

Synthesis and Crystal Structure of Two Copper(II) Halide Complexes with *trans*-1,2-Cycloheptanediol

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The crystal and molecular structures of $\text{CuCl}_2 \cdot 2t\text{-chpd}$ (**1**) and $\text{CuBr}_2 \cdot 2t\text{-chpd}$ (**2**) (*t*-chpd = *trans*-1,2-cycloheptanediol) have been determined from X-ray single-crystal data, and refined to *R*-values of 0.038 for 2202 reflections and 0.035 for 2024 reflections for **1** and **2**, respectively. Both compounds crystallize in the monoclinic space group $P2_1/n$ with two dimeric $[\text{CuX}_2(t\text{-chpd})]_2 \cdot 2t\text{-chpd}$ units (X = Cl or Br) in a cell. Cell parameters are $a = 1531.8(8)$, $b = 778.1(2)$, $c = 1568.2(8)$ pm and $\beta = 105.93(4)^\circ$ for **1** and $a = 1521.5(2)$, $b = 808.8(3)$, $c = 1588.5(2)$ pm and $\beta = 106.07(1)^\circ$ for **2**. The structures are isomorphous. The copper(II) ions have a square-pyramidal coordination sphere. $\text{CuX}_2(t\text{-chpd})$ units are linked to dimers through halogen bridges and hydrogen bonds. Dimeric $[\text{CuX}_2(t\text{-chpd})]_2$ units are polymerised along the *b*-axis through hydrogen bonding of the diols. The OH hydrogens of the coordinated diol molecule form hydrogen bonds with the oxygen atoms of the uncoordinated diol unit, while the OH hydrogens of the uncoordinated diols form hydrogen bonds with the halide ions.

Second-sphere coordination offers a good example of the importance of non-covalent bonds,¹ hydrogen bonding playing a dominant role.²

We have previously found this phenomenon in copper(II) complexes of *trans*-1,2-cyclohexanediol (*t*-chd) and *cis*-1,2-cyclohexanediol (*c*-chd). The complexes studied have the formula $\text{CuCl}_2 \cdot x\text{chd}$, where $x = 0.5, 1, 1.5$ or 2 . The structure consists of $\text{CuCl}_2(\text{chd})$ units which are linked to dimers or polymers through halogen bridges. If $x = 1.5$ or 2 then only one chd molecule is coordinated to the copper(II) ion, and the $\text{CuCl}_2(\text{chd})$ units are linked to the uncoordinated diol molecules through hydrogen bonds.³

Neutral diols and polyols form relatively unstable complexes with metal ions.⁴ In many cases syntheses of these complexes can be accomplished in weakly coordinating solvents such as THF (tetrahydrofuran) or DME (1,2-dimethoxyethane).

We have now extended our work to complexes of *trans*-1,2-cycloheptanediol (*t*-chpd). Syntheses were carried out in acetonitrile. The influence of halide ligands was studied by using either CuCl_2 or CuBr_2 as a starting material. The final aim is to apply copper(II) complexes to the separation of isomeric diols. The present paper describes the syntheses and crystal structures of two Cu(II) complexes of *t*-chpd.

Experimental

Preparation of $\text{CuCl}_2 \cdot 2t\text{-chpd}$ (1). 5.1 mmol of CuCl_2 and

10.2 mmol of *t*-chpd were suspended in 25 cm³ of acetonitrile. The green suspension was stored at 277 K for a few weeks to obtain bright green crystals (990 mg, 50%). The crystals were separated by decantation and washed with ether. Found: Cu 15.9; Cl 17.9. Calc. for $\text{CuCl}_2\text{C}_{14}\text{H}_{28}\text{O}_2$: Cu 16.1; Cl 18.0.

Preparation of $\text{CuBr}_2 \cdot 2t\text{-chpd}$ (2). 4.7 mmol of CuBr_2 and 9.5 mmol of *t*-chpd were dissolved in 20 cm³ of acetonitrile. The brown solution was kept at 255 K for two weeks. Brown crystals formed (520 mg, 23%) were separated by filtration and washed with ether. Found: Cu 12.4; Br 31.9. Calc. for $\text{CuBr}_2\text{C}_{14}\text{H}_{28}\text{O}_2$: Cu 13.1; Br 33.0.

Spectral measurements. The solid-state UV–VIS spectra of the compounds studied were recorded on a Cary 17D spectrometer by using the Nujol mull technique. The spectrum of **1** exhibited a band at 350 nm (28 600 cm⁻¹) and a broad band with two equal peaks at 765 nm (13 100 cm⁻¹) and 895 nm (11 200 cm⁻¹). In the spectrum of **2** the respective bands were at 450 nm (22 200 cm⁻¹) and at 775 nm (12 900 cm⁻¹), with an unresolved shoulder at 900 nm (11 100 cm⁻¹).

The solid-state IR spectra were measured on a Mattson Galaxy FTIR spectrometer by using the Nujol mull technique. The mid-IR spectrum of **1** showed O–H stretchings at 3405(m), 3327(m) and 3133(m) cm⁻¹. Possible C–O stretchings were observed at 1051(s) and 1000(s) cm⁻¹. The far-IR spectrum showed strong bands at 374 and 361 cm⁻¹, possibly due to coupled Cu–O stretchings. Strong Cu–Cl stretching bands were at 276 and 260 cm⁻¹. In the mid-IR

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Table 1. Crystal data and experimental details of the structure determination of $\text{CuCl}_2 \cdot 2t\text{-chpd}$ and $\text{CuBr}_2 \cdot 2t\text{-chpd}$.

Formula	$\text{C}_{14}\text{H}_{28}\text{Cl}_2\text{CuO}_4$	$\text{C}_{14}\text{H}_{28}\text{Br}_2\text{CuO}_4$
M_r	394.82	483.73
Space group	$P2_1/n$ (14)	$P2_1/n$ (14)
Cell parameters at 296 K:		
<i>a</i> /pm	1531.8(8)	1521.5(2)
<i>b</i> /pm	778.1(2)	808.8(3)
<i>c</i> /pm	1568.2(8)	1588.5(2)
β /°	105.93(4)	106.07(1)
<i>U</i> /nm ³	1.797(2)	1.879(1)
Calculated density/g cm ⁻³	1.459	1.710
<i>Z</i>	4	4
$\mu(\text{MoK}_\alpha)/\text{cm}^{-1}$	15.28	53.90
Crystal description	Green, cubic	Brown, prismatic
Crystal dimensions/mm	0.25 × 0.20 × 0.20	0.30 × 0.20 × 0.20
Instrument	Rigaku AFC5S	Rigaku AFC5S
Data collection	$\omega/2\theta$	$\omega/2\theta$
Corrections	Lp, abs., decay (−5.9 %)	Lp, abs., decay (−4.9 %)
Maximum 2θ /°	50.0	50.0
No. of reflexions measured	3435 unique	3569 unique
No. of observations [$I > 3\sigma(I)$]	2202	2024
Solution	Patterson	Patterson
Hydrogen atoms	Refined isotr.	Refined isotr.
Parameters refined	274	274
$R = \sum(F_o - F_c) / \sum F_o $	0.038	0.035
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.044	0.036
E.s.d. of obs. of unit weight	1.63	1.24
Least-square weights	$w = [\sigma^2(F_o)]^{-1}$	$w = [\sigma^2(F_o)]^{-1}$
Highest peak in diff. map/e Å ⁻³	0.42	0.63
Lowest peak in diff. map/e Å ⁻³	−0.48	−0.41

spectrum of **2** O–H stretchings were at 3423(m) and 3327(m) cm^{-1} and possible C–O stretchings were at 1051(s) and 1014(s) cm^{-1} . In the far-IR spectrum four strong bands were detected. Bands at 372 and 358 cm^{-1} possibly result from Cu–O stretchings and those at 258 and 246 cm^{-1} from Cu–Br stretchings.

Crystal structure determination. Single-crystal X-ray measurements were carried out on a Rigaku AFC5S diffractometer with graphite-monochromated MoK_α radiation, $\lambda = 71.069$ pm. The data obtained were corrected for Lorentz and polarization effects. Absorption and decay corrections were also taken into account. The crystal data and experimental details are shown in Table 1.

The lattice parameters were calculated by least-squares refinements of 24 reflections for **1** and 25 reflections for **2**. The structure of **1** was solved by the Patterson method and refined by full-matrix least-squares techniques to an *R*-value of 0.038 ($R_w = 0.044$). The final cycle was based on 2202 independent, observed reflections [$I > 3\sigma(I)$]. The structure of **2** was solved and refined in the same way, to an *R*-value of 0.035 ($R_w = 0.036$) for 2024 independent, observed reflections having $I > 3\sigma(I)$. The heavy atoms were refined anisotropically, and the hydrogen atoms isotropically with fixed temperature factors. Neutral atomic scattering and dispersion factors were taken from Ref. 5. All calculations were performed using TEXSAN⁶ crystallographic software. Figures were drawn with ORTEP.⁷ The

final atomic positional coordinates and equivalent isotropic temperature factors are listed in Tables 2 and 3.

Discussion

The structures of the complexes. The structures of the CuCl_2 and CuBr_2 complexes studied are isomorphous. The dimeric $[\text{CuX}_2(t\text{-chpd})]_2 \cdot 2t\text{-chpd}$ unit ($X = \text{Cl}$ or Br) and atomic numbering are shown in Fig. 1. The bond distances and angles around the Cu atoms are listed in Table 4. The coordination sphere of the copper(II) ion can be described as square pyramidal in both compounds. The copper ions are surrounded by two oxygen atoms of the diol and two halide ions in a distorted square-planar arrangement. The fifth coordination site is occupied by a halide ion that belongs to the adjacent $\text{CuX}_2(\text{diol})$ unit. The copper(II) ion has a similar coordination sphere in these *t*-chpd complexes as found in the Cu(II) complexes of 1,2-cyclohexanediols having the same molar ratio.⁸

The Cu–O distances vary from 196.2(3) to 199.2(4) pm in the compounds studied and from 200.3(3) to 201.2(3) pm in $\text{CuCl}_2 \cdot 2\text{chpd}$ compounds.⁸ The Cu–Cl distances in **1** are 227.2(1) pm for bridged and 221.7(1) pm for terminal chlorine atoms. The corresponding Cu–Br distances in **2** are 239.8(1) and 235.2(1) pm. When the halide ion acts as a bridging atom, the Cu–X bond is generally lengthened. The fifth, axial Cu–Cl and Cu–Br distances in the $\text{CuX}_2 \cdot 2t\text{-chpd}$ compounds are 274.4(1) and 289.7(1) pm, respectively.

Table 2. Atomic positional parameters and equivalent isotropic temperature factors for $\text{CuCl}_2 \cdot 2t\text{-chpd}$.

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$ ^a
Cu	0.00965(4)	0.28334(7)	0.54245(4)	2.90(2)
Cl(1)	-0.08649(7)	0.3978(1)	0.41873(8)	3.32(5)
Cl(2)	-0.08682(8)	0.2686(1)	0.62471(9)	4.16(5)
O(1)	0.0959(2)	0.2147(5)	0.4767(2)	3.2(1)
O(2)	0.1024(2)	0.1557(4)	0.6346(2)	3.4(2)
O(3)	0.1001(3)	0.3537(4)	0.3254(2)	3.6(1)
O(4)	-0.0539(2)	0.1132(4)	0.2780(2)	3.8(1)
C(1)	0.1869(3)	0.1834(6)	0.5319(3)	3.1(2)
C(2)	0.1739(3)	0.0707(6)	0.6047(3)	3.2(2)
C(3)	0.2565(4)	0.0401(7)	0.6803(3)	4.1(2)
C(4)	0.3204(4)	-0.0973(9)	0.6675(5)	5.8(3)
C(5)	0.3520(5)	-0.0936(8)	0.5846(4)	5.9(3)
C(6)	0.3428(3)	0.0709(8)	0.5324(4)	4.3(3)
C(7)	0.2472(3)	0.1150(7)	0.4796(3)	3.7(2)
C(8)	0.0541(3)	0.3005(6)	0.2373(3)	3.3(2)
C(9)	0.0257(3)	0.1156(6)	0.2452(3)	3.1(2)
C(10)	0.0034(4)	0.0092(7)	0.1608(4)	4.2(2)
C(11)	0.0883(5)	-0.0725(8)	0.1430(5)	5.8(3)
C(12)	0.1496(5)	0.052(1)	0.1123(5)	6.2(3)
C(13)	0.1828(4)	0.205(1)	0.1741(6)	6.8(4)
C(14)	0.1106(5)	0.3349(8)	0.1748(4)	5.3(3)
H(1)	0.102(4)	0.254(7)	0.444(3)	3.6
H(2)	0.081(3)	0.113(7)	0.655(3)	3.7
H(3)	0.210(3)	0.304(6)	0.560(3)	3.8
H(4)	0.146(3)	-0.045(6)	0.574(3)	3.6
H(5)	0.236(3)	0.022(6)	0.731(3)	4.8
H(6)	0.296(3)	0.148(7)	0.697(3)	4.8
H(7)	0.378(4)	-0.107(7)	0.726(3)	6.6
H(8)	0.290(4)	-0.198(8)	0.665(4)	7.0
H(9)	0.410(4)	-0.137(8)	0.600(3)	6.5
H(10)	0.312(4)	-0.168(8)	0.546(4)	7.0
H(11)	0.380(3)	0.072(6)	0.494(3)	5.2
H(12)	0.365(3)	0.164(7)	0.575(3)	5.2
H(13)	0.251(3)	0.207(6)	0.436(3)	4.3
H(14)	0.221(3)	0.023(6)	0.447(3)	4.3
H(15)	0.088(4)	0.438(6)	0.327(3)	4.2
H(16)	-0.049(3)	0.187(6)	0.318(3)	4.6
H(17)	-0.002(3)	0.367(6)	0.215(3)	4.4
H(18)	0.080(3)	0.066(6)	0.290(3)	3.8
H(19)	-0.032(3)	0.078(7)	0.109(3)	5.2
H(20)	-0.037(3)	-0.082(6)	0.171(3)	5.2
H(21)	0.129(3)	-0.128(7)	0.204(4)	6.6
H(22)	0.060(3)	-0.162(7)	0.095(3)	6.6
H(23)	0.115(4)	0.101(8)	0.053(4)	7.3
H(24)	0.202(4)	-0.012(8)	0.110(4)	7.3
H(25)	0.212(4)	0.163(8)	0.243(4)	7.7
H(26)	0.221(4)	0.254(9)	0.165(4)	7.7
H(27)	0.075(3)	0.339(7)	0.110(3)	5.8
H(28)	0.142(3)	0.448(7)	0.197(3)	5.8

^aThe equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{\text{eq}} = 4/3 \sum_i \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

The halide bridge system as a whole in the studied compounds is rather similar to that found in $\text{CuX}_2(\text{DMG})$ (DMG = dimethylglyoxime) compounds. The lengths of the bridging copper-halogen bonds are comparable to those in $[\text{Cu}(\text{DMG})\text{Cl}_2]_2$ ⁹ and $[\text{Cu}(\text{DMG})\text{Br}_2]_2$,¹⁰ viz. 223.8(4) and 238.7(1) pm for Cu-Cl and Cu-Br bonds. In the *t*-chpd complexes the Cu-X-Cuⁱ bridge angles are 91.75(5) and 90.17(4)° for the chloride and bromide compounds,

Table 3. Atomic positional parameters and equivalent isotropic temperature factors for $\text{CuBr}_2 \cdot 2t\text{-chpd}$.

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$ ^a
Cu	0.01006(5)	0.2825(1)	0.54401(5)	3.17(3)
Br(1)	-0.09583(4)	0.39628(8)	0.41624(4)	3.62(3)
Br(2)	-0.08933(5)	0.27902(9)	0.63406(5)	4.47(3)
O(1)	0.0944(3)	0.2093(6)	0.4771(3)	3.6(2)
O(2)	0.1033(3)	0.1596(6)	0.6349(3)	3.5(2)
O(3)	0.0954(4)	0.3335(5)	0.3235(3)	4.3(2)
O(4)	-0.0553(3)	0.0979(6)	0.2762(3)	4.2(2)
C(1)	0.1870(4)	0.1799(8)	0.5315(4)	3.1(3)
C(2)	0.1743(4)	0.0738(8)	0.6049(4)	3.2(3)
C(3)	0.2590(5)	0.051(1)	0.6793(4)	4.3(3)
C(4)	0.3225(6)	-0.087(1)	0.6651(6)	5.6(4)
C(5)	0.3523(7)	-0.086(1)	0.5841(6)	6.7(5)
C(6)	0.3429(5)	0.069(1)	0.5307(5)	4.6(4)
C(7)	0.2458(4)	0.110(1)	0.4789(4)	3.9(3)
C(8)	0.0514(5)	0.2808(9)	0.2363(4)	3.9(3)
C(9)	0.0234(5)	0.1050(8)	0.2433(4)	3.6(3)
C(10)	0.0018(6)	0.004(1)	0.1594(5)	4.8(4)
C(11)	0.0841(7)	-0.069(1)	0.1363(6)	6.3(5)
C(12)	0.1437(7)	0.050(2)	0.1065(7)	7.9(6)
C(13)	0.1755(7)	0.201(2)	0.167(1)	9.5(7)
C(14)	0.1079(8)	0.321(1)	0.1756(7)	7.9(6)
H(1)	0.093(5)	0.257(8)	0.435(4)	4.1
H(2)	0.089(5)	0.100(8)	0.659(4)	4.0
H(3)	0.210(4)	0.281(7)	0.561(4)	3.7
H(4)	0.151(4)	-0.044(8)	0.580(3)	4.1
H(5)	0.243(4)	0.029(8)	0.726(4)	5.2
H(6)	0.295(4)	0.158(8)	0.697(4)	5.1
H(7)	0.365(5)	-0.09(1)	0.717(4)	6.5
H(8)	0.290(4)	-0.204(8)	0.675(4)	4.0
H(9)	0.410(6)	-0.13(1)	0.592(5)	7.9
H(10)	0.311(5)	-0.17(1)	0.547(5)	7.9
H(11)	0.381(4)	0.062(8)	0.488(4)	5.6
H(12)	0.364(5)	0.159(8)	0.568(4)	5.6
H(13)	0.245(4)	0.189(8)	0.431(4)	4.7
H(14)	0.213(4)	-0.004(8)	0.444(4)	4.7
H(15)	0.089(5)	0.423(8)	0.326(5)	5.0
H(16)	-0.055(5)	0.170(8)	0.307(4)	4.9
H(17)	-0.006(4)	0.354(8)	0.214(4)	4.8
H(18)	0.074(4)	0.052(7)	0.281(4)	4.3
H(19)	-0.035(5)	0.063(9)	0.113(4)	5.8
H(20)	-0.035(5)	-0.089(8)	0.166(4)	5.8
H(21)	0.115(6)	-0.12(1)	0.187(5)	7.6
H(22)	0.051(5)	-0.16(1)	0.080(5)	7.6
H(23)	0.118(6)	0.10(1)	0.055(6)	9.4
H(24)	0.194(6)	0.02(1)	0.109(6)	9.4
H(25)	0.191(7)	0.20(1)	0.238(6)	11.4
H(26)	0.226(7)	0.26(1)	0.145(6)	11.4
H(27)	0.067(6)	0.29(1)	0.098(6)	9.5
H(28)	0.134(6)	0.43(1)	0.189(5)	9.5

^aThe equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{\text{eq}} = 4/3 \sum_i \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

respectively. In the $\text{CuX}_2(\text{DMG})$ compounds the corresponding angles are 88.0(1) and 85.59(4)°.

The bite distances (O1...O2) are 249.7(4) pm for the chloride, 250.4(6) pm for the bromide and 257.1(4) pm for $\text{CuCl}_2 \cdot 2t\text{-chpd}$.³ In $\text{CuCl}_2(\text{ed})$ (ed = 1,2-ethanediol) and $\text{CuCl}_2(\text{ed}) \cdot \frac{1}{2}\text{H}_2\text{O}$ the bite distances are 251.8(5) and 255.1(4) pm, respectively.¹¹

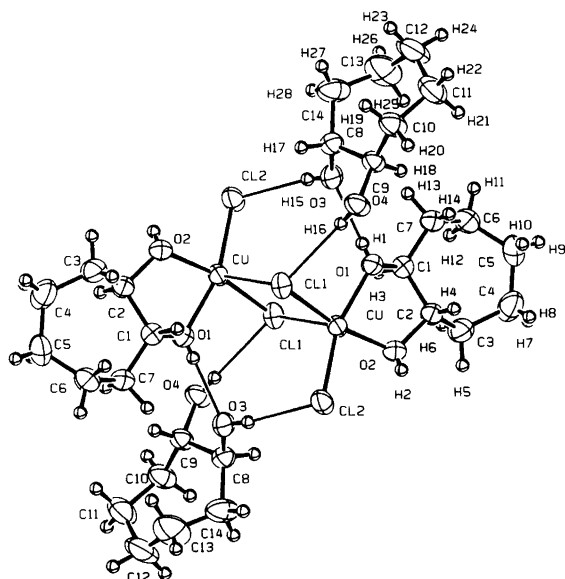


Fig. 1. ORTEP drawing of $\text{CuCl}_2 \cdot 2t\text{-chpd}$ dimer unit showing the atomic labelling scheme. The asymmetric unit is fully labelled. The bromo compound has the same labelling except that chloride ions are replaced by bromide ions.

The O1-Cu-O2 bite angle is $78.3(1)^\circ$ in $\text{CuCl}_2 \cdot 2t\text{-chpd}$ and $78.5(2)^\circ$ in $\text{CuBr}_2 \cdot 2t\text{-chpd}$. The corresponding angle is $79.6(1)^\circ$ in $\text{CuCl}_2 \cdot 2t\text{-chd}$,⁸ $79.1(1)^\circ$ in $\text{CuCl}_2(\text{ed})$ and $79.6(1)^\circ$ in $\text{CuCl}_2(\text{ed}) \cdot \frac{1}{2}\text{H}_2\text{O}$.¹¹ Similarly, the torsion angles are almost equal. This suggests that the O-Cu-O coordination system shows common features in all copper-1,2-diol complexes, and is independent of the diol.

The bonding parameters of the ligand are not markedly changed on going from bromide to chloride. The C-O bonds of the coordinated diols are longer than those of the

Table 4. Selected distances (in pm) and angles (in $^\circ$) around the Cu atom in the studied compounds with standard deviations in parentheses.^a

$\text{CuCl}_2 \cdot 2t\text{-chpd}$		$\text{CuBr}_2 \cdot 2t\text{-chpd}$	
Cu-O1	196.2(3)	Cu-O1	197.0(4)
Cu-O2	199.2(4)	Cu-O2	198.8(5)
Cu-Cl1	227.2(1)	Cu-Br1	239.8(1)
Cu-Cl2	221.7(1)	Cu-Br2	235.2(1)
Cu-Cl1 ⁱ	274.4(1)	Cu-Br1 ⁱ	289.7(1)
Cu...Cu ⁱ	361.0(1)	Cu...Cu ⁱ	376.6(2)
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O1-Cu-O2	78.3(1)	O1-Cu-O2	78.5(2)
O1-Cu-Cl1	91.7(1)	O1-Cu-Br1	92.5(1)
O1-Cu-Cl2	161.1(1)	O1-Cu-Br2	161.6(1)
O1-Cu-Cl1 ⁱ	93.1(1)	O1-Cu-Br1 ⁱ	93.8(1)
O2-Cu-Cl1	169.0(1)	O2-Cu-Br1	169.6(1)
O2-Cu-Cl2	90.4(1)	O2-Cu-Br2	90.1(1)
O2-Cu-Cl1 ⁱ	96.5(1)	O2-Cu-Br1 ⁱ	95.9(1)
Cl1-Cu-Cl2	98.00(5)	Br1-Cu-Br2	97.18(4)
Cl-Cu-Cl1 ⁱ	88.43(5)	Br1-Cu-Br1 ⁱ	89.83(4)
Cl2-Cu-Cl1 ⁱ	103.38(5)	Br2-Cu-Br1 ⁱ	101.83(3)
Cu-Cl1-Cu ⁱ	91.75(5)	Cu-Br1-Cu ⁱ	90.17(4)

^aSymmetry code: $i = -x, 1-y, 1-z$.

uncoordinated diols (Table 5). With the uncoordinated diol, the $\text{O} \cdots \text{O}$ distances are 294.3(5) and 291.6(7) pm in the chloride and bromide compounds. These values are about 50 pm greater than for the coordinated diols. The ligands have different ring conformations, depending on whether they are coordinated to the Cu(II) ion or not. This is seen from the values of the torsion angles (Table 6). The coordinated ligand has a chair conformation, whereas the uncoordinated ligand adopts a twist-chair conformation.¹² The different conformations are also reflected in the

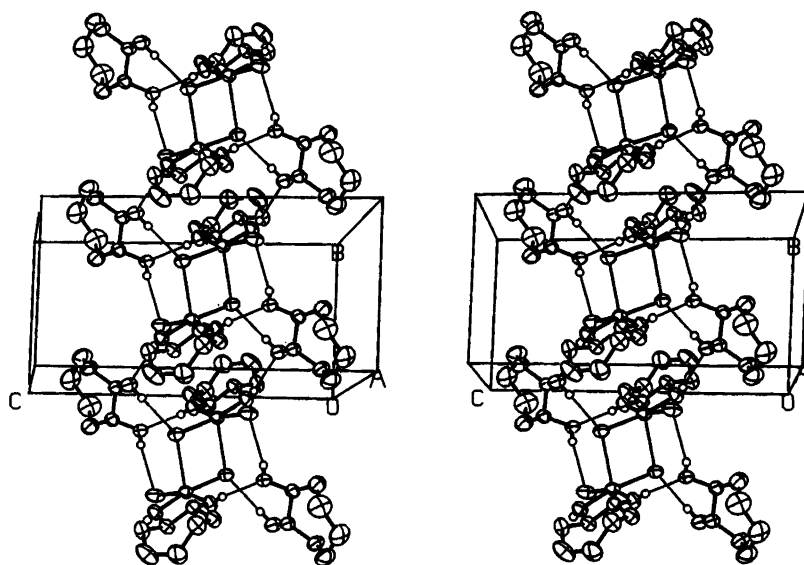


Fig. 2. Stereoscopic ORTEP drawing showing the packing of $[\text{CuX}_2(t\text{-chpd})]_2 \cdot 2t\text{-chpd}$ units along the b -axis.

Table 5. Bond distances (in pm) and angles (in °) in the *t*-chpd molecules with standard deviations in parantheses.

	CuCl ₂ ·2 <i>t</i> -chpd	CuBr ₂ ·2 <i>t</i> -chpd
O1–C1	144.6(5)	145.3(7)
O2–C2	146.5(5)	146.9(7)
O3–C8	143.0(6)	142.7(8)
O4–C9	144.8(5)	143.5(7)
C1–C2	149.6(6)	150.3(8)
C2–C3	149.7(6)	150.0(8)
C3–C4	149.9(8)	153(1)
C4–C5	151.0(9)	148(1)
C5–C6	150.7(8)	149(1)
C6–C7	151.0(7)	151.5(9)
C7–C1	149.3(6)	149.6(8)
C8–C9	151.9(6)	149.7(9)
C9–C10	151.9(6)	151.8(9)
C10–C11	154.1(8)	152(1)
C11–C12	151.9(9)	149(1)
C12–C13	153(1)	154(2)
C13–C14	150(1)	144(1)
C14–C8	150.1(7)	150(1)
Cu–O1–C1	114.1(2)	113.4(3)
Cu–O2–C2	116.1(3)	116.2(3)
O1–C1–C2	104.4(3)	104.0(5)
O1–C1–C7	111.8(4)	111.2(5)
C2–C1–C7	116.3(4)	116.2(5)
O2–C2–C1	104.4(4)	104.2(5)
O2–C2–C3	111.2(4)	110.7(5)
C1–C2–C3	116.0(4)	114.5(6)
C2–C3–C4	116.6(5)	114.5(6)
C3–C4–C5	118.5(5)	118.7(7)
C4–C5–C6	118.8(5)	119.8(7)
C5–C6–C7	115.0(5)	114.5(7)
C6–C7–C1	115.6(4)	115.1(6)
O3–C8–C9	105.8(4)	106.2(5)
O3–C8–C14	111.2(4)	111.2(6)
C9–C8–C14	116.9(4)	118.6(7)
O4–C9–C8	109.2(4)	110.3(5)
O4–C9–C10	107.0(4)	107.3(6)
C8–C9–C10	116.6(4)	116.3(6)
C9–C10–C11	112.6(5)	115.3(7)
C10–C11–C12	114.9(5)	116.1(8)
C11–C12–C13	115.0(5)	115.3(8)
C12–C13–C14	114.3(6)	119(1)
C13–C14–C8	116.4(5)	118.0(9)

O–C–C–O torsion angles, which in CuBr₂·2*t*-chpd for example are –48.5(6) and 75.6(7)° for the coordinated and the uncoordinated diol, respectively.

The structures are formed of [CuX₂(*t*-chpd)]₂·2(*t*-chpd) dimers, which are polymerized along the *b*-axis (Fig. 2) as pillars. The second-sphere coordination has an important role in the formation of the structures of both compounds studied. The OH hydrogens of the coordinated diol molecule form hydrogen bonds to oxygen atoms of the uncoordinated diol. The OH hydrogens of the uncoordinated diol molecule form, in turn, hydrogen bonds to halogen atoms (Table 7). Accordingly, the dimeric units are stabilised by OH...X hydrogen bonds. Between the pillars there are only van der Waals contacts. Evidently the crystal structure

Table 6. Torsion angles (in °) in the *t*-chpd molecules.

	CuCl ₂ ·2 <i>t</i> -chpd	CuBr ₂ ·2 <i>t</i> -chpd
O1–C1–C2–O2	–47.9(4)	–48.5(6)
O1–C1–C2–C3	–170.6(4)	–169.5(5)
O1–C1–C7–C6	–177.4(4)	–177.9(6)
O2–C2–C3–C4	158.7(5)	159.0(6)
O2–C2–C1–C7	–171.5(4)	–171.2(5)
C1–C2–C3–C4	–82.3(6)	–83.6(8)
C2–C3–C4–C5	50.6(9)	53(1)
C3–C4–C5–C6	18(1)	17(1)
C4–C5–C6–C7	–74.0(8)	–74(1)
C5–C6–C7–C1	75.8(7)	76.2(9)
C6–C7–C1–C2	–57.7(6)	–59.1(9)
C7–C1–C2–C3	65.8(6)	67.9(8)
O3–C8–C9–O4	77.9(5)	75.6(7)
O3–C8–C9–C10	–160.7(4)	–161.9(6)
O3–C8–C14–C13	81.3(6)	88(1)
O4–C9–C10–C11	–152.3(4)	–153.5(7)
O4–C9–C8–C14	–157.7(5)	–158.4(7)
C8–C9–C10–C11	85.1(6)	82.4(9)
C9–C10–C11–C12	–73.0(7)	–71(1)
C10–C11–C12–C13	55.6(9)	51(1)
C11–C12–C13–C14	–71.0(8)	–67(1)
C12–C13–C14–C8	85.9(7)	80(1)
C13–C14–C8–C9	–40.3(8)	–36(1)
C14–C8–C9–C10	–36.3(7)	–36(1)

is dependent not only on the stoichiometry of the complex, but also on the nature of the diol. For example, the structure of CuX₂·2*t*-chpd differs clearly from that of CuCl₂·2H₂pin, the former being a halide-bridged dimer and the later a halide-bridged polymer.¹³ Also, the polymerisation of CuX₂·2*t*-chpd dimers is different from that of CuCl₂·2*t*-chd dimers.

UV-VIS spectra. The CuCl₂·2*t*-chpd compound has a broad d–d band with two peaks at 13 100 and 11 200 cm^{–1}. The CuBr₂·2*t*-chpd compound showed a broad band at 12 900 cm^{–1}. Accordingly, the ligand field energies of CuO₂Cl₃ and CuO₂Br₃ chromophores with square-pyramidal struc-

Table 7. Distances (in pm) and angles (in °) involving hydrogen atoms of hydroxyl groups (X = O, Cl or Br) with standard deviations in parentheses.^a

	O–H	H...X	O...X	O–H...X
CuCl ₂ ·2 <i>t</i> -chpd				
O1–H1...O3	63(4)	200(4)	262.7(4)	168(7)
O2–H2...O4 ⁱⁱ	62(5)	215(5)	271.5(4)	154(7)
O3–H15...Cl2 ⁱ	69(5)	241(5)	306.5(4)	161(6)
O4–H16...Cl1	84(5)	246(5)	326.4(3)	162(4)
CuBr ₂ ·2 <i>t</i> -chpd				
O1–H1...O3	77(6)	189(6)	264.3(6)	168(7)
O2–H2...O4 ⁱⁱ	68(6)	205(6)	272.7(6)	173(8)
O3–H15...Br2 ⁱ	73(6)	249(7)	321.2(5)	168(7)
O4–H16...Br1	76(6)	271(6)	345.2(4)	166(7)

^aSymmetry codes: i = –x, 1–y, 1–z; ii = –x, –y, 1–z.

ture around the Cu(II) ion are almost equal to the energies found for CuCl_5 or CuCl_6 chromophores.¹⁴ The CT band is at $28\,600\text{ cm}^{-1}$ for the chloro compound and at $22\,200\text{ cm}^{-1}$ for the bromo compound. These values are consistent with earlier observations for μ -chloro and μ -bromo bridged dimers, in which a band at $20\,400\text{ cm}^{-1}$ for the bromo derivative and at $27\,000\text{ cm}^{-1}$ for the chloro derivative of $[\text{Cu}(\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2)\text{X}_2]_2$ ($\text{X} = \text{Cl}$ or Br) was assigned as a $\text{X} \rightarrow \text{d}_{x^2-y^2}$ charge-transfer band.¹⁵

IR spectra. The IR spectra of both compounds contain more bands than shown in the experimental section. However, the assignment of these additional bands is difficult without isotopic derivatives. Since the high-energy bands at 3405 cm^{-1} in the chloride complex and at 3423 cm^{-1} in the bromide complex are sensitive to the nature of the halogen atom, they can be assigned as a $\nu(\text{O-H})$ stretching of $\text{O-H}\cdots\text{X}$ hydrogen bonds.

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