

Benzotriazole Complexes. VI. The Crystal Structures of Catena- μ -dichlorobis(benzotriazole)-cadmium(II) and Catena- μ -dichlorobis(benzotriazole)-manganese(II)

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The present structure analyses are part of an investigation of benzotriazole complexes.¹⁻⁵ Benzotriazole is henceforth referred to as BTAH. The two structures are as far as possible described in one. Thus, when two numbers or sets of numbers are given, the first refers to the Cd-complex, and the latter to the Mn-complex.

Colourless crystals of $[\text{CdCl}_2(\text{BTAH})_2]$ were precipitated by mixing 4×10^{-4} mol of cadmium chloride monohydrate in 5 ml 0.1 M hydrochloric acid and 3×10^{-3} mol benzotriazole in 5 ml ethanol. Rose crystals of $[\text{MnCl}_2(\text{BTAH})_2]$ were precipitated by mixing 2×10^{-3} mol manganese dichloride tetrahydrate in 5 ml methanol and 3×10^{-3} mol benzotriazole in 10 ml acetone.

The determination of the possible space groups and the data collections were carried out as

described in Refs. 1 and 5, except that the upper limit for θ was 70° . The dimensions of the crystals were $0.02 \times 0.07 \times 0.25$ mm and $0.02 \times 0.05 \times 0.22$ mm. The structures were solved by Patterson technique.⁶ The refinement techniques and the references to the atomic scattering factors are those given in Ref. 1. Crystal data and R -values are listed in Table 1. The final positional parameters with ESD's are listed in Table 2. The labelling of the atoms in the benzotriazole group are as in Ref. 1. Lists of thermal parameters as well as lists of observed and calculated structure factors may be obtained from the authors on request.

Description and discussion of the structures. Bond lengths and bond angles with ESD's are listed in Tables 3 and 4. The Me atoms, situated on two-fold axes, are linked together in the y -direction by double chloride bridges, forming infinite $-\text{Me}-\text{Cl}_2-\text{Me}$ -ribbons. The octahedral coordination is completed by two $\text{Me}-\text{N}_3$ bonds. The plane of the BTAH ligand is almost perpendicular to the plane of the Me and Cl atoms, the angles being 88.2° and 89.2° . Similar coordination occurs in catena- μ -dichlorobis(imidazole)cadmium(II)⁸ and in catena- μ -dichlorobis(pyrazole)manganese(II),⁹ The $\text{Me}-\text{Cl}-\text{Me}$ angles are 92.9 and 93.5° . The $\text{Cl}-\text{Me}-\text{Cl}$ angles are 87.0 and 86.5° , in agreement with the values found in Refs. 8 and 9. The distances between the bridging Cl atoms are $3.663(2)$ and $3.507(1)$ Å, which are somewhat shorter than found in Ref. 8 [$3.785(3)$ Å] and in Ref. 9 [$3.572(1)$ Å].

The Cd-Cl distances of $2.639(2)$ and $2.631(2)$

Table 1. Crystal data.

	$[\text{CdCl}_2(\text{BTAH})_2]$	$[\text{MnCl}_2(\text{BTAH})_2]$
M	421.5	364.1
$\mu(\text{CuK}\alpha)(\text{cm}^{-1})$	159.1	111.8
Crystal system	monoclinic	monoclinic
V (Å ³)	1447.5	1424.3
a (Å)	23.125(4)	23.441(5)
b (Å)	3.818(2)	3.728(1)
c (Å)	16.680(4)	16.480(3)
β (°)	100.61(2)	98.50(2)
Space group	$C 2/c$	$C 2/c$
D_c (g cm ⁻³)	1.93	1.70
Z	4	4
Total number of reflections	1426	1401
Number of independent observations [$I \geq 2\sigma(I)$]	1198	1002
$R = \frac{\sum F_o - F_c }{\sum F_o }$	0.053	0.043
$R = \left[\frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2} \right]^{1/2}$	0.068	0.058

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 . The isotropic temperature factors for the non-hydrogen atoms are estimated from the anisotropic values.⁷

Atom	x	y	z	B_{eq}	x	y	z	B_{eq}
	[CdCl ₂ (BTAH) ₂]				[MnCl ₂ (BTAH) ₂]			
Me	0	1353(2)	2500	2.2	0	1743(3)	2500	2.4
Cl	676(1)	6368(5)	3253(1)	3.2	633(1)	6742(3)	3216(1)	2.2
N1	654(3)	2801(18)	198(4)	3.7	641(2)	2749(11)	200(2)	2.7
N2	286(3)	2880(17)	732(4)	3.5	281(2)	2938(11)	744(2)	2.6
N3	563(3)	1572(16)	1427(3)	3.4	554(1)	1856(11)	1456(2)	2.4
C4	1122(3)	671(19)	1342(4)	3.2	1105(2)	972(11)	1360(2)	2.3
C5	1184(3)	1469(19)	547(4)	3.3	1168(2)	1545(13)	544(2)	2.4
C6	1699(4)	883(23)	246(5)	4.3	1681(2)	895(14)	235(3)	3.3
C7	2162(4)	-512(26)	802(6)	4.8	2134(2)	-269(17)	790(3)	3.5
C8	2108(3)	-1318(23)	1604(5)	4.4	2082(2)	-804(14)	1622(3)	3.4
C9	1595(3)	-772(22)	1902(5)	4.0	1577(2)	-235(15)	1923(3)	3.0
H1	56(5)	392(27)	-41(7)	7.4	51(2)	328(14)	-29(3)	3.9
H2	176(5)	226(33)	-46(7)	10.2	165(2)	140(15)	-33(3)	5.5
H3	268(5)	-106(29)	69(7)	9.9	248(2)	-44(19)	64(3)	5.7
H4	247(4)	-213(24)	204(5)	5.1	242(2)	-177(13)	197(3)	3.3
H5	153(5)	-239(30)	244(7)	6.5	154(2)	-87(14)	247(3)	4.2

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in the metal coordination spheres. Superscripts refer to atoms in the following positions: a $x, y-1, z$; b $-x, y, \frac{1}{2}-z$

Atoms	[CdCl ₂ (BTAH) ₂] Distance or angle	[MnCl ₂ (BTAH) ₂] Distance or angle
Me-N3	2.401(6)	2.305(3)
Me-Cl	2.639(2)	2.559(1)
Me-Cl ^a	2.631(2)	2.560(1)
Cl-Me-N3	88.5(1)	88.8(1)
Cl-Me-N3 ^b	88.6(1)	89.7(1)
Cl-Me-Cl ^a	92.8(1)	93.5(1)
Cl-Me-Cl ^b	87.0(1)	86.5(1)
N3-Me-Cl ^a	91.4(1)	90.3(1)
N3 ^b -Me-Cl ^a	91.5(1)	91.2(1)

Å are shorter than the distances of 2.706(2) and 2.731(2) Å found in [CdCl₂(ImH₂)],⁸ but may be compared to the distances [2.60–2.73 Å] observed in polymeric- μ -imidazolocadmium (II).¹⁰ The Cd-N3 distance of 2.401(6) Å is significantly longer than those observed in imidazole complexes [2.24–2.37 Å],^{8,10-14} but falls within the range of 2.29–2.50 Å found in other octahedral complexes.¹⁵⁻¹⁸ The Cd atom lies in the least-squares plane of the BTAH ligand.

The Mn-Cl distances of 2.559(1) and 2.560(1) Å are significantly shorter than the distances of

2.592(2) and 2.594(2) Å observed in [MnCl₂py₂],⁹ but in agreement with the distances [2.48–2.61 Å] found in [Mn(glycine)Cl₂-(H₂O)₂]_n.¹⁹ The Mn-N3 distance of 2.305(3) Å is significantly longer than the distance of 2.201(3) Å found in the pyrazole complex,⁹ but lies in the interval 2.24–2.32 Å found in imidazole complexes^{20,21} and in 1,2,4-triazole complexes.^{22,23} The Mn atom lies 0.09 Å from the least-squares plane through the BTAH ligand.

The BTAH ligands in both complexes are

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

Atoms	[CdCl ₂ (BTAH) ₂] Distance or angle	[MnCl ₂ (BTAH) ₂] Distance or angle
N1–N2	1.341(9)	1.321(5)
N2–N3	1.316(8)	1.314(5)
N3–C4	1.370(9)	1.363(5)
C4–C5	1.394(10)	1.391(6)
C5–N1	1.354(9)	1.357(5)
C5–C6	1.393(11)	1.396(7)
C6–C7	1.388(11)	1.366(6)
C7–C8	1.400(13)	1.409(7)
C8–C9	1.384(12)	1.366(7)
C9–C4	1.413(10)	1.409(6)
N1–H1	1.08(11)	0.84(5)
C6–H2	1.32(12)	0.94(6)
C7–H3	1.27(12)	0.89(6)
C8–H4	1.05(8)	0.98(4)
C9–H5	1.12(12)	0.95(5)
C5–N1–N2	110.9(6)	111.5(3)
N1–N2–N3	108.1(6)	108.3(3)
N2–N3–C4	108.7(6)	108.4(3)
N3–C4–C5	107.9(5)	108.2(3)
C4–C5–N1	104.4(6)	103.6(4)
C4–C5–C6	123.5(6)	123.2(4)
C5–C6–C7	115.3(8)	115.9(4)
C6–C7–C8	121.9(8)	121.8(5)
C7–C8–C9	122.9(7)	122.4(4)
C8–C9–C4	115.6(7)	116.7(4)
C9–C4–C5	120.8(7)	119.9(4)

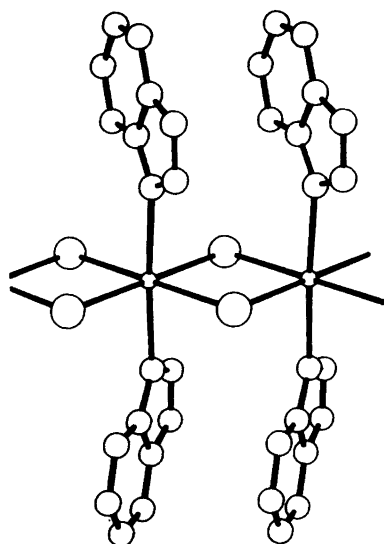


Fig. 1. The coordination around the metal atoms.²⁵

nearly planar, the deviations of the atoms from the least-squares plane through them being less than 0.01 and 0.02 Å. The sum of the endocyclic angles at C4 and C5 (Table 4) may be compared to idealized values (Ref. 3, Table 6 and Ref. 4). A comparison shows that the angles in the triazole group of the two complexes correspond to intermediates between 1- and 1,3-substituted compounds, however more to 1-substituted compounds. This is in agreement with the rather long Me–N bond observed in both complexes.

The packing of the structure is shown in Fig. 2. The angles between the *ac*-plane and the plane through BTAH are 23.2 and 19.3° for the two compounds. The angles between the BTAH planes and the *ab*- and *bc*-plane range from 71 to 78°. The distances between the least-squares planes are 3.509 and 3.520 Å. The hydrogen-bonding distances between BTAH and Cl are the N1–Cl(*x*, 1–*y*, *z*–½) distances of 3.267(7) and 3.271(4) Å. The N1–N2(–*x*, 1–*y*, –*z*) distances of 2.934(9) and 2.947(5) Å constitute hydrogen bonds between two BTAH groups belonging to

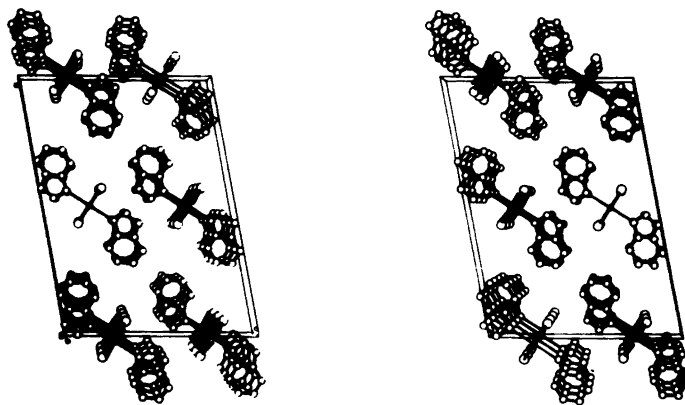


Fig. 2. Stereo view along the *b*-axis of the structure.

different chains. They are, however, rather weak compared to those found in other compounds.²⁴ The shortest non-bonded distances [3.724(12) and 3.743(7) Å] between the chains at $x=0$ and $x=\frac{1}{2}$ are found from C8($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$).

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