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# Synthesis and Crystal Structure of Copper(II) Chloride Complexes with (±)*trans*-1,2-Cyclohexanediol and Tetrahydrofuran in the Molar Ratio 1:½:1. A Ferromagnetic polymer.

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*The copper(II) chloride complex with (±)*trans-*1,2-cyclohexanediol (*trans-*chd) and tetrahydrofuran (THF) in the molar ratio 1:½:1 has been prepared and its crystal structure determined by X-ray methods. The molecular formula of the compound is* $Cu_2Cl_4$(trans-*chd)*$(THF)_2$ *and it crystallizes in the monoclinic space group C2/*c *with Z = 4. The unit cell parameters are* a = *16.561(3) Å,* b = *13.217(2) Å,* c = *13.290(3) Å, β = 134.05(1)°. The structure is formed of alternating* $CuCl_2$(trans-*chd) and* $CuCl_2(THF)_2$ *units, which are joined together by two chloride bridges and one OH···O(THF) hydrogen bond. The formed polymeric structure contains three copper atoms in line, after which the direction of the line changes. Both copper(II) ions are six-coordinated with four short bonds in a plane and two longer bonds perpendicular to that plane. One Cu atom lies on a two-fold axis and the other in a center of symmetry. There are rather short distances from the Cl(1) atom to both copper atoms: the bond length Cu(1)–Cl(1) is 2.288(2) Å and the bond length Cu(2)–Cl(1) is 2.350(2) Å.*

*Magnetic susceptibility measurements of the compound were made from 298 K to 80 K. The obtained results suggest that the complex is ferromagnetic with J/k = 33(4) K.*

## Introduction

We have previously studied coordination compounds of copper(II) chloride with 1,2-cyclohexanediols as neutral ligands. When synthesized in tetrahydrofuran the compounds often contain this solvent. Previously we have reported the preparation and crystal structures of $CuCl_2\cdot2$*trans*-chd and $CuCl_2\cdot1.5$*trans*-chd·0.5THF [1, 2], where *trans*-chd is (±)*trans*-1,2-cyclohexanediol and THF is tetrahydrofuran. In the present work the preparation, crystal structure and magnetic properties of $CuCl_2\cdot0.5$*trans*-chd·THF are reported.

## Experimental

### *Synthesis of the Complex*

The diol [3] (1.369 g, 11.8 mmol) and $CuCl_2$ (936 mg, 6.98 mmol) were dissolved in 50 ml of tetrahydrofuran (THF) and 40 ml of hexane was added. The solution was allowed to stand for one day at room temperature. Brown crystals were separated by decantation and washed twice with ethyl ether. The yield was 1.20 g (65.0%). The analyses of the crystals were performed by the standard titrimetric methods. *Anal.* Found: Cu, 23.9; Cl, 26.7; diol, 21.6%. Calc. for $CuCl_2C_7H_{14}O_2$: Cu, 24.0; Cl, 26.8; diol, 22.0%.

### *Magnetic Measurements*

Magnetic susceptibility was measured by a variable temperature Gouy balance Mk-II instrument (Newport Instruments, England), from 298 K to 80 K. As reference substance $HgCo(SCN)_4$ was used. All susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal constants [4] and for temperature-independent paramagnetism (TIP) of copper. The used TIP value was $754\cdot10^{-12}$ m$^3$ mol$^{-1}$ [5].

### *X-ray Measurements*

The single crystal X-ray diffraction measurements were made with the SYNTEX P$2_1$ (FORTRAN version) automatic four-circle diffractometer employing graphite monochromatized Mo–$K_\alpha$ radia-

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TABLE I. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å$^2$) with their e.s.d.'s for the atoms of $CuCl_2 \cdot 0.5$*trans*-chd·THF. The equivalent temperature coefficients are of the form $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13} \cdot \cos\beta)/3$.

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Cu(1) | 0.5000 | 0.5892(1) | 0.2500 | 0.0214(3) |
| Cu(2) | 0.5000 | 0.5000 | 0.5000 | 0.0229(3) |
| Cl(1) | 0.5971(1) | 0.4768(1) | 0.4319(1) | 0.0277(4) |
| Cl(2) | 0.3685(1) | 0.5886(1) | 0.3039(1) | 0.0267(4) |
| O(1) | 0.5871(3) | 0.7033(2) | 0.3855(3) | 0.0255(11) |
| O(2) | 0.3800(3) | 0.3252(3) | 0.3884(3) | 0.0331(13) |
| C(1) | 0.5262(4) | 0.7980(3) | 0.3244(4) | 0.0237(16) |
| C(2) | 0.6003(5) | 0.8898(4) | 0.4020(5) | 0.0347(20) |
| C(3) | 0.5297(8) | 0.9849(4) | 0.3260(7) | 0.0466(34) |
| C(4) | 0.2650(4) | 0.3392(4) | 0.2616(5) | 0.0338(19) |
| C(5) | 0.2610(7) | 0.3155(7) | 0.1477(7) | 0.0582(32) |
| C(6) | 0.3491(8) | 0.2416(8) | 0.2088(8) | 0.0655(39) |
| C(7) | 0.4270(6) | 0.2516(5) | 0.3624(6) | 0.0418(26) |
| H(O1) | 0.599(4) | 0.693(4) | 0.450(6) | 0.041(14) |
| H(C1) | 0.465(5) | 0.798(4) | 0.322(7) | 0.066(8) |
| H(1C2) | 0.622(5) | 0.889(5) | 0.491(7) | 0.066(8) |
| H(2C2) | 0.653(6) | 0.899(5) | 0.402(6) | 0.066(8) |
| H(1C3) | 0.472(6) | 0.982(5) | 0.334(7) | 0.066(8) |
| H(2C3) | 0.583(5) | 0.045(5) | 0.378(6) | 0.066(8) |
| H(1C4) | 0.213(7) | 0.303(6) | 0.257(8) | 0.101(9) |
| H(2C4) | 0.242(7) | 0.412(6) | 0.265(8) | 0.101(9) |
| H(1C5) | 0.245(9) | 0.356(8) | 0.119(10) | 0.101(9) |
| H(2C5) | 0.196(7) | 0.260(6) | 0.075(9) | 0.101(9) |
| H(1C6) | 0.331(7) | 0.161(7) | 0.238(9) | 0.101(9) |
| H(2C6) | 0.370(8) | 0.224(6) | 0.184(9) | 0.101(9) |
| H(1C7) | 0.503(8) | 0.249(6) | 0.427(9) | 0.101(9) |
| H(2C7) | 0.403(7) | 0.186(7) | 0.363(9) | 0.101(9) |

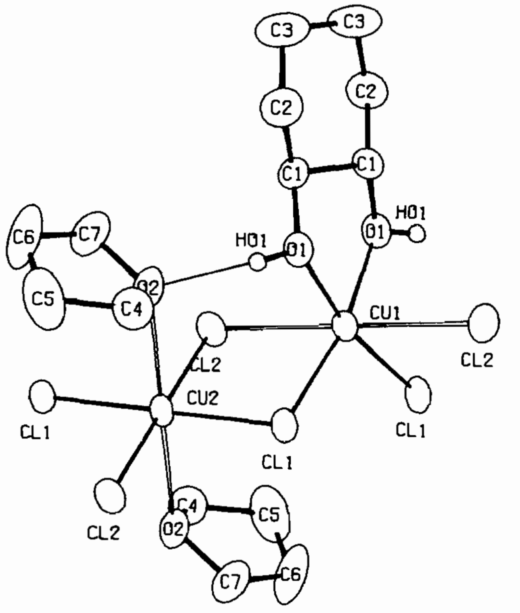

Fig. 1. A part of the structure of $[CuCl_2($*trans*-chd$)CuCl_2(THF)_2]$ showing the atom numbering scheme. Ring hydrogen atoms are not shown.

tion. The unit cell parameters were calculated by 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$^{-1}$). The systematic absences in the hkl-indices showed that the space group is $C2/c$.

*Crystal data* $Cu_2Cl_4C_{14}H_{28}O_4$; $M_r = 529.28$; space group $C2/c$; $a = 16.561(3)$ Å, $b = 13.217(2)$ Å, $c = 13.290(3)$ Å, $\beta = 134.05(1)°$; $Z = 4$; $V = 2091.0$ Å$^3$; $D_c = 1.671$ g cm$^{-3}$, $D_m$ (flotation) = 1.68(1) gcm$^{-3}$; $\mu$(Mo–K$_\alpha$) = 24.6 cm$^{-1}$.

The intensity of one check reflection showed no loss of intensity. The corrections for Lp and absorption were applied. Out of 2423 independent reflections 1873 intensities having $I > 3.0\sigma(I)$ were accepted as observed.

The structure was solved by direct methods [6], which gave positional parameters for Cu and Cl atoms. The atomic scattering factors and anomalous dispersion correction factors for heavy atoms were taken from 'International Tables' [7]. The structure was refined with heavy atoms having anisotropic temperature factors and hydrogen atoms having isotropic ones. Omission of 9 poorly-agreeing reflections led to a final $R = 0.047$ and $R_w = 0.050$, where $R = \Sigma\Delta/\Sigma F_o$, $R_w = \Sigma\sqrt{w}\Delta/\Sigma\sqrt{w}F_o$, $\Delta = |F_o - F_c|$ and $w = 2.356/(\sigma^2(F_o) + 0.0004F_o^2)$.

Crystallographical calculations were performed by the program SHELX-76 [8] and the figures were drawn by ORTEP [9].

## Results and Discussion

The final positional parameters with equivalent temperature factors for atoms of the complex are given in Table I. The labelling of the atoms is indicated in Fig. 1, where the basic structural unit can also be seen.

The structure is formed of nearly planar $CuCl_2$(*trans*-chd) and $CuCl_2(THF)_2$ units, which are alternatingly tied together by two chlorobridges and one hydrogen bond, forming an infinite chain along the $c$-axis. In this chain there are three copper atoms on the same line. These lines form a zigzag type trace. The bonding parameters of the Cu atoms are presented in Table II. The Cu–O and Cu–Cl bond lengths are in agreement with other diol complexes [1, 10]. Around the copper atoms there is an elongated tetragonal distorted six-coordination giving typical '4 + 2' coordination geometry. The inplane ligands around Cu(1) are the atoms O(1), O(1$^i$), Cl(1) and Cl(1$^i$), and around Cu(2) the atoms Cl(1), Cl(1$^{ii}$), Cl(2) and Cl(2$^{ii}$). The out-of-plane ligands are Cl(2) and Cl(2$^i$) around Cu(1), and O(2)

TABLE II. Distances (Å) and Bond Angles (°) around the Copper Atoms in the Complex.

| | | | |
|---|---|---|---|
| Cu(1)–Cl(1) | 2.288(2) | Cu(2)–Cl(2) | 2.240(2) |
| Cu(1)–Cl(1$^{i}$) | 2.288(2) | Cu(2)–Cl(2$^{ii}$) | 2.240(2) |
| Cu(1)–Cl(2) | 2.726(3) | Cu(2)–Cl(1) | 2.350(3) |
| Cu(1)–Cl(2$^{i}$) | 2.726(3) | Cu(2)–Cl(1$^{ii}$) | 2.350(3) |
| Cu(1)–O(1) | 1.996(4) | Cu(2)–O(2) | 2.719(4) |
| Cu(1)–O(1$^{i}$) | 1.996(4) | Cu(2)–O(2$^{ii}$) | 2.719(4) |
| Cu(1)•••Cu(2) | 3.525(2) | | |
| Cl(1)–Cu(1)–Cl(1$^{i}$) | 99.0(1) | Cl(2)–Cu(2)–Cl(1) | 89.6(1) |
| Cl(1)–Cu(1)–Cl(2) | 79.8(1) | Cl(2)–Cu(2)–Cl(1$^{ii}$) | 90.4(1) |
| Cl(1)–Cu(1)–Cl(2$^{i}$) | 100.0(1) | Cl(2)–Cu(2)–Cl(2$^{ii}$) | 180.0(1) |
| Cl(1)–Cu(1)–O(1) | 90.1(1) | Cl(2)–Cu(2)–O(2) | 93.4(1) |
| Cl(1)–Cu(1)–O(1$^{i}$) | 168.6(1) | Cl(2)–Cu(2)–O(2$^{ii}$) | 86.6(1) |
| Cl(2)–Cu(1)–Cl(2$^{i}$) | 179.7(1) | Cl(1)–Cu(2)–Cl(1$^{i}$) | 180.0(1) |
| Cl(2)–Cu(1)–O(1) | 88.5(2) | Cl(1)–Cu(2)–O(2) | 96.6(1) |
| Cl(2)–Cu(1)–O(1$^{i}$) | 91.8(2) | Cl(1)–Cu(2)–O(2$^{ii}$) | 83.4(1) |
| O(1)–Cu(1)–O(1$^{i}$) | 81.9(2) | O(2)–Cu(2)–O(2$^{ii}$) | 180.0(2) |
| Cu(1)–Cl(1)–Cu(2) | 99.0(1) | Cu(1)–Cl(2)–Cu(2) | 89.9(1) |

Symmetry codes: (i) 1 – x, y, ½ – z; (ii) 1 – x, 1 – y, 1 – z

TABLE III. Distances (Å) and Bond Angles (°) around the Oxygen and Carbon Atoms of the Organic Molecules.

| | | | |
|---|---|---|---|
| Diol | | | |
| C(1)–O(1) | 1.450(6) | O(1)–C(1)–C(1$^{i}$) | 106.1(4) |
| C(1)–C(1$^{i}$) | 1.509(6) | O(1)–C(1)–C(2) | 113.1(5) |
| C(1)–C(2) | 1.511(8) | C(1)–C(1$^{i}$)–C(2$^{i}$) | 110.4(5) |
| C(2)–C(3) | 1.525(10) | C(1)–C(2)–C(3) | 109.0(6) |
| C(3)–C(3$^{i}$) | 1.512(11) | C(2)–C(3)–C(3$^{i}$) | 111.9(7) |
| O(1)–H(O1) | 0.75(7) | | |
| O(1)•••O(1$^{i}$) | 2.616(4) | | |
| THF | | | |
| C(4)–O(2) | 1.428(7) | O(2)–C(4)–C(5) | 104.5(7) |
| C(7)–O(2) | 1.430(11) | C(4)–C(5)–C(6) | 104.8(6) |
| C(4)–C(5) | 1.502(12) | C(5)–C(6)–C(7) | 106.6(9) |
| C(5)–C(6) | 1.447(16) | C(6)–C(7)–O(2) | 107.2(7) |
| C(6)–C(7) | 1.480(10) | C(6)–O(2)–C(7) | 107.9(4) |

Symmetry code: (i) 1 – x, y, ½ – z

and O(2$^{ii}$) around Cu(2). The distortions from the ideal six-coordination are severe as seen from Table II, but not unusual for Cu(II) compounds.

These different Cu chromophores are linked into discrete chains nearly parallel to the *c*-axis, as shown in the stereoscopic Fig. 2. The chain contains alternatingly centrosymmetric $CuCl_2Cl_2{}'O_2$ and $C_2$-symmetric $CuCl_2O_2Cl_2{}'$ units. This leads to a structure with two Cu–Cl–Cu bridges between the adjacent Cu atoms and three Cu atoms on the same line. In the structure these lines make a zigzag trace with an angle of 140.9(1)°. The bridge angles Cu(1)–Cl(1)–Cu(2) and Cu(1)–Cl(2)–Cu(2) are 99.0(1)° and 89.9(1)°, respectively. The distances from Cl(1) to both copper atoms are rather short: 2.288(2) Å for Cu(1)–Cl(1) and 2.350(2) Å for Cu(2)–Cl(1). The Cu•••Cu distance is 3.525(2) Å. The chain is stabilized by an intrachain hydrogen bond from H(O1) to O(2) with the distance O(1)••• O(2$^{ii}$) of 2.681(6) Å and the angle O(1)–H(O1)••• O(2$^{ii}$) of 176(7)°.

The bonding parameters of the organic molecules are given in Table III. The diol molecule has a *chair* conformation. The torsion angles in the ring are from 54.7° to –62.0°. The torsion angle O(1)–C(1)–C(1$^{i}$)–O(1$^{i}$) is 52.2°. The THF molecule exhibits an *envelope* conformation ($C_s$ symmetry) with C(4) as 'flap' atom [11]. The average value (1.476 Å) of the distance C–C of the THF molecule differs from the corresponding average value (1.531 Å) obtained from free THF molecule with $C_2$-symmetry in the solid state [12]. The mean distance C–O (1.429 Å) agrees well with the corresponding distance (1.435 Å) of free THF molecule in the solid state [12]. The bonding parameters of the organic molecules show that these molecules are not strained in this structure, and thus this unique compound can be formed.

A least squares fit of the magnetic susceptibility data to the Curie-Weiss equation gave $\theta$ = 24.5 K and g = 2.22. The positive Weiss constant is indicative of predominant ferromagnetic interactions. The data

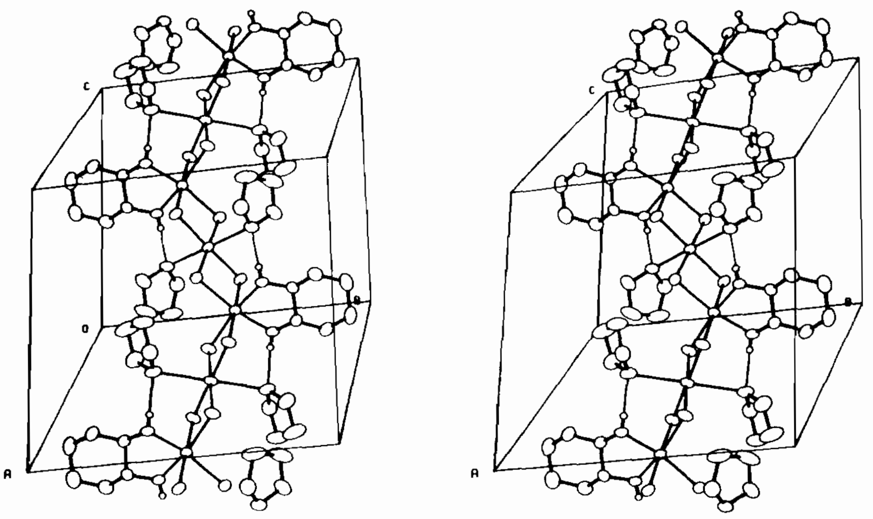

Fig. 2. A stereoscopic view of $[CuCl_2(trans\text{-chd})CuCl_2(THF)_2]_n$ showing the polymeric structure along *c*-axis.

were also fitted by a minimization procedure to the approximate expression of Baker *et al.* [13] for the one-dimensional ferromagnetic linear chain. This analysis yields J/k = 33(4) K and g = 2.21(3). Thus the high temperature magnetic susceptibility data of $CuCl_2 \cdot 0.5$*trans*-chd·THF can be described as ferromagnetic. However, the susceptibilities should be measured to much lower temperatures to get a complete picture of the magnetic behaviour of this compound.

Ferromagnetic behaviour is found also in the $CuCl_2$(TMSO) and $CuCl_2$(DMSO) complexes having three bridging atoms [14]. All these three ferromagnetic compounds contain a chloride bridge with two almost equally short Cu–Cl distances, but the Cu–Cl–Cu angles are quite different. The distances Cu···Cu in the TMSO and DMSO complexes are 3.209(6) Å and 3.238(1) Å respectively. In the studied complex the Cu···Cu distance is 3.525(2) Å. The only structure that could explain the ferromagnetic behaviour of $CuCl_2 \cdot 0.5$*trans*-chd·THF, is the bridge Cu–Cl–Cu with short Cu–Cl distances.

## Acknowledgement

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## Supplementary Material Available

Table S1 contains thermal parameters for the heavy atoms of the complex (1 page). The list of observed and calculated structure factors for the complex (11 pages) is in Table S2. This material is available from the writers (R.S.) on request.

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