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Benzotriazole Complexes. II. The Crystal Structures of Benzotriazolium Tetrachlorocobaltate(II), Bis(benzotriazole)-dichlorozinc(II) and Polymeric Tetrakis(benzotriazolato)dizinc(II)

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The crystal structures of the title compounds, $(C_6H_6N_3)_2[CoCl_4]$, $[ZnCl_2(C_6H_5N_3)_2]$ and $[Zn_2(C_6H_4N_3)_4]_n$, have been investigated by X-ray diffraction techniques. The crystals are all monoclinic. The space group of $(C_6H_6N_3)_2[CoCl_4]$ is $C2/c$, with $a=15.344(9)$ Å, $b=7.560(6)$ Å, $c=15.098(9)$ Å and $\beta=91.83(9)°$. The space group of the second compound is $P2_1/n$, with $a=7.747(4)$ Å, $b=13.982(2)$ Å, $c=13.791(3)$ Å and $\beta=92.58(6)°$. The last compound crystallizes in space group $P2_1/c$, with $a=10.030(2)$ Å, $b=21.115(3)$ Å, $c=19.912(8)$ Å and $\beta=94.10(5)°$. The structures were refined to R-values of 0.025, 0.026 and 0.038, respectively. The Co-compound consists of planar benzotriazolium cations and $CoCl_4^{2-}$ anions, with the Co-atoms tetrahedrally coordinated to the Cl-atoms (average Co–Cl distance: 2.263 Å). The bis(benzotriazole)dichlorozinc(II) compound consists of monomeric $[ZnCl_2(C_6H_5N_3)_2]$-units, with the Zn-atom tetrahedrally coordinated to two Cl-atoms [average distance 2.238(3) Å] and two N3-atoms [average distance 2.024(10) Å]. The coordination to zinc has only a small effect on the geometry of the benzotriazole group. In the polymeric $[Zn_2(C_6H_4N_3)_4]$-compound each benzotriazolate ligand is shared by two Zn-atoms, the Zn-atoms being tetrahedrally coordinated to the marginal nitrogen atoms of the triazole groups [average distance 2.004(4) Å]. The compound $(C_6H_6N_3)_2[ZnCl_4]$ was found to be isostructural with $(C_6H_6N_3)_2[CoCl_4]$.

The present structure analyses are part of an investigation of benzotriazole complexes.[1] Benzotriazolium, benzotriazole and benzotriazolate are henceforth referred to as $BTAH_2$, BTAH and BTA, respectively.

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EXPERIMENTAL

Blue crystals of $(BTAH_2)_2[CoCl_4]$ were prepared by mixing 4×10^{-4} mol cobaltous chloride hexahydrate in 1 ml 2 M hydrochloric acid and 3×10^{-3} mol benzotriazole in 3 ml 2 M hydrochloric acid. Colourless crystals of $(BTAH_2)_2[ZnCl_4]$ were prepared by mixing 6×10^{-4} mol zinc chloride in 6 ml 2 M hydrochloric acid and 3×10^{-3} mol benzotriazole in 6 ml 2 M hydrochloric acid. Colourless crystals of $[ZnCl_2(BTAH)_2]$ were prepared by mixing 6×10^{-4} mol zinc chloride in 0.5 ml 7 M ammonia + 4.5 ml 2 M hydrochloric acid and 3×10^{-3} mol benzotriazole in 0.5 ml 7 M ammonia + 4.5 ml 2 M hydrochloric acid. Colourless crystals of $[Zn_2(BTA)_4]_n$ were prepared by mixing 6×10^{-4} mol zinc chloride in 6 ml 7 M ammonia and 3×10^{-3} mol benzotriazole in 6 ml 7 M ammonia. Determination of the possible space groups and the data collection were carried out as described in Ref. 1. The dimensions of the crystals were $0.13\times0.18\times0.25$ mm, $0.13\times0.18\times0.25$ mm and $0.05\times0.10\times0.15$ mm for $(BTAH_2)_2[CoCl_4]$, $[ZnCl_2(BTAH)_2]$ and $[Zn_2(BTA)_4]_n$, respectively. All structures were solved by Patterson technique.[2] The refinement technique and the references to the atomic scattering factors are those given in Ref. 1. To confirm that $(BTAH_2)_2[ZnCl_4]$ and $(BTAH_2)_2[CoCl_4]$ are isostructural, a rough data set was collected on the Zn-compound and refined to $R=0.053$. Crystal data and R-values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2. The labelling of the BTAH-atoms are shown in Fig. 1. Lists of thermal parameters and observed and calculated structure factors may be obtained from the authors on request.

Table 1. Crystal data.

	$(BTAH_2)_2[CoCl_4]$	$(BTAH_2)_2[ZnCl_4]$	$[ZnCl_2(BTAH)_2]$	$[Zn_2(BTA)_4]_n$
M	441.0	447.4	374.5	603.2
μ(Mo$K\alpha$) (cm^{-1})	16.0	20.6	20.5	20.8
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
V(Å^3)	1750.5	1746.1	1492.3	2413.4
a(Å)	15.344(9)	15.305(5)	7.747(4)	10.030(2)
b(Å)	7.560(6)	7.558(2)	13.982(2)	21.115(3)
c(Å)	15.098(9)	15.101(4)	13.791(3)	19.912(8)
β(°)	91.83(9)	91.69(4)	92.58(6)	94.10(5)
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/c$
D_c (g cm^{-3})	1.67	1.70	1.67	1.66
Z	4	4	4	4
Total number of reflections	1122	1218	2623	6982
Number of independent observations [$I \geq 2\sigma(I)$]	918	824	2099	3088
$R = \sum\|\|F_o\| - \|F_c\|\| / \sum\|F_o\|$	0.025		0.026	0.038
$R_w = \left[\frac{\sum w(\|F_o\| - \|F_c\|)^2}{\sum w\|F_o\|^2}\right]^{\frac{1}{2}}$	0.033		0.031	0.037

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Bond lengths and bond angles with their estimated standard deviations are listed in Tables 3, 4 and 5. The Co-compound is built from $BTAH_2$ and $CoCl_4^{2-}$ ions. The $BTAH_2$ ion is nearly planar, the deviations of the atoms from the least-squares plane through them being less than 0.02 Å. The metrical details of the ion are compared with those of benzotriazole[3] in Table 5. The bond lengths and bond angles in the average groups were found as in Ref. 1. The $BTAH_2$ ion nearly has C_{2v} symmetry, the H atoms being bonded to N1 and N3. The N–H and C–H bond lengths lie between 0.85 and 1.01 Å. The Co atom is situated on a two-fold axis and is coordinated to four Cl atoms forming an almost regular tetrahedron. For the Zn-compound

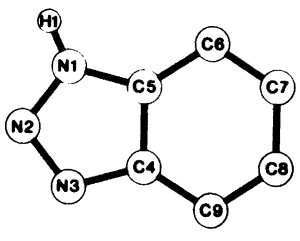

Fig. 1. The benzotriazole molecule.

the Zn–Cl distances are 2.217(4) and 2.307(4) Å with an average value of 2.262 Å. The average Co–Cl distance is 2.263 Å. The bond lengths and angles are in good agreement with the results of studies on Zn complexes.[4] The distance between the $BTAH_2$ ions (x,y,z) and ($\frac{1}{2}$-x,$\frac{1}{2}$-y,1-z), related by a center of symmetry (Fig. 2) is ~3.5 Å. The hydrogen-bonding distances between the $CoCl_4^{2-}$ ion and the $BTAH_2$ ion are the N1–Cl2($\frac{1}{2}+x$,$\frac{1}{2}+y$, z) distance of 3.217(3) Å and the N3–Cl2 distance of 3.266(3) Å.

The structure of $[ZnCl_2(BTAH)_2]$ consists of well-separated molecular units (Fig. 3). The Zn atom is coordinated to two Cl atoms and two N3 atoms forming a nearly regular tetrahedron. The Zn–Cl bond lengths are in good agreement with the results of other studies on Zn-complexes.[4] The Zn–N bond lengths fall within values normally found in Zn-complexes. The BTAH ligands are nearly planar, the deviations of the atoms from the least-squares plane through them being less then 0.02 Å. The metrical details of the BTAH ligand are compared with those of benzotriazole[3] in Table 5. A comparison of the angles of the BTAH ligand in the present structure to those in other structures is carried out in Ref. 5.

The angle between the planes through BTAH1 and BTAH2 is 41.8°. The BTAH2 and BTAH1

Table 2. Final atomic coordinates $\times 10^4$. The estimated standard deviations $\times 10^4$ are in parentheses. The value of the hydrogen atoms are multiplied by 10^3.

Atom	x	y	z	x	y	z	x	y	z
	$(BTAH_2)_2[CoCl_4]$			$[ZnCl_2(BTAH)_2]$ BTAH1			$[ZnCl_2(BTAH)_2]$ BTAH2		
Me	0	1011(1)	2500	2514(1)	718(1)	2209(1)			
Cl1	1076(1)	2486(1)	1868(1)	−189(1)	144(1)	2172(1)			
Cl2	627(1)	−912(1)	3508(1)	4587(1)	−362(1)	2536(1)			
N1	3756(2)	2186(4)	3589(2)	3670(3)	3189(2)	3584(2)	3756(3)	1041(2)	−562(2)
N2	3081(2)	1941(4)	3048(2)	3584(3)	2582(2)	2846(2)	3623(3)	630(2)	298(2)
N3	2527(2)	1034(4)	3513(2)	2828(3)	1808(2)	3155(2)	2886(3)	1251(2)	862(2)
C4	2833(2)	697(4)	4352(2)	2436(3)	1917(2)	4109(2)	2542(3)	2080(2)	358(2)
C5	3653(2)	1480(4)	4407(2)	2977(4)	2828(2)	4384(2)	3119(3)	1945(2)	−577(2)
C6	4178(2)	1432(5)	5179(2)	2747(5)	3180(3)	5325(3)	2995(4)	2660(3)	−1289(2)
C7	3838(2)	533(5)	5870(2)	1988(5)	2576(4)	5936(3)	2256(4)	3486(3)	−1022(3)
C8	3007(2)	−264(5)	5811(2)	1469(5)	1647(4)	5674(2)	1650(4)	3634(2)	−85(3)
C9	2485(2)	−200(4)	5069(2)	1676(4)	1295(3)	4758(2)	1787(4)	2944(2)	620(2)
H	196(3)	86(6)	324(3)						
H1	419(2)	275(4)	340(2)	416(5)	369(3)	345(3)	427(4)	73(2)	−101(3)
H2	473(3)	199(5)	522(3)	308(4)	380(3)	550(3)	348(4)	256(2)	−192(3)
H3	422(2)	49(5)	637(3)	178(6)	280(3)	654(3)	213(4)	399(3)	−138(3)
H4	278(3)	−90(5)	633(3)	96(5)	126(3)	618(3)	115(4)	425(2)	6(2)
H5	192(2)	−67(5)	503(2)	139(4)	66(2)	454(2)	136(4)	304(2)	123(2)

Atom	x	y	z	x	y	z
	$[Zn_2(BTA)_4]_n$ BTA 1			$[Zn_2(BTA)_4]_n$ BTA 2		
Zn1 and 2	3009(1)	4419(1)	3443(1)	1878(1)	1619(1)	1063(1)
N1	4927(4)	4730(3)	3308(2)	1964(4)	5622(3)	3849(2)
N2	5602(4)	5538(4)	3645(2)	647(4)	5624(4)	3699(2)
N3	6880(4)	5515(3)	3503(2)	37(4)	6166(3)	4174(2)
C4	7051(4)	4660(4)	3058(2)	995(4)	6507(4)	4656(2)
C5	5799(4)	4168(4)	2936(2)	2221(5)	6169(4)	4444(2)
C6	5636(5)	3253(5)	2508(3)	3425(5)	6398(4)	4826(3)
C7	6744(6)	2886(5)	2209(3)	3320(5)	6962(5)	5412(3)
C8	7992(5)	3387(5)	2341(3)	2088(6)	7270(5)	5637(3)
C9	8178(5)	4265(4)	2761(3)	907(5)	7068(5)	5268(2)
H2	478(5)	299(4)	244(2)	422(5)	617(5)	469(3)
H3	660(6)	233(5)	191(3)	411(5)	706(4)	568(2)
H4	871(5)	313(4)	211(2)	213(6)	771(5)	601(3)
H5	907(4)	460(4)	286(2)	4(5)	725(4)	541(2)
	BTA 3			BTA 4		
N1	2900(4)	3257(3)	4157(2)	2135(4)	3984(3)	2551(2)
N2	2569(4)	3652(3)	4748(2)	2316(4)	2979(4)	2290(2)
N3	2596(4)	2845(3)	5203(2)	1688(4)	2919(3)	1679(2)
C4	2966(4)	1886(4)	4900(2)	1069(4)	3914(4)	1537(2)
C5	3155(5)	2153(4)	4232(2)	1375(4)	4595(4)	2089(2)
C6	3521(6)	1355(5)	3769(3)	889(5)	5677(4)	2107(2)
C7	3674(6)	297(5)	4008(3)	102(6)	6029(5)	1559(3)
C8	3487(6)	25(5)	4684(3)	−202(5)	5330(5)	1002(3)
C9	3152(5)	801(4)	5141(3)	261(5)	4274(5)	973(2)
H2	364(5)	148(5)	332(3)	101(5)	614(4)	253(2)
H3	392(6)	−27(5)	373(3)	−35(6)	675(5)	155(3)
H4	364(6)	−71(5)	484(3)	−80(5)	563(4)	64(2)
H5	317(5)	65(5)	563(3)	5(5)	373(5)	58(3)

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in the metal coordination spheres. The primed atoms are related to the unprimed atoms by a two-fold axis. The figures in parentheses refer to numbers of the BTAH or BTA ligands. Superscripts refer to atoms in the following positions: a $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; b $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; c $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

Atoms	Distance or angle	Atoms	Distance or angle
	$(BTAH_2)_2[CoCl_4]$		$[ZnCl_2(BTAH)_2]$
Co – Cl1	2.232(1)	Zn – Cl1	2.241(1)
Co – Cl2	2.294(1)	Zn – Cl2	2.235(1)
Cl1 – Co – Cl2	107.48(5)	Zn – N3(1)	2.014(2)
Cl1 – Co – Cl1′	120.06(6)	Zn – N3(2)	2.034(2)
Cl1 – Co – Cl2′	109.44(5)	Cl1 – Zn – Cl2	115.14(4)
Cl2 – Co – Cl2′	101.34(7)	Cl1 – Zn – N3(1)	111.80(7)
		Cl1 – Zn – N3(2)	106.33(7)
		Cl2 – Zn – N3(1)	108.39(7)
		Cl2 – Zn – N3(2)	107.57(7)
		N3(1) – Zn – N3(2)	107.23(9)
	$[Zn_2(BTA)_4]_n$		
	Zn1		Zn2
Zn – N1(1)	1.997(4)	Zn – N3(1^a)	1.984(4)
Zn – N1(2)	1.999(4)	Zn – N3(2^b)	2.021(4)
Zn – N1(3)	2.010(4)	Zn – N3(3^c)	2.011(4)
Zn – N1(4)	1.995(4)	Zn – N3(4)	2.013(4)
	$[Zn_2(BTA)_4]_n$		
	Zn1		Zn2
N1(1) – Zn – N1(2)	117.1(2)	N3(1^a) – Zn – N3(2^b)	118.3(2)
N1(1) – Zn – N1(3)	109.2(2)	N3(1^a) – Zn – N3(3^c)	109.7(2)
N1(1) – Zn – N1(4)	107.2(2)	N3(1^a) – Zn – N3(4)	110.2(2)
N1(2) – Zn – N1(3)	99.7(2)	N3(2^b) – Zn – N3(3^c)	106.4(2)
N1(2) – Zn – N1(4)	110.1(2)	N3(2^b) – Zn – N3(4)	103.0(2)
N1(3) – Zn – N1(4)	113.7(2)	N3(3^c) – Zn – N3(4)	108.8(2)

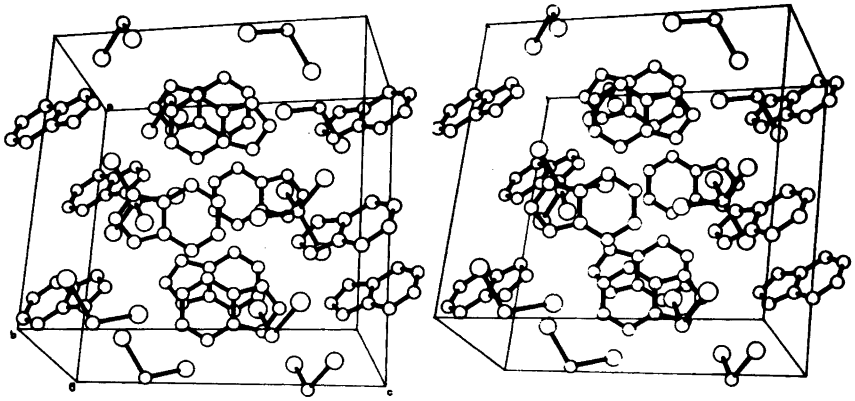

Fig. 2. Stereo view along the *b*-axis of the structure of $(BTAH_2)_2[CoCl_4]$.

Table 4. Bond distances (Å) and bond angles (°) with estimated standard deviations in the BTAH and BTA ligands.

Atoms	BTAH 1 Distance or angle	BTAH 2 Distance or angle	BTA 1 Distance or angle	BTA 2 Distance or angle	BTA 3 Distance or angle	BTA 4 Distance or angle
N1 – N2	1.325(3)	1.326(3)	1.342(6)	1.333(5)	1.334(5)	1.340(6)
N2 – N3	1.311(3)	1.313(3)	1.333(5)	1.334(6)	1.332(5)	1.332(5)
N3 – C4	1.371(3)	1.372(3)	1.381(6)	1.372(6)	1.372(6)	1.376(6)
C4 – C5	1.389(4)	1.396(4)	1.396(6)	1.390(7)	1.394(7)	1.391(6)
C5 – N1	1.347(4)	1.357(4)	1.367(6)	1.367(6)	1.369(6)	1.370(6)
C5 – C6	1.407(5)	1.401(4)	1.402(7)	1.408(7)	1.404(8)	1.399(7)
C6 – C7	1.347(6)	1.349(5)	1.371(8)	1.362(8)	1.372(8)	1.368(7)
C7 – C8	1.403(7)	1.410(5)	1.399(8)	1.395(8)	1.412(9)	1.411(8)
C8 – C9	1.371(5)	1.370(5)	1.357(8)	1.370(8)	1.366(9)	1.364(8)
C9 – C4	1.397(4)	1.398(4)	1.397(7)	1.404(7)	1.407(7)	1.405(6)
N1 – H1	0.82(4)	0.86(4)				
C6 – H2	0.93(4)	0.97(4)	0.92(5)	0.90(5)	0.93(6)	1.01(5)
C7 – H3	0.91(5)	0.87(4)	0.90(6)	0.94(5)	0.93(6)	0.99(7)
C8 – H4	0.97(4)	0.97(3)	0.93(5)	0.92(6)	0.95(6)	0.97(5)
C9 – H5	0.95(3)	0.93(3)	0.99(4)	0.95(5)	1.00(6)	1.03(6)
C5 – N1 – N2	112.4(2)	111.9(2)	108.4(3)	108.4(4)	108.1(4)	108.4(3)
N1 – N2 – N3	106.6(2)	107.3(2)	109.7(4)	109.9(3)	110.0(4)	109.6(4)
N2 – N3 – C4	110.0(2)	109.7(2)	108.5(4)	108.1(4)	108.4(4)	108.4(4)
N3 – C4 – C5	106.7(2)	106.9(2)	106.3(4)	106.8(4)	106.4(4)	106.7(4)
C4 – C5 – N1	104.3(2)	104.1(2)	107.2(4)	106.8(4)	107.1(4)	106.9(4)
C4 – C5 – C6	121.6(3)	122.4(3)	120.5(4)	121.4(4)	121.8(5)	121.2(4)
C5 – C6 – C7	115.8(4)	115.9(3)	117.3(5)	116.5(5)	116.3(5)	116.9(4)
C6 – C7 – C8	123.2(4)	122.6(3)	121.3(5)	122.2(5)	122.0(6)	121.3(5)
C7 – C8 – C9	121.7(4)	121.9(3)	122.5(5)	122.1(5)	122.0(6)	122.7(5)
C8 – C9 – C4	116.0(3)	116.4(3)	116.7(5)	116.5(5)	116.7(5)	115.8(5)
C9 – C4 – C5	121.7(3)	120.7(2)	121.7(4)	121.2(4)	121.2(4)	121.9(4)

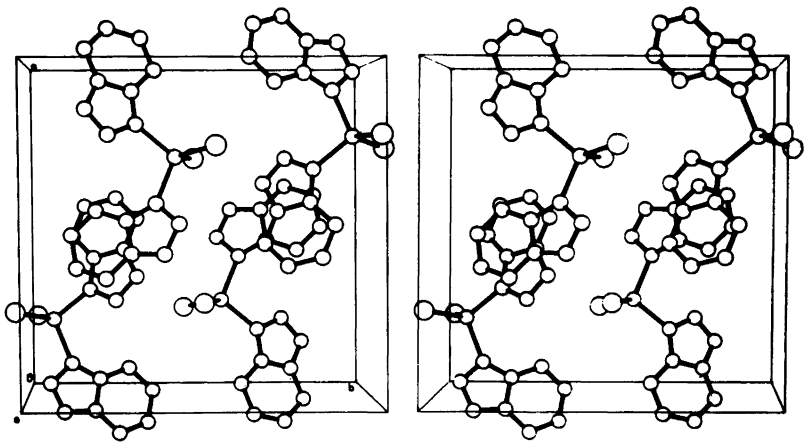

Fig. 3. Stereo view along the *a*-axis of the structure of $[Zn(BTAH)_2Cl_2]$.

Table 5. Comparison of $BTAH_2$ in $(BTAH_2)_2[CoCl_4]$, BTAH in $[ZnCl_2(BTAH)_2]$ and BTA in $[Zn_2(BTA)_4]_n$ with benzotriazole. Average values of two independent molecules for $[ZnCl_2(BTAH)_2]$ and four independent molecules for $[Zn_2(BTA)_4]_n$ and benzotriazole.

Distance (Å) or angle (°)	$(BTAH_2)_2[CoCl_4]$	$[ZnCl_2(BTAH)_2]$	$[Zn_2(BTA)_4]_n$	Benzotriazole [3]
N1–N2	1.311(4)	1.326(1)	1.337(2)	1.346(5)
N2–N3	1.313(4)	1.312(1)	1.333(1)	1.310(4)
N3–C4	1.361(4)	1.372(1)	1.375(2)	1.377(6)
C4–C5	1.390(4)	1.393(4)	1.393(1)	1.389(5)
C5–N1	1.359(4)	1.352(5)	1.368(1)	1.366(7)
C5–C6	1.397(4)	1.403(3)	1.403(2)	1.404(4)
C6–C7	1.362(5)	1.348(1)	1.368(2)	1.367(3)
C7–C8	1.410(6)	1.408(3)	1.404(4)	1.405(5)
C8–C9	1.357(5)	1.371(1)	1.364(3)	1.368(5)
C9–C4	1.398(4)	1.398(1)	1.403(2)	1.409(5)
C5–N1–N2	113.4(3)	112.2(3)	108.3(1)	110.3(7)
N1–N2–N3	104.6(3)	107.0(4)	109.8(1)	108.8(4)
N2–N3–C4	112.7(2)	109.9(2)	108.4(1)	108.2(2)
N3–C4–C5	105.1(2)	106.8(1)	106.6(1)	108.4(2)
C4–C5–N1	104.1(2)	104.2(1)	107.0(1)	104.2(4)
C4–C5–C6	122.4(3)	122.0(4)	121.2(3)	122.7(4)
C5–C6–C7	115.2(3)	115.9(1)	116.8(2)	115.3(3)
C6–C7–C8	122.2(3)	122.8(3)	121.7(2)	122.7(1)
C7–C8–C9	123.1(3)	121.8(1)	122.4(2)	122.2(2)
C8–C9–C4	115.3(3)	116.2(2)	116.4(2)	116.2(4)
C9–C4–C5	121.8(3)	121.0(5)	121.5(2)	120.9(2)

$(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$ groups are parallel, the angle between them being 0.6°. The Cl–Zn–Cl planes are therefore situated between parallel layers of BTAH ligands, but because of the tetrahedral coordination of Zn, the covering of the $ZnCl_2$-unit by benzotriazole is less pronounced than observed in the corresponding copper complex.[1] The distance between the planes through the parallel BTAH ligands is ~3.5 Å. The hydrogen-bonding distances between BTAH and Cl are the N1(BTAH1) $-Cl2(1-x,-y,-z)$ distance of 3.205(3) Å and the N1(BTAH2)$-Cl1(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ distance of 3.171(3) Å.

In the structure of $[Zn_2(BTA)_4]_n$ the Zn atoms are coordinated to four BTA ligands forming a nearly regular tetrahedron. The Zn–N bond lengths fall within values of Zn–N distances normally found in Zn-complexes. Every BTA ligand is shared by two Zn atoms forming a three-dimensional network, the N1 and N3 always being coordinated to Zn1 and Zn2, respectively (Fig. 4). The BTA ligands are almost planar, the deviations of the atoms from the least-squares plane through them being less than 0.03 Å. The metrical details of the BTA ligand are compared to those of benzotriazole[3] and $BTAH_2$ in Table 5. As the $BTAH_2$ ion the BTA ion almost

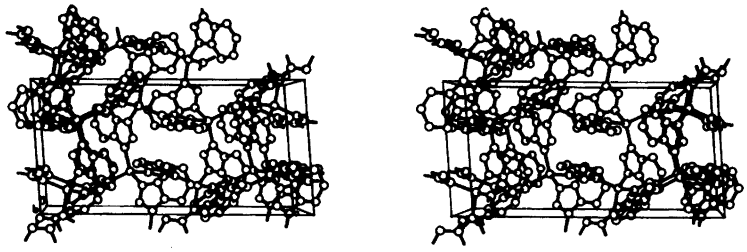

Fig. 4. Stereo view along the *b*-axis of the structure of $[Zn_2(BTA)_4]$.

has C_{2v} symmetry. A comparison of the angles of the BTA ligand in the present structure to those in other structures is carried out in Ref. 5.

THE GEOMETRY OF THE TRIAZOLE RING IN $BTAH_2$

The angles in the triazole ring of $BTAH_2$ ion resemble those found in 1,3-disubstituted 1,2,3-triazoles.[6-8] Despite individual differences in the endocyclic angles at C4 and C5 due to different substituents the sum of the two angles (209.2°) is close to the value expected for 1,3-disubstituted compounds (209.5°). The angle at N2 (104.6°) is 1.5° larger than found in the latter compounds, but an increase of this order is what would be expected by ring closure of the carbon substituents.[9] Of the distances only the C4–C5 and N2–N3 distances are comparable. When comparing the distances in $BTAH_2$ to BTA and 2*H*-triazole as determined by *ab initio* calculations,[10] the order of magnitude of the N–N bonds (average values) is 2*H*-triazole (1.352 Å) > BTA (1.334 Å) > $BTAH_2$ (1.312 Å). The C4–C5 distances for BTAH and BTA are identical (1.390 Å and 1.393 Å) but less than the one in 2*H*-triazole (1.412 Å). The order of magnitude of the C–N bonds is BTA (1.369 Å) ≥ $BTAH_2$ (1.360 Å) > 2*H*-triazole (1.317 Å). The relation between $BTAH_2$ and 2*H*-triazole are as expected from an analyses of their resonance structures. In this respect also the N–N distance of BTA fits in, whereas the C–N distance seems too large, possibly an effect of the metal atom.

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