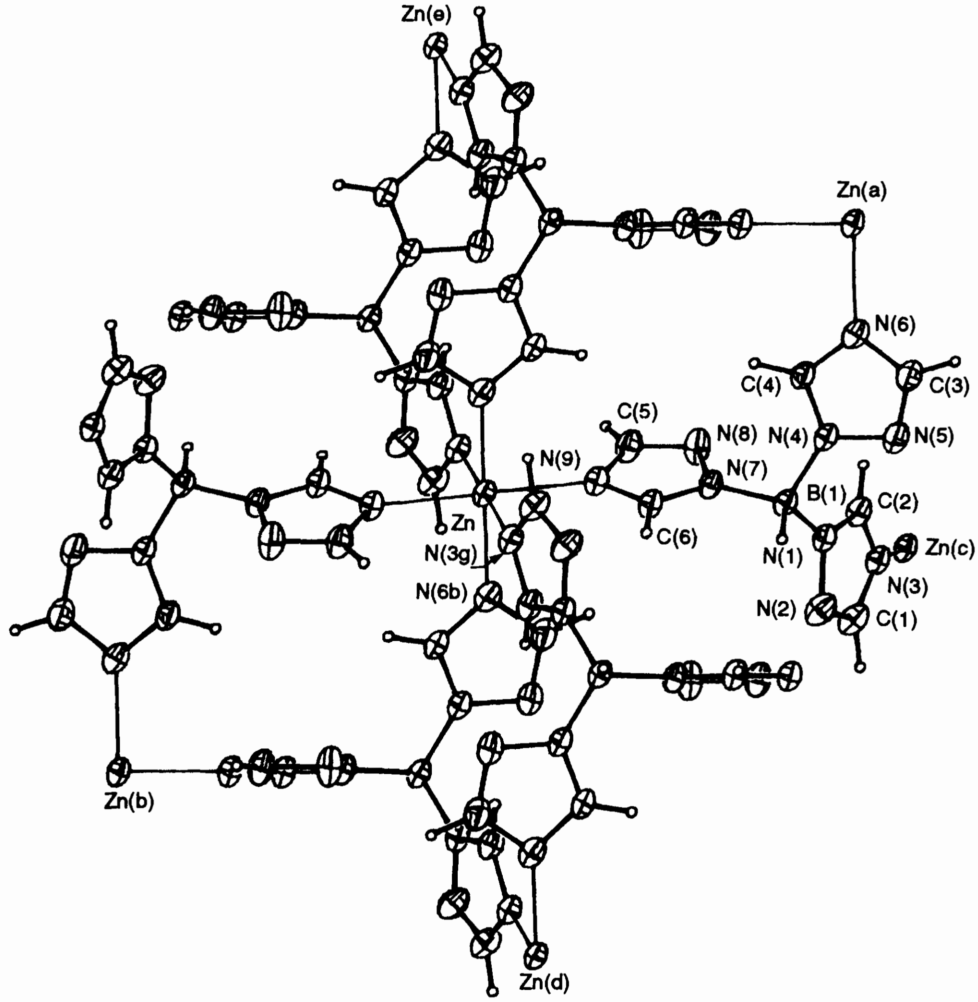

Fig. 6 Section of the three-dimensional co-ordination polymer **1b** with the atom numbering (ORTEP).[15] Symmetry operations: a $-x, y, \frac{1}{2} - z$; b $x, -y, \frac{1}{2} + z$; c $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; d $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; e $\frac{1}{2} + x, \frac{1}{2} + y, z$; g $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; h $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

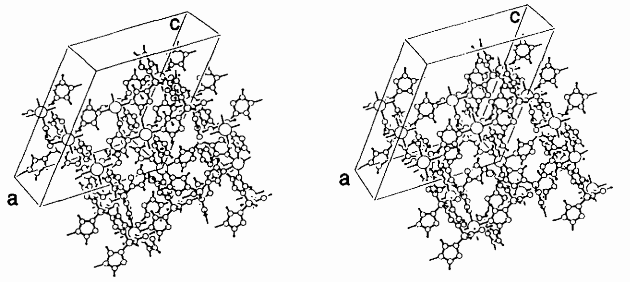

Fig. 7 Stereoview of the crystal structure of compound **1b** (PLUTON plot).[12] The voids in the lattice are filled with water molecules which are severely disordered in this room-temperature structure and have been omitted for clarity

temperature water-layer structures of the closely related iron and cobalt complexes.[8]

The crystalline modification **1b** is a three-dimensional co-ordination polymer built up from hydrotris(1,2,4-triazolyl)borate ions bridging three zinc centres through the exodentate nitrogen atoms. Fig. 6 shows a section of this array to illustrate the atom numbering. It also shows the octahedral co-ordination around the zinc and that each zinc shares two ligands with four of its neighbours, while each ligand connects three metal atoms. A stereoscopic view of the lattice is given in Fig. 7. Selected bond distances and angles are in Table 1. Fig. 7 shows the formation of infinite channels extending through the crystal lattice with a potential solvent area of 336 Å^3 or 15.4% per unit-cell volume of 2177 Å^3 for the solvent-free framework. The largest hole (within the unit cell) is calculated to be 79.6 Å^3. This can be compared to an expected volume for a hydrogen-bonded water molecule of 40 Å^3 (PLATON-93 [12]).

We view the supramolecular architecture of compound **1a** and **1b** as examples of the spontaneous self-organization of molecular building blocks.[16] Furthermore, both **1a** and **1b** together manifest a case of linkage isomerism for the ambidentate borate and demonstrate that the exodentate nitrogens can very well function as donor atoms in accordance with the results of the theoretical calculation presented in Fig. 1. The ready formation of octahedral chelate complexes with Fe, Co,[8] Cu[9] and in part Zn may be explained by a combination of chelate and kinetic effects as well as by the difficulty of crystallizing a three-dimensional co-ordination polymer. We are now attacking the problem of utilizing both donor atoms at the same time in *e.g.* a mixed-metal complex.

Experimental

Doubly distilled or deionized water was used as a solvent. Instruments employed: CHN analysis, Perkin-Elmer Series II CHNS/O Analyser 2400; IR spectroscopy, Nicolet Magna 750; mass spectrometry, Varian MAT 311A. The salt K[HB$(C_2H_2N_3)_3$] was synthesized from KBH_4 and triazole according to refs. 1 and 17.

Table 3 Crystal data and details of measurement for complexes **1a** and **1b**

	1a	**1b**
Formula	$C_{12}H_{26}B_2N_{18}O_6Zn$	$C_{12}H_{17}B_2N_{18}O_{1.5}Zn$
M	605.46	524.39
Crystal size/mm	0.25 × 0.40 × 0.40	0.10 × 0.15 × 0.38
Crystal system	Orthorhombic	Monoclinic
Space group	*Pmcn*	*C*2/*c* (no. 15)
	(non-standard setting of *Pnma*, no. 62)	
a/Å	20.980(11)	15.975(13)
b/Å	10.734(6)	8.900(6)
c/Å	11.747(3)	17.930(15)
β/°	—	121.36(5)
U/Å^3	2645(3)	2177(3)
Z	4	4
D_c/g cm^{-3}	1.520	1.600
F(000)	1248	1068
μ(Mo-Kα)/cm^{-1}	10.1	12.0
Absorption correction	None	DIFABS[18]
maximum, minimum, average	—	1.211, 0.902, 1.017
Measured reflections	5168	2170
Unique reflections	2367 (R_{int} = 0.0279)	2103 (R_{int} = 0.0412)
Observed reflections [$F > 4\sigma(F)$]	1980	1553
Parameters refined	253	195
Maximum, minimum $\Delta\rho^a$/e Å^{-3}	0.67, −0.64	0.43, −0.36
R, R'^b	0.048, 0.044	0.039, 0.036
Weighting scheme^c	Unit weights	k = 1.8735, g = 0.000

[a] Residual electron density. [b] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [c] $w = k/[\sigma^2(F) + g(F)]$.

Table 4 Fractional atomic coordinates for complex **1a**

Atom	x	y	z
Zn	0.245 31(3)	0.25	0.502 32(5)
N(1)	0.197 26(19)	0.25	0.259 6(3)
N(2)	0.252 78(19)	0.25	0.321 5(3)
N(3)	0.277 1(2)	0.25	0.135 9(3)
N(4)	0.126 99(12)	0.134 0(3)	0.395 1(2)
N(5)	0.172 06(13)	0.112 8(3)	0.477 7(2)
N(6)	0.097 48(15)	−0.036 2(3)	0.486 5(3)
N(7)	0.295 0(2)	0.25	0.745 7(3)
N(8)	0.239 5(2)	0.25	0.683 5(3)
N(9)	0.216 1(2)	0.25	0.868 3(3)
N(10)	0.364 67(15)	0.135 2(4)	0.609 6(3)
N(11)	0.320 07(14)	0.114 4(3)	0.526 7(3)
N(12)	0.394 35(19)	−0.033 2(4)	0.516 7(4)
C(1)	0.298 2(2)	0.25	0.244 4(4)
C(2)	0.213 9(2)	0.25	0.149 9(3)
C(3)	0.152 11(18)	0.010 9(3)	0.528 8(3)
C(4)	0.083 89(17)	0.043 9(3)	0.403 6(3)
C(5)	0.194 0(2)	0.25	0.760 0(4)
C(6)	0.278 3(3)	0.25	0.854 1(4)
C(7)	0.340 4(2)	0.012 3(4)	0.475 1(4)
C(8)	0.406 9(2)	0.041 5(5)	0.598 0(4)
B(1)	0.131 5(3)	0.25	0.318 3(4)
B(2)	0.360 1(3)	0.25	0.686 2(4)
O(1)	0.466 98(18)	0.25	0.073 6(3)
O(2)	0.051 3(2)	0.25	0.620 5(3)
O(3)	0.027 5(2)	0.25	0.993 6(4)
O(4)	0.043 00(17)	0.048 6(4)	0.763 1(3)
O(5)*	0.451 3(3)	0.182 5(4)	0.313 4(4)

* Disordered atom.

Synthesis of Bis[*hydrotris*(1,2,4-*triazolyl*)*borato*]*zinc*(II) *Hexahydrate* **1a** *and Hydrate* **1b**.—Zinc chloride (0.18 g, 1.3 mmol) or $Zn(O_2CMe)_2\cdot 2H_2O$ (0.29 g) dissolved in water (10 cm^3) was carefully overlayered in a test-tube with $K[HB(C_2H_2N_3)_3]$ (0.66 g, 2.6 mmol) dissolved in water (20 cm^3). Some amorphous precipitate was formed in the overlayering process. Slow diffusion of the solutions then led to the formation of clear, colourless cubic platelets of $[Zn\{HB(C_2H_2N_3)_3\}_2]\cdot 6H_2O$ **1a** [0.1 g, 15% from $ZnCl_2$; 0.38 g, 60% from $Zn(O_2CMe)_2$] as the first crystal batch within a few days. When removed from the water phase the crystals quickly turn opaque with loss of crystallinity due to the evaporation of crystal water. When the platelets are stored in water at room temperature over a period of months they dissolve again with the appearance of a second crystalline modification in the form of more or less well shaped parallelepipeds **1b** (0.45 g, 70% based on $ZnCl_2$). These colourless crystals can be dried and stored at room temperature for weeks without loss of crystallinity.

The dried platelets **1a** analysed as $[Zn\{HB(C_2H_2N_3)_3\}_2]$, m.p. *ca* 310 °C (decomp.) (Found: C, 28.85; H, 2.60; N, 50.60. $C_{12}H_{14}B_2N_{18}Zn$ requires C, 29.00; H, 2.85; N, 50.70%); $\tilde{\nu}_{max}$/cm^{-1} 3126w, 3103w, 3089w, 2515w, 2494w, 1509s, 1410m, 1328m, 1321m, 1287s, 1227w, 1216w, 1193s, 1150s, 1103w, 1047m, 1030s, 968(sh), 961s, 926w, 906(sh), 896w, 874w, 782w, 730(sh), 720s, 673s and 664(sh) (CsI); *m*/*z* (electron impact, EI; 220 °C) 496 (80, $M^{\bullet +}$), 428 (54, $[M - C_2H_2N_3]^+$), 426 (22, $[M - C_2H_2N_3 - 2H]^+$), 359 (95, $[M - 2C_2H_2N_3 - H]^+$), 358 (43, $[M - 2C_2H_2N_3 - 2H]^{\bullet +}$), 332 (13, $[M - 2C_2H_2N_3 - H - HCN]^+$), 280 (64, $[M - HB(C_2H_2N_3)_3]^+ = [Zn\{HB(C_2H_2N_3)_3\}]^+$), 211 (52, $[Zn\{HB(C_2H_2N_3)_3\} - C_2H_2N_3 - H]^+$), 184 (31, $[Zn\{HB(C_2H_2N_3)_3\} - C_2H_2N_3 - H - HCN]^+$), 157 (13, $[Zn\{HB(C_2H_2N_3)_3\} - C_2H_2N_3 - H - 2HCN]^+$) and 69 (100%, $[C_2H_3N_3]^{\bullet +}$).

The crystalline parallelepipeds **1b** analysed as $[Zn\{HB(C_2H_2N_3)_3\}_2]\cdot$ *ca*. 1.5 H_2O, m.p. *ca*. 305 °C (decomp.) (Found: C, 26.75; H, 3.10; N, 47.30. $C_{12}H_{17}B_2N_{18}O_{1.5}Zn$ requires C, 27.50; H, 3.25; N, 48.10%) the exact amount of water could not be determined, see above); $\tilde{\nu}_{max}$/cm^{-1} 3430m(br) [ν(OH)], 3150w, 3133w, 3118w, 2503w, 1514s, 1428w, 1337w, 1329w, 1278m, 1230w, 1217w, 1190m, 1136s, 1119(sh), 1095w, 1082w, 1017w, 1008w, 988m, 904w, 876w, 773w, 739m, 727m, 676m, 667(sh) and 652w (CsI); *m*/*z* (EI, 270 °C) 495 (8, $[M - H]^+$), 428 (6, $[M - C_2H_2N_3]^+$), 427 (3, $[M - C_2H_2N_3 - H]^{\bullet +}$), 359 (9, $[M - 2C_2H_2N_3 - H]^+$), 358 (4, $[M - 2C_2H_2N_3 - H_2]^{\bullet +}$), 280 (6, $[M - HB(C_2H_2N_3)_3]^+ = [Zn\{HB(C_2H_2N_3)_3\}]^+$), 211 (3, $[Zn\{HB(C_2H_2N_3)_3\} - C_2H_2N_3 - H]^+$), 184 (2, $[Zn\{HB(C_2H_2N_3)_3\} - C_2H_2N_3 - H - HCN]^+$) and 69 (100%, $[C_2H_3N_3]^{\bullet +}$) (peaks given refer to the most abundant isotope combination ^{64}Zn, ^{11}B).

Crystal Structure Determination of Complexes **1a** *and* **1b**.—The crystal of compound **1a** was taken out of the mother-liquor at room temperature and quickly transferred to the cold nitrogen stream of the diffractometer. Crystal data and details of measurements for complexes **1a** and **1b** are given in Table 3. Diffraction intensities were collected at 173 K on a CAD4 diffractometer for **1a** with the ω–2θ scan mode ($5 \leqslant 2\theta \leqslant 50°$) and at room temperature on a STOE diffractometer for **1b** with the ω scan mode ($4 \leqslant 2\theta \leqslant 54°$). Graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) was employed in each case. No decay correction was made.

Both structures were solved by direct methods (SHELXS 86)[19] and refined by full-matrix least squares (SHELX 76)[19] with all non-hydrogen atoms anisotropic. The hydrogens were found and refined, except for those in the disordered water molecules of **1b**. Final positional parameters for non-hydrogen atoms are listed in Tables 4 and 5 for **1a** and **1b**, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 5 Non-hydrogen positional parameters for complex **1b**

Atom	*x*	*y*	*z*
Zn	0	0	0.5
N(1)	−0.357 64(15)	0.073 82(19)	0.088 08(13)
N(2)	−0.432 20(15)	0.050 2(2)	0.104 18(14)
N(3)	−0.457 35(15)	0.265 99(19)	0.030 54(13)
N(4)	−0.225 34(15)	−0.030 65(19)	0.066 51(13)
N(5)	−0.282 93(16)	−0.059 8(2)	−0.020 73(14)
N(6)	−0.126 99(15)	−0.036 15(19)	0.013 89(14)
N(7)	−0.190 28(14)	0.027 28(19)	0.217 75(13)
N(8)	−0.153 75(16)	0.170 5(2)	0.231 74(14)
N(9)	−0.089 80(15)	0.047 60(19)	0.359 63(13)
C(1)	−0.489 06(17)	0.167 5(2)	0.068 53(16)
C(2)	−0.375 55(17)	0.201 5(2)	0.044 27(15)
C(3)	−0.220 97(17)	−0.060 3(2)	−0.047 60(16)
C(4)	−0.133 70(16)	−0.017 1(2)	0.085 30(15)
C(5)	−0.094 52(18)	0.176 0(2)	0.316 88(16)
C(6)	−0.151 08(17)	−0.041 8(2)	0.294 51(15)
B	−0.268 49(18)	−0.032 5(2)	0.126 82(17)
O(1)*	0.5	0.226 0(2)	0.25
O(2)*	0.413 2(2)	−0.056 6(3)	0.196 7(2)
O(3)*	−0.578 9(2)	0.105 6(3)	0.223 2(2)

* Owing to the high disorder of the water molecules the occupancy of the oxygen centres could not be clearly determined. They were eventually refined with the following site occupation factors: O(1) 0.25; O(2) 0.30; O(3) 0.20, giving a total of 1.5 water molecules per zinc centre.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (grant Ja466/4-1), the Fonds der Chemischen Industrie, the Freunde der TU Berlin, and through the graduate program 'Synthesis and structure elucidation of molecular compounds'. Dr. D. Lentz is cordially thanked for collecting the crystallographic data set for compound **1b** and Professor H. Schumann for his continuing support.

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Received 13*th April* 1994; *Paper* 4/02189D