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Crystal and Molecular Structure of Chlorodithiabendazolecopper(II) Chloride Dihydrate

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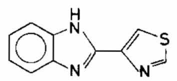
The crystal and molecular structure of chlorodithiabendazolecopper(II) chloride dihydrate was determined by three-dimensional X-ray diffraction studies and least squares methods. The pale green crystals are monoclinic, space group $P2_1/c$ with unit cell parameters, a = 14.778(3), b = 11.713(2), c = 14.100(3) Å, β = 101.61(2)° and Z = 4. The structure was solved by direct methods from 2098 reflections collected on a four-circle diffractometer and was refined to an R index of 0.049. Each thiabendazole molecule is bidentate chelating and is bonded to copper through the nitrogen atoms of the thiazolyl and benzimidazole rings in cis-*configuration. The coordination around copper is completed by one of the two chlorine atoms resulting in a distorted trigonal bipyramidal arrangement. There is an extensive hydrogen bonding involving the water molecules, chlorine atoms and the protonated nitrogen atoms of the ligand.*

Introduction

2-(4′-Thiazolyl)-benzimidazole, also known as thiabendazole is a widely used [1] anthelmintic and



fungistatic agent and is useful in the treatment of parasitic diseases of human beings and animals. Though its chelating ability is known quite some time back [1], interest is shown in recent years [2–5] to isolate and characterize its metal complexes, particularly the water soluble complexes which are suitable for oral administration. The structural informations on its metal complexes suggest that thiabendazole resembles ligands such as 2,2′-dipyridine and 1,10-phenanthroline in its bonding to metal atoms. In this paper we report the crystal and molecular structure of chlorodithiabendazolecopper(II) chloride dihydrate.

Experimental

Chlorodithiabendazolecopper(II) chloride dihydrate was prepared by adding an alcoholic solution of copper(II) chloride to a hot alcoholic solution of thiabendazole in 1:2 molar ratio. The mixture was then stirred for some time and the precipitated pale green product was filtered, washed with acetone and ether. Single crystals of the sample were obtained by slow evaporation of the methanolic solution of the complex. *Anal.*: found: C 41.87, H 3.38, N 15.44, Cu 11.15; calcd. for $[CuC_{20}H_{18}N_6S_2O_2Cl_2]$: C 41.92, H 3.17, N 14.67, Cu 11.09%.

Preliminary Weissenberg and precession photographs suggested the crystals belonging to the monoclinic system. The systematic absences 0k0, k = 2n + 1, h0l, l = 2n + 1 indicated the space group $P2_1/c$ (C^5_{2h}, No. 14). The crystal data after least squares refinement of the diffractometer coordinates for 15 reflections are a = 14.778(3), b = 11.713(2), c = 14.100(3) Å, β = 101.61(2)°, V = 2390.7 Å^3. There are four molecules per unit cell and the calculated and measured densities are 1.592 and 1.58(1) g/cm^3 respectively.

X-ray intensity data of a prismatic crystal of approximate dimensions 0.01 × 0.09 × 0.12 mm^3 were collected at 22 °C on a Syntex $P2_1$ four-circle diffractometer using monochromated MoKα radiation (λKα_1 0.70926 Å, λKα_2 0.71354 Å, ω–2θ scan, scintillation counter, take-off angle 6°). The sampling interval for each reflection was from 1.0° (in 2θ) below the calculated MoKα_1 maximum to 1.0° above the MoKα_2 maximum. Depending on the intensity of the reflection, the scan rate was varied from 2° min^{-1} to 15° min^{-1} (in 2θ). Background measurements with the total time for background counts being equal to the scan time were made at the starting and end of each scan with the counter stationary. A reference reflection was measured for every 50 reflections. A complete set of 3770 unique reflections was measured up to $(\sin\theta)/\lambda$ = 0.57 Å^{-1}, out of which 2098 reflections were accepted as statistically above background on the basis that $I \geqslant 1.96\ \sigma(I)$. The linear absorption coefficient was calculated to be 13.7 cm^{-1} and hence no absorption

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TABLE I. Coordinates of the Atoms in the Unit Cell of Chlorodithiabendazolecopper(II) Chloride Dihydrate.[a]

	x	y	z
Cu	0.74178(6)	0.47621(8)	0.30403(7)
Cl1	0.68089(14)	0.54845(17)	0.43046(14)
Cl2	0.20570(14)	0.42841(18)	0.16235(16)
S1	0.64033(16)	0.09793(18)	0.20997(16)
S2	0.92127(16)	0.56119(21)	0.08047(16)
O1	0.3413(4)	0.3270(5)	0.0489(5)
O2	0.1844(4)	0.3642(6)	0.3700(5)
N1	0.6913(4)	0.3009(5)	0.2583(4)
N2	0.4944(4)	0.4575(6)	0.1198(4)
N3	0.6293(4)	0.5105(6)	0.2087(4)
N4	0.8294(4)	0.5154(5)	0.2094(4)
N5	0.0087(4)	0.3923(6)	0.3956(5)
N6	0.8598(4)	0.4237(5)	0.3828(4)
C1	0.7162(5)	0.1952(8)	0.2715(6)
C2	0.5693(6)	0.2074(7)	0.1637(6)
C3	0.6072(5)	0.3071(7)	0.1973(5)
C4	0.5748(5)	0.4241(7)	0.1757(5)
C5	0.4953(5)	0.5752(8)	0.1166(5)
C6	0.4302(6)	0.6544(8)	0.0700(5)
C7	0.4543(7)	0.7678(9)	0.0830(6)
C8	0.5394(8)	0.7992(8)	0.1370(8)
C9	0.6038(6)	0.7218(8)	0.1831(6)
C10	0.5803(6)	0.6070(7)	0.1732(6)
C11	0.8222(5)	0.5592(7)	0.1240(7)
C12	0.9774(5)	0.5020(7)	0.1864(6)
C13	0.9192(5)	0.4828(6)	0.2458(5)
C14	0.9318(5)	0.4333(6)	0.3412(5)
C15	0.9871(5)	0.3528(6)	0.4806(5)
C16	0.0412(6)	0.3047(7)	0.5632(6)
C17	0.9961(7)	0.2758(7)	0.6360(6)
C18	0.9020(7)	0.2939(8)	0.6262(7)
C19	0.8488(6)	0.3424(7)	0.5467(6)
C20	0.8932(5)	0.3729(6)	0.4717(6)
H1	0.773(5)	0.172(6)	0.314(5)
H2	0.519(4)	0.193(6)	0.116(5)
H3	0.449(5)	0.413(6)	0.097(5)
H4	0.353(4)	0.624(5)	0.026(4)
H5	0.405(4)	0.825(5)	0.051(4)
H6	0.554(5)	0.870(6)	0.133(5)
H7	0.663(4)	0.743(5)	0.227(5)
H8	0.766(4)	0.583(6)	0.089(5)
H9	0.035(4)	0.484(6)	0.196(5)
H10	0.057(5)	0.389(6)	0.385(5)
H11	0.110(5)	0.298(5)	0.571(5)
H12	0.029(4)	0.247(5)	0.697(5)
H13	0.875(4)	0.275(6)	0.679(5)
H14	0.779(5)	0.355(5)	0.536(5)
H15	0.336(5)	0.256(6)	0.052(5)
H16	0.307(5)	0.344(6)	0.089(5)
H17	0.216(5)	0.394(7)	0.416(5)
H18	0.192(5)	0.381(6)	0.312(5)

[a] Estimated standard deviations are given in all tables in parentheses in units of the last significant digits.

correction was made. Data reduction was done applying Lorentz and polarization corrections including a Wilson plot.

Determination and Refinement of the Structure

The structure was solved by direct methods, using the MULTAN programme system [6]. Most of the non-hydrogen atoms were located from the E-map and the remaining ones from the subsequent difference Fourier map. All hydrogen atoms were found from ΔF-maps calculated after isotropic refinement of the non-hydrogen atoms. The atomic scattering factors for Cu, Cl, S, O, N, C and H were taken from the International Tables [7]. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors fixed at 6.0 for the hydrogen atoms converged to residuals of $R_1 = 0.049$ (including unobserved data: 0.087), $R_2 = 0.038$ where $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The anisotropic refinement of O, N, and C was justified according to Hamilton's statistical test. The weighting scheme was based on the counting statistics of the intensities. Reflections with $F_o \leqslant 3.92\sigma(F_o)$ were given zero weight. The shifts in the final cycle were below 0.02σ. The final difference Fourier map had no significant features. The final positional and thermal parameters of the atoms are given in Tables I

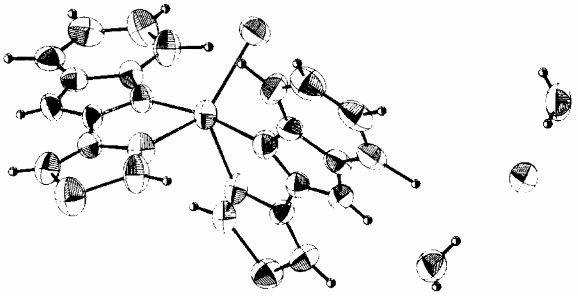

Figure 1a. ORTEP plot of the asymmetric unit of the chlorodithiabendazolecopper(II) chloride dihydrate structure (ellipsoids drawn to 50% probability, except hydrogen).

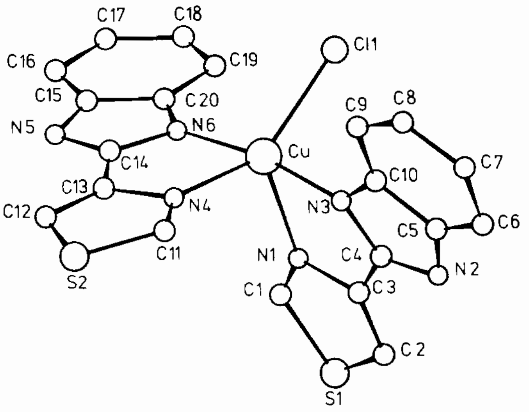

Figure 1b. Chlorodithiabendazolecopper(II) cation with atom numbering.

TABLE II. Coefficients of the Anisotropic Temperature Factors[a] of the Atoms in the Chlorodithiabendazolecopper(II) Chloride Dihydrate Structure.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.47(4)	3.72(5)	3.80(5)	0.19(4)	0.38(4)	0.27(5)
Cl1	4.47(11)	4.69(12)	4.10(11)	0.84(9)	1.01(9)	−0.44(9)
Cl2	3.97(11)	5.24(14)	6.12(13)	−0.45(9)	1.00(10)	−1.32(10)
S1	4.88(2)	3.30(11)	4.99(12)	−0.14(10)	1.15(10)	−0.14(9)
S2	4.78(12)	6.84(16)	4.48(12)	0.32(11)	1.52(10)	1.79(10)
O1	4.4(3)	4.2(3)	5.6(4)	−0.4(3)	1.1(3)	−0.3(3)
O2	3.1(3)	8.5(5)	5.5(4)	0.2(3)	0.7(3)	−0.1(4)
N1	2.7(3)	3.5(4)	4.1(4)	0.0(3)	0.4(3)	0.7(3)
N2	2.9(4)	3.4(5)	3.8(4)	−0.1(3)	0.6(3)	−0.1(3)
N3	3.0(3)	3.5(4)	4.0(3)	−0.1(3)	0.6(3)	−0.2(3)
N4	3.4(3)	3.5(3)	3.3(3)	0.3(3)	0.6(3)	1.4(3)
N5	2.7(4)	3.5(3)	3.5(4)	0.6(3)	0.9(3)	0.0(3)
N6	2.6(3)	3.2(3)	3.1(3)	0.4(3)	0.5(3)	0.5(3)
C1	2.7(4)	4.4(5)	4.0(5)	0.1(4)	0.6(4)	0.8(4)
C2	3.8(5)	4.2(5)	3.2(4)	−0.5(4)	−0.4(3)	−0.5(4)
C3	2.8(4)	3.3(4)	2.9(4)	−0.6(3)	0.5(3)	−0.1(3)
C4	2.4(4)	3.7(5)	2.6(4)	0.4(4)	0.6(3)	0.4(3)
C5	3.7(5)	3.8(5)	2.4(4)	0.9(4)	0.8(3)	−0.1(3)
C6	3.9(5)	5.0(5)	2.7(4)	1.7(4)	0.7(3)	−0.2(4)
C7	5.7(6)	4.6(6)	4.2(5)	1.7(5)	1.5(5)	0.2(4)
C8	6.7(7)	4.3(6)	6.0(6)	0.2(6)	2.8(5)	0.4(5)
C9	3.4(5)	4.4(6)	4.5(5)	−0.4(4)	0.2(4)	−0.3(4)
C10	3.3(5)	3.2(5)	3.4(4)	0.3(4)	0.7(4)	−0.5(4)
C11	3.0(4)	5.2(5)	5.3(5)	0.8(4)	0.4(4)	1.9(4)
C12	2.7(4)	4.7(5)	4.3(4)	0.1(4)	0.2(4)	0.4(4)
C13	2.6(4)	3.0(4)	3.2(4)	0.3(3)	0.5(3)	0.2(3)
C14	2.1(3)	2.5(4)	3.7(4)	0.4(3)	0.4(3)	−0.2(3)
C15	3.4(5)	2.1(4)	3.1(5)	0.3(3)	0.3(4)	−0.0(3)
C16	4.0(5)	3.1(4)	4.0(5)	0.7(4)	0.2(4)	−0.9(4)
C17	5.7(6)	3.9(5)	3.6(5)	1.2(4)	0.7(4)	0.3(4)
C18	5.0(6)	4.9(5)	5.0(6)	0.5(4)	2.0(5)	1.7(4)
C19	3.1(4)	4.8(5)	4.8(5)	0.7(4)	0.6(4)	1.4(4)
C20	2.8(4)	2.7(4)	3.6(4)	0.1(3)	0.9(3)	0.4(3)

[a] The anisotropic temperature factors are expressed in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

and II. A Table of the calculated and observed structure factors is available from the Editor.

Results and Discussion

The crystal structure consists of $[CuCl(thiabendazole)_2]^+$ units linked through hydrogen bonds involving the protonated nitrogen atoms of the benzimidazole rings, water molecules and chlorine atoms. A view of the complete $[CuCl(thiabendazole)_2]^+$ ion is shown in Fig. 1a, the atom designations being given in Fig. 1b. It is clear from Fig. 1 that both ligand molecules are bonded to the copper atom through a nitrogen atom of the thiazolyl ring and one of the nitrogen atoms of the benzimidazole ring in *cis* configuration to form two 5-membered bidentate chelate rings. One of the chlorine atoms completes the 5-coordinated geometrical arrangement around copper. The coordination polyhedron of copper may be described as a distorted trigonal bipyramid.

A distorted trigonal basal plane is formed by the atoms Cl1, N1, and N4. The corresponding least squares equation of the plane containing Cu is $-0.6487x + 0.3889y - 0.6542z + 7.1284 = 0$, where x, y and z are related to the monoclinic axes of the crystal in Å units. The maximum deviations from the plane are 0.02 Å for N1 and N4. However, the trigonal angles deviate from 120° in the sense that the *trans* direction to the weakly bonded N1 is avoided by the other ligand atoms (Table III). The other two ligating atoms, N3 and N6, approach the basal plane approximately at right angles. To a very rough approximation, the Cu coordination can also be considered as being tetragonal pyramidal with a Cl1–N3–N4–N6 basal plane (however large deviations

TABLE III. Interatomic Distances and Bond Angles.

Distances (Å)		*Angles* (°)	
Cu Coordination			
Cu–Cl1	2.313(2)	Cl1–Cu–N1	113.6(2)
Cu–N1	2.235(6)	Cl1–Cu–N3	92.6(2)
Cu–N3	1.958(6)	Cl1–Cu–N4	143.1(2)
Cu–N4	2.088(6)	Cl1–Cu–N6	96.7(2)
Cu–N6	1.968(6)	N1–Cu–N3	78.6(2)
		N1–Cu–N4	103.4(2)
		N1–Cu–N6	94.7(2)
		N3–Cu–N4	93.8(2)
		N3–Cu–N6	170.1(3)
		N4–Cu–N6	80.6(2)
Thiabendazole Molecules			
C1–S1	1.708(9)	C1–S1–C2	89.1(4)
C2–S1	1.701(9)	C11–S2–C12	88.9(4)
C11–S2	1.698(9)	Cu–N1–C1	140.2(6)
C12–S2	1.704(8)	Cu–N1–C3	110.0(5)
C1–N1	1.294(11)	C1–N1–C3	109.8(7)
C3–N1	1.363(10)	Cu–N3–C4	117.3(5)
C4–N2	1.345(10)	Cu–N3–C10	136.7(5)
C4–N3	1.319(10)	C4–N3–C10	105.2(6)
C5–N2	1.380(11)	C4–N2–C5	107.3(6)
C10–N3	1.380(11)	Cu–N4–C11	137.5(5)
C11–N4	1.294(11)	Cu–N4–C13	112.1(4)
C13–N4	1.378(9)	C11–N4–C13	110.4(6)
C14–N5	1.326(10)	Cu–N6–C14	115.1(5)
C14–N6	1.320(9)	Cu–N6–C20	139.4(5)
C15–N5	1.380(10)	C14–N6–C20	105.5(6)
C20–N6	1.385(10)	C14–N5–C15	107.7(6)
C2–C3	1.341(12)	N1–C1–S1	115.3(6)
C3–C4	1.463(11)	C3–C2–S1	109.8(6)
C5–C6	1.401(12)	C2–C3–N1	116.1(7)
C5–C10	1.397(11)	C2–C3–C4	130.3(8)
C6–C7	1.378(14)	C4–C3–N1	113.6(7)
C7–C8	1.383(15)	C3–C4–N2	127.4(7)
C8–C9	1.378(14)	C3–C4–N3	119.6(7)
C9–C10	1.389(13)	N2–C4–N3	112.9(7)
C12–C13	1.334(10)	C6–C5–N2	131.8(8)
C13–C14	1.442(10)	C6–C5–C10	123.1(8)
C15–C16	1.392(11)	C10–C5–N2	105.1(7)
C16–C17	1.374(13)	C7–C6–C5	116.1(8)
C17–C18	1.386(14)	C6–C7–C8	120.8(9)
C18–C19	1.357(13)	C7–C8–C9	123.4(10)
C19–C20	1.398(12)	C8–C9–C10	117.0(9)
		C9–C10–C5	119.5(8)
		C9–C10–N3	130.9(8)
		C5–C10–N3	109.6(7)
		N4–C11–S2	115.3(6)
		C13–C12–S2	110.9(6)
		C12–C13–N4	114.5(7)
		C12–C13–C14	132.4(7)
		C14–C13–N4	113.1(6)
		C13–C14–N5	128.3(7)
		C13–C14–N6	119.1(6)
		N5–C14–N6	112.6(6)
		C16–C15–C20	127.7(7)
		N5–C15–C20	105.4(6)
		N5–C15–C16	131.9(7)
		C15–C16–C17	116.2(8)
		C16–C17–C18	121.0(9)
		C17–C18–C19	123.3(9)
		C18–C19–C20	116.7(8)
		C19–C20–N6	131.1(7)
		C19–C20–C15	120.0(7)
		C15–C20–N6	108.8(6)

of up to 0.54 Å for N4 from the best plane) and with N1 at the apex.

The Cu–Cl and Cu–N bond distances (Table III) in the complex are comparable with those found in other similar copper(II) complexes [8–12]. The Cu–Cl1 distance of 2.313(2) is close to the sum of the covalent radii (2.27 Å) given by Pauling [13]. The lengthening of the distance may be ascribed partly to the hydrogen bonding involving the Cl1 atom. The other chlorine atom is separated by 5.360(2) Å from copper. Bonded neighbors to this ionic Cl2 are, besides the hydrogen-bonded O1–H16 and O2–H18 groups (Table IV) one S1 (distance 3.273(3) Å) and one S2 (3.560(3) Å) out of neighboring thiabendazol ligands. The distances Cu–N3, Cu–N4 and Cu–N6 are normal, being in line with bond lengths ranging from 1.95 to 2.03 Å reported for Cu–N complexes of neutral bidentate ligands [14–19]. The "axial" bond length Cu–N1 (2.235(6) Å) is significantly longer than the others. Similarly it is reported [20] that the apical bond distances in the complex tris(2,2′-bipyridyl)copper(II) perchlorate are 2.226(7) and 2.450(7).

Due to bond participation of lone pair electrons from the secondary nitrogen and sulphur atoms, the delocalized π system makes the thiabendazole molecule virtually planar [21]. The least squares equations of the planes through all non-hydrogen atoms of the thiabendazol ligands containing S1 and S2 are $0.6083x + 0.0119y - 0.7936z - 3.0794 = 0$ and $-0.1213x - 0.9068y - 0.4037z + 8.0389 = 0$. The maximum deviation of atoms within the planes is 0.14 and 0.02 Å, respectively. The angle between the normals to the planes is 79.4°. The large deviation in the first case is due to a twist of 6.5° of the (precisely planar) benzimidazol and thiazolyl parts of the molecule around the C3–C4 bond.

The bond lengths and bond angles in the two ligand molecules are not deviating significantly from those found in the free ligand [21]. As expected, due to the highly conjugated system, the C–N bond distances involving the nitrogen atom bonded to copper, are not influenced much by complex formation. However, it is interesting to note that in the free ligand the protonated benzimidazole nitrogen

TABLE IV. Hydrogen Bonding in the Crystal Structure of Chlorodithiabendazolecopper(II) Chloride Dihydrate.

Distances (Å)				*Angles* (°)
A–H...B	A–H	H...B	A...B	AHB
O1–H15...Cl1	0.84(6)	2.46(6)	3.297(6)	172(6)
O1–H16...Cl2	0.85(7)	2.22(7)	3.046(7)	163(7)
O2–H17...Cl1	0.80(7)	2.48(7)	3.267(7)	170(7)
O2–H18...Cl2	0.87(7)	2.23(7)	3.100(7)	178(7)
N2–H3...O1	0.87(7)	1.89(7)	2.747(9)	174(7)
N5–H10...O2	0.76(7)	1.96(7)	2.713(9)	172(8)

and the thiazolyl nitrogen atoms are in *cis*-configuration [21] whereas in the complex the two are *trans* to each other. Experimental C–H and N–H bond distances are observed between 0.76(7) and 1.21(7) Å.

In Table IV the hydrogen bond distances and angles are listed. It can be clearly seen that the water molecules are strongly hydrogen bonded to the ionic chlorine atom, [O1...C12, 3.046(7), O2...C12, 3.100(7)] and weakly hydrogen bonded to the coordinated chlorine atom [O2...Cl1, 3.297(6), O2...Cl1, 3.267(7)]. Further, each water oxygen atom accepts a hydrogen bond from the imino group of the ligand.

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