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Syntheses and Crystal Structures of Two Copper(II) Chloride Complexes with 2,3-Dimethyl-2,3-butanediol

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The crystal and molecular structures of the complexes [$CuCl_2(H_2pin)]_2$ (H_2pin = 2,3-dimethyl-2,3-butanediol = pinacol) (1) and [$CuCl_2(H_2pin)]\cdot H_2pin$ (2) have been determined. The compound (1) crystallizes in the orthorhombic space group Pbcn with $a = 20.710(2)$, $b = 11.401(6)$, $c = 17.469(4)$, and $Z = 8$. The dimeric [$CuCl_2(H_2pin)]_2$ molecules consist of two five-coordinated Cu(II) ions with two different CuO_2Cl_2Cl' chromophores. The symmetry around one copper atom can be described as a distorted square based pyramid, and around the other as a distorted trigonal bipyramid. The dimers are held together by hydrogen bonds. The compound (2) crystallizes in the monoclinic space group C2/c with $a = 18.878(18)$, $b = 12.115(3)$, $c = 7.541(2)$, $\beta = 104.94(5)$, and $Z = 4$. The structure of (2) is a polymer. The copper atom is surrounded by two oxygen atoms of one H_2pin molecule and by two chloride ions (Cu–Cl = 2.223 Å). Two extra chloride ions from adjacent $CuCl_2(H_2pin)$ units are at the distance of 3.223 Å. The coordination number of copper(II) ion is 4 + 2 with an elongated rhombic octahedral symmetry. The second H_2pin molecule is not coordinated to copper atom, but has an anti *conformation and connects $CuCl_2(H_2pin)$ units together by hydrogen bonds.*

Investigation of the interaction of metal ions with weakly coordinating neutral ligands has led to many useful applications in chemistry [1]. Recently we prepared some diol adducts of copper(II) chloride and determined their structures [2, 3]. In this work I report the preparations and the crystal structures of two copper(II) chloride complexes with pinacol (=2,3-dimethyl-2,3-butanediol, abbr. as H_2pin).

H_2pin can exist in three different forms, one of which has the *anti* conformation while the other two have the *gauche* conformation [4]. Pinacol forms two clatrates with water. The structures of $H_2pin\cdot 6H_2O$ and $H_2pin\cdot H_2O$ show that the H_2pin molecules have an *anti* conformation in these compounds [5, 6].

Pinacol has been found to coordinate as a neutral, a monoanionic, or a dianionic ligand. As a neutral ligand H_2pin acts in $Co(NO_3)_2\cdot 3H_2pin\cdot 2H_2O$, $CoBr_2\cdot 3H_2pin\cdot 2H_2O$, and $CoCl_2\cdot 1.5H_2pin$ [7]. The structures of these are unknown. In $[Mo(MeO)(Hpin)O_2]\cdot 2MeOH$ pinacol coordinates as a monoanionic ligand [8]. In the complexes $(OsO_2pin)_2$ and $[(\eta^5\text{-}C_5H_5)Cl_2Ti]_2pin$ pinacol acts as a dianionic ligand [9, 10]. In the former compound the conformation of the ligand is *gauche*, but in the latter it is *anti*. The structure of the compound $[Mo_2(pin)_2(Hpin)_2O_3]$ shows that there are in the dimer unit two monoanionic and two dianionic pinacol groups [11].

The now prepared complexes have molecular formulas of $CuCl_2\cdot H_2pin$ and $CuCl_2\cdot 2H_2pin$ with the pinacol molecules as neutral ligands. The compounds are a part of our study about coordination chemistry of diols (polyols) as neutral ligands.

Experimental

Preparation of the Complexes—Complex (1)

H_2pin (448 mg, 3.79 mmol) and $CuCl_2$ (350 mg, 2.60 mmol) were dissolved in 10 ml DME (1,2-dimethoxyethane) and 4 ml hexane was added. The solution was allowed to stand for one week at room temperature. Dark green crystals were separated by decantation and washed twice with ethyl ether. The yield was 277 mg (41.5%). The crystals were stored in a desiccator. The analysis of the crystals was performed by standard titrimetric methods. (Found: Cu, 25.3; Cl, 28.2; and diol, 46.0. $CuCl_2\cdot C_6H_{14}O_2$ requires Cu, 25.2; Cl, 28.1; and diol, 46.7.)

Complex (2)

H_2pin (1.642 g, 12.2 mmol) and $CuCl_2$ (735 mg, 5.47 mmol) were dissolved in 25 ml DME. The solvent was allowed slowly to evaporate through $CaCl_2$ tube in a fume hood for six weeks. Green crystals were separated by decantation, washed twice with ethyl ether and stored in a desiccator. The yield was 625 mg (30.8 %). (Found: Cu, 17.3;

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Cl, 19.1; and diol, 64.1. $CuCl_2 \cdot C_{12}H_{28}O_4$ requires Cu, 17.1; Cl, 19.1; and diol, 63.7.)

Crystal Data

Crystal data for (*1*) and (*2*) are summarized in Table I. The X-ray diffraction measurements were made with a SYNTEX $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite monochromatized Mo-K_α-radiation. The unit cell parameters were calculated by least squares refinements of 25 reflections. The intensities were recorded using the ω-scanning mode with varying scan speed (3.0–29.3° min^{-1}) depending on the peak intensity of the reflection. The systematic absences in the *hkl*-indices showed that the space group is Pbcn for (*1*) and C2/c for (*2*).

TABLE I. Crystal Data.

Complex	$[CuCl_2(H_2pin)]_2$	$[CuCl_2(H_2pin)] \cdot H_2pin$
Crystal system	orthorhombic	monoclinic
Space group	Pbcn	C2/*c*
a (Å)	20.710(2)	18.878(18)
b (Å)	11.401(6)	12.115(3)
c (Å)	17.469(4)	7.541(2)
β (°)		104.94(5)
V ($Å^3$)	4124.69	1666.38
M_r	505.26	370.80
z	8	4
$D_c/g\ cm^{-3}$	1.627	1.478
$D_m/g\ cm^{-3}$ (flotation)	1.62(1)	1.46(1)
F(000)	2064	780
μ (cm^{-1})	24.91	15.62
Number of collected unique reflections	3662	2511
Number of refined reflections	2359	2070
R	0.037	0.045
R_w	0.039	0.046

The 2459 intensities out of 3662 independent reflections for $[CuCl_2(H_2pin)]_2$, having $I > 2.5\sigma(I)$, were used in the refinements. Two check reflections showed no crystal decay. Intensities were corrected only for Lp, but not for absorption. Out of 2511 independent reflections for $[CuCl_2(H_2pin)] \cdot H_2pin$ the 2131 intensities with $I > 3.0\sigma(I)$ were used in the refinements. One check reflection decreased by 22%. Corrections for crystal decay and Lp were applied, but not for absorption. The structures were solved by the direct methods, which gave positional parameters for the Cu and Cl atoms. The scattering factors were taken from ref. 12. Anomalous dispersion correction was made for all nonhydrogen atom scattering factors [13]. The structure of (*1*) was refined with non-H atoms having anisotropic temperature factors and methyl hydrogens considered as rigid groups (C–H = 1.00 Å) with the same isotropic temperature factor. Hydroxyl hydrogens were allowed to refine freely with isotropic temperature factors. Omission of 100 poorly agreeing weak reflections and application of an empirical extinction correction ($F_c^* = F_c(1 - xF_c^2/\sin\theta)$, $x = 3.2 \times 10^{-8}$) led to final R = 0.037 and $R_w = 0.039$, where $R = \Sigma\Delta/\Sigma F_o$, $R_w = \Sigma\sqrt{w}\Delta/\Sigma\sqrt{w}F_o$, $\Delta = |F_o - F_c|$ and $w = 1.1959/(\sigma^2(F_o) + 6.87 \times 10^{-4}F_o^2)$. Without omitting those 100 weak reflections R = 0.047 and $R_w = 0.050$. However, the analysis of variances showed a better straight line and the methyl groups had more reliable structural parameters after omitting these 100 reflections.

The structure of (*2*) was refined with all non-H atoms having anisotropic temperature factors and hydrogen atoms having isotropic temperature factors. Omission of 61 poorly agreeing weak reflections and application of an experimental extinction correction ($x = 2.0 \times 10^{-7}$) led to final R = 0.045 and R_w = 0.046 with $w = 1/(\sigma^2(F_o) + 0.002F_o^2)$. Without omitting 61 reflections R = 0.050 and R_w = 0.054. The omission of these 61 reflections is thought to be reasonable on the same basis as in the case of (*1*). All crystallographic calculations were performed by the program SHELX-76 [14] and the figures of molecules were drawn by ORTEP [15].

Results and Discussion

Structure of $[CuCl_2(H_2pin)]_2$ (1)

The final positional parameters for the non-H atoms in compound (*1*) are given in Table IIa. The labelling of the atoms is indicated in Fig. 1. In the discrete dimer unit $[CuCl_2(H_2pin)]_2$ the copper atoms exhibit a distorted five-coordination. The $CuCl_2(H_2pin)$ units are joined together by two chloride bridges and an intramolecular hydrogen bond. The distances and bond angles around the copper atoms are presented in Table III.

The symmetry around Cu(1) can be described as a distorted square based pyramid and around Cu(2) as a distorted trigonal bipyramid. The Cu–Cu distance of 3.647(1) Å indicates a very weak Cu–Cu dimer interaction. Most of the possible Cu–Cu interaction might go through the Cu(1)–Cl(1)–Cu(2) pathway, for the Cu(2)–Cl(1) distance is 2.664(2) Å and the Cu(1)–Cl(3) distance is 3.080(2) Å. However, the Cu–Cl–Cu angle also plays an important role [16]. The Cu–O and short Cu–Cl distances are of the same order as in ref. 2, 3, and 17, and the values are normal for the Cu–O and Cu–Cl bonds.

The coordinated pinacol molecules have a *gauche* conformation with the torsion angles of −44.8(5)° for O(1)–C(1)–C(2)–O(2) and −41.3(7)° for O(3)–C(7)–C(8)–O(4). The distances and bond angles

TABLE II. Fractional Atomic Coordinates for Complexes (*1*) and (*2*) with Estimated Standard Deviations in Parentheses.[a]

(a) Complex (*1*)

Atom	x/*a*	y/*b*	z/*c*
Cu(1)	0.13270(3)	0.06238(6)	0.22428(3)
Cu(2)	0.12853(3)	0.38197(6)	0.23246(4)
Cl(1)	0.07872(7)	0.19789(11)	0.15938(8)
Cl(2)	0.17654(6)	−0.02821(13)	0.12594(7)
Cl(3)	0.21620(6)	0.27805(14)	0.26262(9)
Cl(4)	0.07796(7)	0.37446(13)	0.34684(8)
O(1)	0.0883(2)	0.1005(4)	0.3192(2)
O(2)	0.1640(2)	−0.0601(4)	0.2950(2)
O(3)	0.1779(2)	0.4826(4)	0.1616(3)
O(4)	0.0603(2)	0.4802(4)	0.1862(3)
C(1)	0.0878(2)	0.0142(4)	0.3815(3)
C(2)	0.1560(2)	−0.0406(4)	0.3775(3)
C(3)	0.0344(3)	−0.0712(5)	0.3636(3)
C(4)	0.0744(3)	0.0776(5)	0.4555(3)
C(5)	0.2090(3)	0.0420(6)	0.4044(3)
C(6)	0.1599(3)	−0.1588(5)	0.4186(3)
C(7)	0.1435(3)	0.5448(5)	0.1020(4)
C(8)	0.0811(3)	0.5797(6)	0.1405(4)
C(9)	0.1267(4)	0.4541(6)	0.0373(4)
C(10)	0.1827(3)	0.6428(5)	0.0696(4)
C(11)	0.0971(5)	0.6758(7)	0.2022(5)
C(12)	0.0291(3)	0.6235(6)	0.0902(4)

(b) Complex (*2*)

Atom	x/*a*	y/*b*	z/*c*
Cu	0.50000	0.57098(2)	0.25000
Cl	0.42033(3)	0.45420(4)	0.31928(7)
O(1)	0.5645(1)	0.6989(1)	0.2362(2)
O(2)	0.6590(1)	0.7057(1)	0.0172(2)
C(1)	0.5293(1)	0.8061(1)	0.1949(2)
C(2)	0.4963(1)	0.8149(2)	−0.0111(3)
C(3)	0.5865(1)	0.8957(2)	0.2611(3)
C(4)	0.7379(1)	0.7063(2)	0.0633(2)
C(5)	0.7651(1)	0.5906(2)	0.0375(4)
C(6)	0.7629(1)	0.7390(2)	0.2647(3)

[a]Tables of hydrogen atom positions, thermal parameters for all atoms and lists of observed and calculated structure factors for both compounds are available as supplementary material.

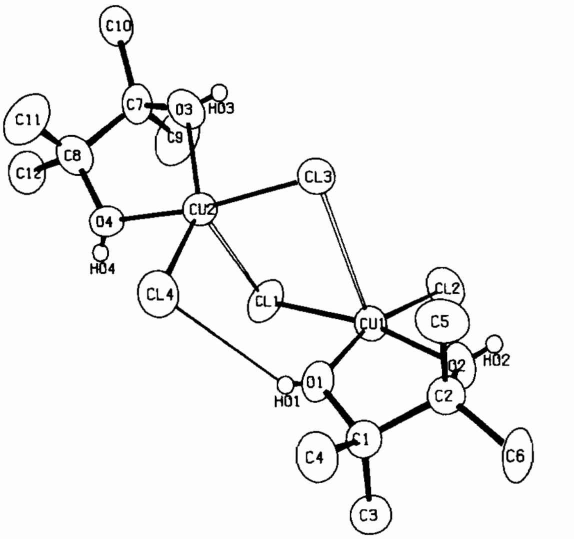

Fig. 1. Molecular structure of $[CuCl_2(H_2pin)]_2$ showing the atom numbering scheme. Methyl hydrogen atoms are not shown.

TABLE III. Distances (Å) and Bond Angles (°) Around the Cu Atoms in $[CuCl_2(H_2pin)]_2$.

Cu(1)–Cl(1)	2.218(1)	Cu(2)–Cl(3)	2.231(2)
Cu(1)–Cl(2)	2.201(1)	Cu(2)–Cl(4)	2.258(1)
Cu(1)–Cl(3)	3.080(2)	Cu(2)–Cl(1)	2.664(2)
Cu(1)–O(1)	1.946(5)	Cu(2)–O(3)	1.972(4)
Cu(1)–O(2)	1.974(4)	Cu(2)–O(4)	1.976(4)
Cu(1)···Cu(2)	3.647(1)		
Cl(1)–Cu(1)–Cl(2)	97.8(1)	Cl(3)–Cu(2)–Cl(4)	98.5(1)
Cl(1)–Cu(1)–Cl(3)	80.7(1)	Cl(3)–Cu(2)–Cl(1)	90.6(1)
Cl(1)–Cu(1)–O(1)	92.4(1)	Cl(3)–Cu(2)–O(3)	92.0(1)
Cl(1)–Cu(1)–O(2)	167.9(1)	Cl(3)–Cu(2)–O(4)	168.4(1)
Cl(2)–Cu(1)–Cl(3)	108.2(1)	Cl(4)–Cu(2)–Cl(1)	102.4(1)
Cl(2)–Cu(1)–O(1)	164.9(1)	Cl(4)–Cu(2)–O(3)	144.9(2)
Cl(2)–Cu(1)–O(2)	91.2(1)	Cl(4)–Cu(2)–O(4)	93.0(1)
Cl(3)–Cu(1)–O(1)	84.4(1)	Cl(1)–Cu(2)–O(3)	111.0(2)
Cl(3)–Cu(1)–O(2)	104.1(1)	Cl(1)–Cu(2)–O(4)	88.5(1)
O(1)–Cu(1)–O(2)	77.3(2)	O(3)–Cu(2)–O(4)	77.6(2)
Cu(1)–Cl(1)–Cu(2)	108.9(1)	Cu(1)–Cl(3)–Cu(2)	85.1(1)

in the H_2pin molecules are shown in Table IV. The C–O bond lengths in the complexes are slightly longer than in the free diol molecules [4]. The mean C–O bond length in pinacol is 1.435 Å, and in this compound it is 1.459 Å. This seems to show that the coordination of the oxygen atom in a neutral OH group to copper lengthens the C–O bond. In the second pinacol molecule the C–C bond lengths are more distorted than in the first. The values agree within experimental errors with the values found in the pinacolates [8, 9, 11].

The dimer molecules are held together by hydrogen bonds. The parameters for the hydrogen bonds are presented in Table V. The O–H distances are abnormally short, a common observation in many X-ray works. If the O–H bond length is normalized to 0.96 Å, the values for the H···Cl distances and O–H···Cl angle become more realistic. Revised values are also given in Table V. The Cl···O distances are of the same order as found in the same type of compounds [2, 3, 17].

Structure of [CuCl$_2$(H$_2$pin)]·H$_2$pin (2)

The final positional parameters for the non-H atoms in compound (*2*) are given in Table IIb. The labelling of the atoms is indicated in Fig. 2. The structure of (*2*) is a polymer. The $CuCl_2(H_2pin)$ units are packed along *c* axis forming a uniformly spaced

TABLE IV. Distances (Å) and Bond Angles (°) around the Oxygen and Carbon Atoms in the Pinacol Units in $[CuCl_2(H_2pin)]_2$.

Molecule 1		Molecule 2	
C(1)–O(1)	1.466(6)	C(7)–O(3)	1.447(7)
C(2)–O(2)	1.468(6)	C(8)–O(4)	1.453(7)
C(1)–C(2)	1.547(7)	C(7)–C(8)	1.508(8)
C(1)–C(3)	1.506(7)	C(7)–C(9)	1.571(9)
C(1)–C(4)	1.506(6)	C(7)–C(10)	1.494(8)
C(2)–C(5)	1.520(7)	C(8)–C(11)	1.572(10)
C(2)–C(6)	1.529(7)	C(8)–C(12)	1.477(8)
O(1)–H(O1)	0.56(6)	O(3)–H(O3)	0.65(5)
O(2)–H(O2)	0.70(5)	O(4)–H(O4)	0.65(5)
O(1)•••O(2)	2.447(6)	O(3)•••O(4)	2.473(6)
O(1)–C(1)–C(2)	103.3(4)	O(3)–C(7)–C(8)	103.3(5)
O(1)–C(1)–C(3)	106.6(4)	O(3)–C(7)–C(9)	107.7(5)
O(1)–C(1)–C(4)	108.4(4)	O(3)–C(7)–C(10)	111.8(5)
C(2)–C(1)–C(3)	106.6(4)	C(8)–C(7)–C(9)	107.7(6)
C(2)–C(1)–C(4)	113.6(4)	C(8)–C(7)–C(10)	115.9(5)
C(3)–C(1)–C(4)	110.7(4)	C(9)–C(7)–C(10)	109.9(6)
O(2)–C(2)–C(1)	102.0(4)	O(4)–C(8)–C(7)	107.0(5)
O(2)–C(2)–C(5)	108.4(4)	O(4)–C(8)–C(11)	103.3(5)
O(2)–C(2)–C(6)	108.8(4)	O(4)–C(8)–C(12)	112.0(5)
C(1)–C(2)–C(5)	113.3(5)	C(7)–C(8)–C(11)	108.0(6)
C(1)–C(2)–C(6)	112.5(4)	C(7)–C(8)–C(12)	116.6(6)
C(5)–C(2)–C(6)	111.3(5)	C(11)–C(8)–C(12)	109.0(6)

TABLE V. Distances (Å) and Angles (°) Associated with the Possible Hydrogen Bonds of $[CuCl_2(H_2pin)]_2$.

X–H•••Y	X–H	H•••Y	X•••Y	∢X–H•••Y
O(1)–H(O1)•••Cl(4)	0.56(6)	2.72(6) 2.43†	3.168(5)	140(9) 134
O(2)–H(O2)•••Cl(3^{i})	0.70(5)	2.47(5) 2.22	3.143(4)	162(5) 160
O(3)–H(O3)•••Cl(2^{ii})	0.65(5)	2.51(5) 2.25	3.082(5)	148(5) 145
O(4)–H(O4)•••Cl(4^{iii})	0.65(5)	2.50(5) 2.20	3.159(4)	177(5) 177

†The lower values have been calculated assuming 0.96 Å for OH–bond lengths. Symmetry codes: (i) 1/2 – x, y – 1/2, z; (ii) 1/2 – x, 1/2 + y, z; (iii) –x, y, 1/2 – z.

alternatingly bridged linear chain. The chains are kept together by hydrogen-bonded uncoordinated pinacol molecules, which have an *anti* conformation. A stereo view of the packing is shown in Fig. 3. The structure has similarities with the compound *catena*-dichloro-(3,6-dithiaoctane)copper(II), which has an alternatingly spaced and bridged chain structure [18].

The copper atom has an elongated rhombic octahedral symmetry. The bond lengths and angles

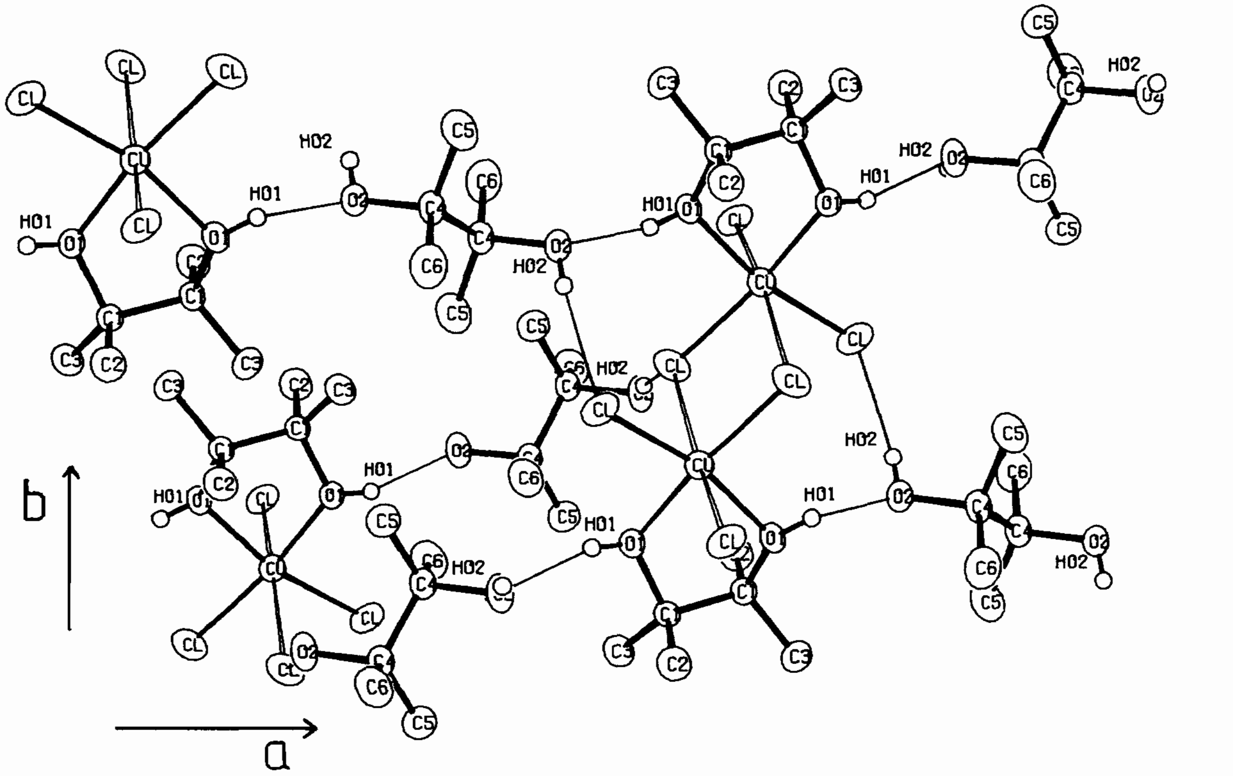

Fig. 2. A part of the molecular packing and the atom numbering scheme in $[CuCl_2(H_2pin)]\cdot H_2pin$. Methyl hydrogen atoms are not shown.

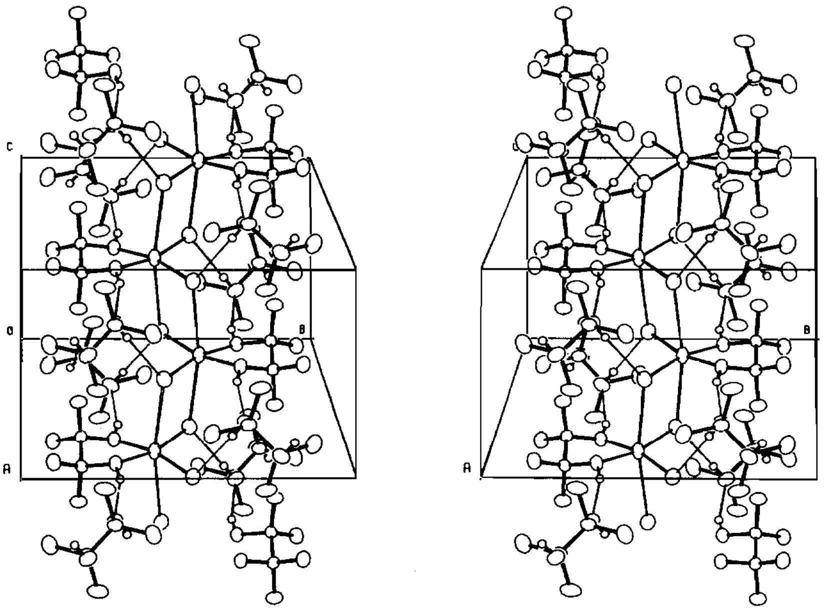

Fig. 3. A stereoscopic view of $[\mathrm{CuCl_2(H_2pin)}]\cdot\mathrm{H_2pin}$ showing the packing along *c*-axis.

around the copper atom are presented in Table VI. The $\mathrm{CuCl_2(H_2pin)}$ units have a C_2-symmetry: the C_2 axis is going through the Cu atom and the midpoint of the $C(1)$–$C(1^{i})$ bond. The *trans* O–Cu–Cl bond angle is 165.5(1)°. This shows that the $\mathrm{CuO_2Cl_2}$ unit is not planar but tetrahedrally distorted. Also the O–Cu–O^{i} and Cl–Cu–Cl^{i} bond angles are distorted from the square planar values. The former angle has the value of 77.7(1)° and the latter 101.0(1)°.

The coordinated pinacol molecule has a *gauche* conformation. The torsion angle $O(1)$–$C(1)$–$C(1^{i})$–$O(1^{i})$ is 46.7(2)°. In the uncoordinated pinacol molecule the equivalent torsion angle has the value of 180.0(1)°. This value is consistent with the *anti* conformation. The distances and bond angles in the pinacol molecules are presented in Table VII. The C–O distance of the coordinated diol is longer than the C–O distance of the uncoordinated diol. The values are 1.455(2) Å and 1.439(2) Å, respectively. The $C(1)$–$C(1^{i})$ bond length is of the same order as found in the structure of (*1*), but the $C(4)$–$C(4^{i})$ distance is 1.570(4) Å. This is very close to the value of 1.565(5) Å found for the same type of C–C bond in the compound $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2Ti}]_2\mathrm{pin}$ [10]. Also in this compound the pinacol molecule has an *anti* conformation. The methyl–C distances are very similar in these two compounds.

TABLE VI. Distances (Å) and Angles (°) around Cu Atom in $[\mathrm{CuCl_2(H_2pin)}]\cdot\mathrm{H_2pin}$.

Cu–Cl	2.223(1)	Cu–O(1)	1.991(1)
Cu–Cl^{i}	2.223(1)	Cu–O(1^{i})	1.991(1)
Cu–Cl^{ii}	3.223(1)	Cu···Cu^{ii}	4.144(1)
Cu–Cl^{iii}	3.223(1)		
Cl–Cu–Cl^{i}	101.0(1)	O–Cu–Cl^{ii}	89.6(1)
Cl–Cu–Cl^{ii}	82.6(1)	O–Cu–Cl^{iii}	98.9(1)
Cl–Cu–Cl^{iii}	90.5(1)	O–Cu–O(1^{i})	77.7(1)
Cl–Cu–O	165.5(1)	Cl^{ii}–Cu–Cl^{iii}	169.1(1)
Cl–Cu–O^{i}	91.3(1)	Cu–Cl–Cu^{ii}	97.4(1)

Symmetry codes: (i) 1 – x, y, 1/2 – z; (ii) 1 – x, 1 – y, 1 – z; (iii) x, 1 – y, z – 1/2.

TABLE VII. Distances (Å) and Angles (°) in the Pinacol Molecules of $[\mathrm{CuCl_2(H_2pin)}]\cdot\mathrm{H_2pin}$.

Molecule 1		Molecule 2	
C(1)–O(1)	1.455(2)	C(4)–O(2)	1.439(2)
C(1)–C(1^{i})	1.544(3)	C(4)–C(4^{iv})	1.570(4)
C(1)–C(2)	1.521(2)	C(4)–C(5)	1.523(3)
C(1)–C(3)	1.522(2)	C(4)–C(6)	1.522(3)
O(1)–H(O1)	0.81(4)	O(2)–H(O2)	0.76(3)
O(1)···O(1^{i})	2.497(2)	O(2)···O(2^{iv})	3.671(3)
O(1)–C(1)–C(1^{i})	103.7(1)	O(2)–C(4)–C(4^{iv})	107.5(1)
O(1)–C(1)–C(2)	109.0(1)	O(2)–C(4–C(5)	109.0(2)
O(1)–C(1)–C(3)	108.6(1)	O(2)–C(4)–C(6)	106.1(1)
C(1^{i})–C(1)–C(2)	112.9(1)	C(4^{iv})–C(4)–C(5)	112.5(2)
C(1^{i})–C(1)–C(3)	111.7(2)	C(4^{iv})–C(4)–C(6)	111.6(2)
C(2)–C(1)–C(3)	110.7(2)	C(5)–C(4)–C(6)	109.8(2)

Symmetry codes: (iv) 1/2 – x, 1/2 – y, –z; (i), (ii) and (iii) as in Table VI.

One may also compare the atomic distances in the C–O bonds in these two compounds. The Ti complex contains a coordinated $-\mathrm{CO}^-$ group, but the present Cu complex has a coordinated –COH group. In the former the C–O distance is 1.430(3) Å and in the latter it is 1.455(2) Å. This could mean that the coordination of the diol to metal as a neutral ligand affects more strongly the diol molecule than its coordination as an alkoxide ion.

The hydrogen bond angles in compound (*2*) for O(1)–H(O1)···O(2) and for O(2)–H(O2)···Cl^{v} are 160(2)° and 172(2)°, respectively (the symmetry code v is 1 – x, 1 – y, –z). The distances O(1)···O(2) and O(2)···Cl^{v} are 2.727(2) Å and 3.236(1) Å.

Conclusion

On the basis of the present structural studies the following conclusions may be presented.

When the un-ionized OH-groups of a diol molecule are coordinated to copper through the oxygen atoms, the hydrogen atoms of these groups become more positive and have a stronger tendency to form hydrogen bonds than they have in the free diol molecule. As a result of the plasticity of copper(II) ion [19] copper can modify its coordination sphere so that the most stable hydrogen bonding system (and thus the most stable packing) can be formed. This may be the reason why the two copper(II) ions in compound (*1*) have dissimilar coordination environments.

In compound (*2*) the OH-hydrogens of the coordinated pinacol molecule form hydrogen bonds with the oxygen atoms of the uncoordinated pinacol molecule. In this case the minimum energy of the system is reached if copper has a distorted six-coordination and the uncoordinated pinacol adopts the *anti* conformation.

It seems likely that the coordination ability of the neutral diol molecules is too weak for the formation of compounds in which more than one diol molecule are coordinated to copper, when chloride is as an anion. A similar observation was made when $CuCl_2 \cdot 2H_2O$ was dissolved in 1,2-ethanediol. Only complexes $CuCl_2$(1,2-ethanediol) and $CuCl_2$(1,2-ethanediol)$\cdot 0.5H_2O$ were obtained [17].

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Suplementary Material Available

Tables SI and SII contain thermal parameters for (*1*) and (*2*) (2 pages). Tables SIII and SIV contain positional and thermal parameters for hydrogen atoms in (*1*) and (*2*) (2 pages). The lists of observed and calculated structure factors for (*1*) (14 pages) and for (*2*) (12 pages) are in Tables SV and SVI. This material is available from the writer on request.

References

1 N. S. Poonia and A. V. Bajaj, *Chem. Rev., 79*, 389 (1979).

2 R. Sillanpää, M. Leskelä and L. Hiltunen, *Acta Crystallogr., 38*, 1591 (1982).

3 L. Hiltunen, M. Leskelä, L. Niinistö and R. Sillanpää, *Acta Chem. Scand., Ser. A*, to be published.

4 G. A. Jeffrey and A. Robbins, *Acta Crystallogr., B34*, 3817 (1978).

5 H. S. Kim and G. A. Jeffrey, *J. Chem. Phys., 53*, 3610 (1970).

6 A. J. O'Connors, *M. Sc. Thesis*, Sheffield University, 1969.

7 Ad. Grün and E. Boedecker, *Chem. Ber., 43*, 1051 (1910).

8 C. B. Knobler, B. R. Penfold, W. T. Robinson and C. J. Wilkins, *Acta Crystallogr., B37*, 942 (1981).

9 F. L. Phillips and A. C. Skapski, *J.C.S. Dalton*, 2586 (1975).

10 J. C. Huffman, K. G. Moloy, J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc., 102*, 3009 (1980).

11 A. J. Matheson and B. R. Penfold, *Acta Crystallogr., B35*, 2707 (1979).

12 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, 1974, Vol. IV.

13 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53*, 1891 (1970).

14 G. M. Sheldrick, 'SHELX-76, Program for Crystal Structure Determination', University of Cambridge, 1976.

15 C. K. Johnson, 'ORTEP-II, A Fortran Thermal-ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-5138', Oak Ridge National Laboratory, Tenn., 1976.

16 W. E. Hatfield, *Comments Inorg. Chem., 1*, 105 (1981).

17 B.-M. Antti, *Acta Chem. Scand., Ser. A, 30*, 405 (1976).

18 M. M. Olmstead, W. K. Musker, L. W. Ter Haar and W. E. Hatfield, *J. Am. Chem. Soc., 104*, 6627 (1982).

19 J. Gažo, I. B. Bersuker, J. Garaj, M. Kabešova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator and F. Valach, *Coord. Chem. Rev., 19*, 253 (1976).