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Short Communication

Preparation and Crystal Structure of Copper(II) Chloride Complex with (±)-*trans*-1,2-Cyclohexanediol and Tetrahydrofuran in the Molar Ratio $1{:}1\frac{1}{2}{:}\frac{1}{2}$

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We have prepared coordination compounds of copper(II) chloride that have 1,2-cyclohexanediols as neutral ligands. When trying to prepare compounds that have the formula $CuCl_2 \cdot$ 2diol (diol=(±)-*trans*- or *cis*-1,2-cyclohexanediol), it was found difficult to obtain well-defined compounds in tetrahydrofuran (THF). However, good crystals of $CuCl_2 \cdot$ 2diol compounds can be grown in 1,2-dimethoxyethane (DME), and their molecular and crystal structures have been studied.[1] From the THF solution, however, it is possible to isolate compounds that have the formula $CuCl_2 \cdot$ 1.5diol · 0.5THF. In this paper we describe the preparation and the molecular and crystal structure of the complex $CuCl_2 \cdot$ 1.5*trans*-chd · 0.5THF.

The compound was prepared by dissolving diol[2] (22.4 mmol) and $CuCl_2$ (11.2 mmol) in 50 ml of THF, and 20 ml of hexane was added. The solution was allowed to stand for two weeks at room temperature in a closed vessel. Green crystals were separated by decantation and washed twice with ethyl ether. The yield was 1.60 g (41.4 %). Analysis for Cu, Cl and diol was performed by standard titrimetric methods. Found: Cu 18.4; Cl 20.8; diol 51.2. Calc. for $Cu_2Cl_4C_{22}H_{44}O_7$: Cu 18.4; Cl 20.6; diol 50.5.

Single-crystal X-ray diffraction measurements were made with SYNTEX $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite-monochromatized MoK_α radiation. Unit cell parameters were calculated using least squares refinements of 24 reflections. The intensities were recorded using the $\theta/2\theta$ scan technique with varying scan speed (1.5–29.3° min^{-1}) depending on the peak intensity of the reflection. Systematic absences in the reflections showed that the space group is $P2_1/c$.

The crystals of $Cu_2Cl_4C_{22}H_{44}O_7$ are monoclinic with the following cell dimensions: a=8.120(2) Å, b=34.90(2) Å, c=11.132(4) Å, β=105.71(2)°. There are four formula units in the unit cell (D_m=1.50(2) gcm^{-3}, D_c=1.495 gcm^{-3}) and μ(MoK_α) is 17.1 cm^{-1}.

The intensity of one check reflection decreased by 34 %. Correction was applied for crystal decay and Lp, but not for absorption. Out of 5390 independent reflections 2660 intensities having $I>2.0\sigma(I)$ were considered as observed.

The structure was solved with direct methods, which gave positional parameters for Cu and Cl atoms. The atomic scattering factors and anomalous dispersion correction factors for non-hydrogen atoms were taken from *International Tables*.[3] The structure was refined with non-hydrogen and hydrogen atoms having anisotropic and isotropic temperature factors, respectively. As all the C–H hydrogen atoms could not be found in the difference map, their positions were calculated assuming the C–H distances to be 1.0 Å. The coordinates of H(O3) were fixed to those found in the difference map. Omission of 86 poorly agreeing reflections led to final R and R_w values of 0.055 and 0.045, respectively, where $R=\Sigma\Delta/\Sigma F_o$, $R_w=\Sigma\sqrt{w}\Delta/\Sigma\sqrt{w}F_o$, $\Delta=|F_o-F_c|$ and $w=2.916/(\sigma^2(F_o)+0.0003F_o^2)$. Omission of 86 reflections was thought to be reasonable on the basis of the analysis of variances.

All crystallographic computations were performed with program SHELX-76[4] and the figure was drawn with ORTEP-II.[5] The final positional parameters with equivalent temperature factors for non-hydrogen atoms of the complex are given in Table 1.

The temperature factors for the C–H hydrogen atoms refined to the range 0.07(1)–0.19(2) $Å^2$ and for all O–H hydrogen atoms to 0.06(1) $Å^2$. The structure factors and anisotropic thermal parameters may be obtained from the authors (R.S.). The labelling of the atoms is indicated in Fig. 1, where an asymmetric unit is depicted.

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2) with their e.s.d.'s for the non-hydrogen atoms of $CuCl_2$ · 1.5*trans*-chd · 0.5THF. The temperature factors are of the form $U_{eq}=(U_{11}+U_{22}+U_{33}+2U_{13}\cos\beta)/3$.

	x	y	z	U_{eq}
Cu(1)	0.10759(12)	0.38173(3)	0.65858(9)	0.04659(36)
Cu(2)	0.53615(12)	0.36749(3)	0.82631(9)	0.04335(35)
Cl(1)	0.2499(2)	0.4103(1)	0.8404(2)	0.0488(7)
Cl(2)	0.1910(3)	0.4234(1)	0.5357(2)	0.0738(10)
Cl(3)	0.3536(3)	0.3284(1)	0.6939(2)	0.0528(8)
Cl(4)	0.5810(3)	0.3326(1)	0.9967(2)	0.0604(9)
O(1)	−0.0190(7)	0.3473(2)	0.7442(5)	0.0468(21)
O(2)	−0.0609(7)	0.3598(2)	0.5097(5)	0.0547(23)
O(3)	0.5511(6)	0.3992(1)	0.6813(4)	0.0477(20)
O(4)	0.7206(7)	0.4046(2)	0.9125(5)	0.0482(22)
O(5)	0.1716(8)	0.3138(2)	0.9408(5)	0.0567(24)
O(6)	0.0427(8)	0.3813(2)	1.0328(5)	0.0594(25)
O(7)	−0.2523(8)	0.4091(2)	0.3503(6)	0.0867(29)
C(1)	−0.0899(10)	0.3161(2)	0.6634(7)	0.0470(31)
C(2)	−0.1827(10)	0.3334(2)	0.5433(8)	0.0515(32)
C(3)	−0.2523(11)	0.3040(2)	0.4444(7)	0.0559(33)
C(4)	−0.3683(11)	0.2760(3)	0.4926(9)	0.0729(41)
C(5)	−0.2831(11)	0.2601(2)	0.6158(8)	0.0648(38)
C(6)	−0.2044(10)	0.2903(2)	0.7138(7)	0.0491(32)
C(7)	0.6224(10)	0.4363(2)	0.7196(7)	0.0442(30)
C(8)	0.7750(10)	0.4291(2)	0.8266(7)	0.0478(31)
C(9)	0.8570(11)	0.4655(2)	0.8841(8)	0.0599(37)
C(10)	0.9035(13)	0.4898(3)	0.7852(9)	0.0764(42)
C(11)	0.7524(13)	0.4963(3)	0.6715(9)	0.0843(49)
C(12)	0.6688(11)	0.4589(3)	0.6185(8)	0.0635(38)
C(13)	0.1260(12)	0.3142(2)	1.0588(8)	0.0556(36)
C(14)	0.1452(11)	0.3531(3)	1.1150(7)	0.0553(34)
C(15)	0.0957(12)	0.3532(3)	1.2369(8)	0.0694(39)
C(16)	0.1996(13)	0.3243(4)	1.3257(8)	0.0851(49)
C(17)	0.1789(13)	0.2853(3)	1.2696(9)	0.0810(46)
C(18)	0.2237(11)	0.2841(3)	1.1443(8)	0.0615(37)
C(19)	−0.1961(14)	0.4416(4)	0.2984(12)	0.1176(60)
C(20)	−0.3379(15)	0.4588(4)	0.2118(13)	0.1221(66)
C(21)	−0.4736(16)	0.4294(4)	0.1821(11)	0.1058(58)
C(22)	−0.4219(14)	0.4004(4)	0.2846(11)	0.1050(54)

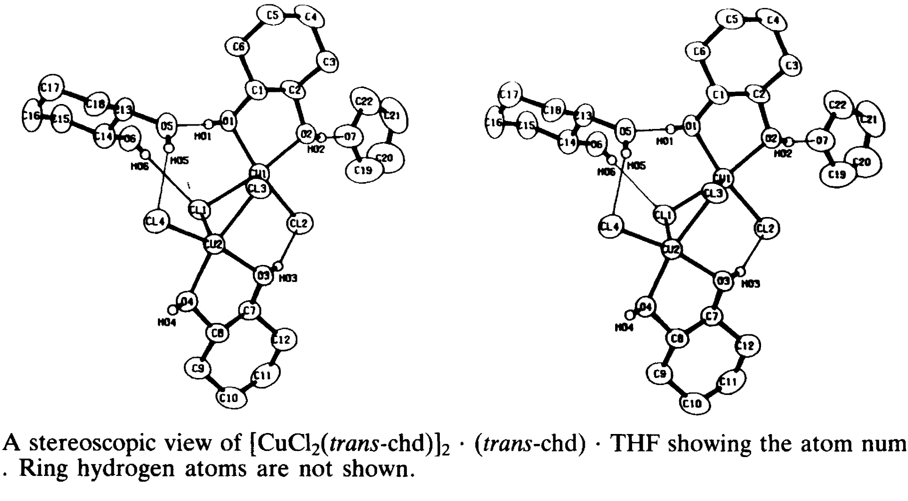

Fig. 1. A stereoscopic view of $[CuCl_2(trans\text{-chd})]_2$ · (*trans*-chd) · THF showing the atom numbering scheme. Ring hydrogen atoms are not shown.

Table 2. Distances (Å) and bond angles (°) around the copper atoms in the complex.

Cu(1)–Cl(1)	2.272(2)	Cu(2)–Cl(3)	2.247(2)
Cu(1)–Cl(2)	2.225(2)	Cu(2)–Cl(4)	2.199(2)
Cu(1)–Cl(3)	2.680(2)	Cu(2)–Cl(1)	2.804(2)
Cu(1)–O(1)	1.984(6)	Cu(2)–O(3)	1.988(5)
Cu(1)–O(2)	1.995(5)	Cu(2)–O(4)	2.016(5)
Cu(1)···Cu(2)	3.511(1)		
Cl(1)–Cu(1)–Cl(2)	95.4(1)	Cl(3)–Cu(2)–Cl(4)	99.0(1)
Cl(1)–Cu(1)–Cl(3)	89.7(1)	Cl(3)–Cu(2)–Cl(1)	87.2(1)
Cl(1)–Cu(1)–O(1)	92.5(2)	Cl(3)–Cu(2)–O(3)	88.8(2)
Cl(1)–Cu(1)–O(2)	168.0(2)	Cl(3)–Cu(2)–O(4)	167.3(2)
Cl(2)–Cu(1)–Cl(3)	101.9(1)	Cl(4)–Cu(2)–Cl(1)	101.1(1)
Cl(2)–Cu(1)–O(1)	167.1(2)	Cl(4)–Cu(2)–O(3)	167.4(2)
Cl(2)–Cu(1)–O(2)	89.7(2)	Cl(4)–Cu(2)–O(4)	90.9(2)
Cl(3)–Cu(1)–O(1)	88.4(2)	Cl(1)–Cu(2)–O(3)	89.0(2)
Cl(3)–Cu(1)–O(2)	99.9(2)	Cl(1)–Cu(2)–O(4)	98.7(2)
Cl(1)–Cu(1)–O(2)	80.7(2)	O(3)–Cu(2)–O(4)	80.1(2)
Cu(1)–Cl(1)–Cu(2)	86.8(1)	Cu(1)–Cl(3)–Cu(2)	90.4(1)

Table 3. Distances (Å) and bond angles (°) around the oxygen and carbon atoms of the coordinated diol units in the complex.

Diol 1		Diol 2	
C(1)–O(1)	1.429(9)	C(7)–O(3)	1.435(8)
C(2)–O(2)	1.471(9)	C(8)–O(4)	1.439(9)
C(1)–C(2)	1.474(10)	C(7)–C(8)	1.489(10)
C(2)–C(3)	1.500(10)	C(8)–C(9)	1.496(10)
C(3)–C(4)	1.551(12)	C(9)–C(10)	1.516(12)
C(4)–C(5)	1.468(12)	C(10)–C(11)	1.522(12)
C(5)–C(6)	1.526(10)	C(11)–C(12)	1.516(12)
C(6)–C(1)	1.508(10)	C(12)–C(7)	1.504(11)
O(1)–H(O1)	0.72(8)	O(3)–H(O3)	0.93
O(2)–H(O2)	0.91(7)	O(4)–H(O4)	0.77(7)
O(1)···O(2)	2.576(7)	O(3)···O(4)	2.577(7)
O(1)–C(1)–C(2)	106.2(6)	O(3)–C(7)–C(8)	105.5(6)
O(1)–C(1)–C(6)	113.9(6)	O(3)–C(7)–C(12)	114.4(7)
O(2)–C(2)–C(1)	105.8(6)	O(4)–C(8)–C(7)	107.0(6)
O(2)–C(2)–C(3)	112.7(7)	O(4)–C(8)–C(9)	113.7(7)
C(1)–C(2)–C(3)	112.7(7)	C(7)–C(8)–C(9)	112.2(7)
C(2)–C(3)–C(4)	108.7(7)	C(8)–C(9)–C(10)	109.5(7)
C(3)–C(4)–C(5)	112.7(7)	C(9)–C(10)–C(11)	112.6(8)
C(4)–C(5)–C(6)	114.0(7)	C(10)–C(11)–C(12)	111.7(8)
C(5)–C(6)–C(1)	109.2(7)	C(11)–C(12)–C(7)	109.7(8)
C(6)–C(1)–C(2)	111.5(7)	C(12)–C(7)–C(8)	111.3(7)

Table 4. Distances (Å) and bond angles (°) around the oxygen and carbon atoms of the uncoordinated molecules in the complex.

Diol 3			
C(13)–O(5)	1.458(9)	O(5)–C(13)–C(14)	111.4(7)
C(14)–O(6)	1.444(9)	O(5)–C(13)–C(18)	110.3(7)
C(13)–C(14)	1.484(11)	O(6)–C(14)–C(13)	112.2(7)
C(14)–C(15)	1.515(11)	O(6)–C(14)–C(15)	108.6(7)
C(15)–C(16)	1.502(12)	C(13)–C(14)–C(15)	110.9(8)
C(16)–C(17)	1.486(13)	C(14)–C(15)–C(16)	110.5(8)
C(17)–C(18)	1.534(12)	C(15)–C(16)–C(17)	110.9(8)
C(18)–C(13)	1.493(11)	C(16)–C(17)–C(18)	112.3(8)
C(5)–H(O5)	0.81(8)	C(17)–C(18)–C(13)	110.2(8)
O(6)–H(O6)	0.72(8)	C(18)–C(13)–C(14)	113.4(7)
O(5)···O(6)	2.874(9)		
THF			
C(19)–O(7)	1.404(11)	C(19)–O(7)–C(22)	109.9(8)
C(22)–O(7)	1.407(11)	O(7)–C(19)–C(20)	109.2(9)
C(19)–C(20)	1.420(14)	C(19)–C(20)–C(21)	106.0(10)
C(20)–C(21)	1.477(15)	C(20)–C(21)–C(22)	105.2(9)
C(21)–C(22)	1.498(15)	C(21)–C(22)–O(7)	106.5(10)

Table 5. Parameters for possible hydrogen bonds in the complex.[a]

O–H···X	H···X (Å)	O···X (Å)	∠O–H···X (°)
O(1)–H(O1)···O(5)	1.91(8)	2.592(8)	159(8)
O(2)–H(O2)···O(7)	1.75(8)	2.651(9)	170(5)
O(3)–H(O3)···Cl(2)	2.18	3.054(7)	158
O(4)–H(O4)···O(6^{i})	2.00(8)	2.720(8)	157(8)
O(5)–H(O5)···Cl(4)	2.49(8)	3.278(7)	165(7)
O(6)–H(O6)···Cl(1)	2.52(9)	3.224(7)	168(7)

[a] Symmetry code: (i) $1+x,y,z$

The structure consists of chloro-bridged non-centrosymmetric $[CuCl_2(\textit{trans}\text{-chd})]_2$ dimers to which one diol and one THF molecule are attached by hydrogen bonds. These clusters are held together by one interclustral hydrogen bond and by Van der Waals forces.

The bonding parameters of the Cu atoms are presented in Table 2. The Cu–O and Cu–Cl bond lengths are normal as found in this type of compounds.[1,6] The coordination geometry around the two copper(II) ions is a distorted square base pyramid. The greatest difference in the bonding parameters of the two copper(II) ions is found between the values of the angles Cl(1)–Cu(1)–O(1) and Cl(3)–Cu(2)–O(3), of which the former is 92.5° and the latter 88.8°. The distance Cu···Cu is 3.511(1) Å.

In the coordinated *trans*-chd molecule the torsion angles O(1)-C(1)–C(2)–O(2) and O(3)–C(7)–C(8)–O(4) are 51.4° and –50.3°, respectively, and in the uncoordinated *trans*-chd the torsion angle O(5)–C(13)–C(14)–O(6) is 57.7°. The torsion angle values of 51.4° and –50.3° in the *trans*-chd molecules reveal that the $[CuCl_2(\textit{trans}\text{-chd})]_2$ dimer contains different *trans*-chd enantiomers.

The bond distances and angles in the organic molecules are presented in Tables 3 and 4. It can be seen from the tables that the coordinated *trans*-chd molecules are more distorted than the uncoordinated ones. The six-membered rings have a *chair* conformation. The hydrogen bonded THF molecule has an *envelope* conformation with C(20) as the "flap" atom. As the torsion angles of the THF molecule are of the size of 1.2°–17.6°, the ring is flattened from the ideal *envelope* conformation of cyclopentane.[7] However, THF is a flexible molecule with many conformations of nearly equal energy.

There exists an extensive hydrogen bond system which contributes to the stability of the structure in the solid state. The hydrogen bond parameters are given in Table 5.

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