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The Molecular and Crystal Structures of $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$; Two Compounds Containing Neutral Dichloro(1,2-ethanediol)copper(II) Molecules

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The crystal structures of the title compounds have been determined and refined using X-ray diffraction data. $[CuCl_2(C_2H_6O_2)]$ is monoclinic, space group $P2_1/c$, $Z=4$ and unit cell $a=7.424$ (1) Å, $b=10.939(5)$ Å, $c=7.518(1)$ Å and $\beta=95.666(9)°$. $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ is orthorhombic, space group $Pcnb$ (D_{2h}^{14}), with $Z=8$ and cell dimensions $a=10.198(1)$ Å, $b=18.769$ (1) Å and $c=7.043(1)$ Å. The structures were refined by full-matrix least-squares techniques to R-values of 0.042 (1739 reflexions) and 0.047 (2388 reflexions) for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$, respectively. Both structures are built from discrete $CuCl_2(C_2H_6O_2)$ molecules with approximately planar coordination around Cu. The Cu – Cl distances range between 2.232 and 2.267 Å and the Cu – O distances between 1.958 and 2.004 Å. Adjacent molecules are connected by longer Cu···Cl contacts thus forming infinite layers in $[CuCl_2(C_2H_6O_2)]$ and chains in $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$.

In two recent papers the structures of $[MnCl_2(C_2H_6O_2)_2]$ [1] and $[Me_2Cl_2(C_2H_6O_2)_4]Cl_2$ (Me = Co, Ni) [2] were presented. In the manganese compound the structure consists of discrete neutral molecules $[MnCl_2(C_2H_6O_2)_2]$ whereas the isostructural cobalt and nickel compounds are built from dimeric $[Me_2Cl_2(C_2H_6O_2)_4]^{2+}$-ions and Cl^--ions. The present work was undertaken in order to elucidate what structural changes would occur if copper was introduced as metal ion.

EXPERIMENTAL

The compounds were prepared by dissolving as much as possible of $CuCl_2.2H_2O$ in 1,2-ethanediol (glycol) (molar ratio 1:2) on the waterbath and placing the solution obtained in a desiccator over sulfuric acid. The space groups were derived from Weissenberg films and the densities determined by the flotation method using bromoform and xylene.

Tabular, light green and extremely hygroscopic crystals of $[CuCl_2(C_2H_6O_2)]$ separated after several weeks. IR-spectrum was recorded on a sample, which had been mulled in nujol and placed between NaCl-plates. From the spectrum it was clear that the sample had taken up water; the spectrum was in fact identical with that of $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ in the recorded wavenumber region (4000 – 625 cm^{-1}). Because of the extreme hygroscopicity, no analyses have been made so far. The systematic extinctions corresponded to space group $P2_1/c$ (No. 14). The cell parameters were refined from rotation photographs (a, b and c) and from omega scan on the diffractometer (a, c and β). The following parameters were obtained: $a=7.424(1)$ Å, $b=10.939(5)$ Å, $c=7.518(1)$ Å and $\beta=95.666(9)°$. The density is 2.14(1) g cm^{-3}; calc. for $[CuCl_2(C_2H_6O_2)]$ 2.148 g cm^{-3}.

$[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ separated overnight as light-green, tabular crystals. If they were kept over sulfuric acid too long they lost their water content. Systematic extinctions uniqely determined the space group to be $Pcnb$ (D_{2h}^{14} No. 60) with the following coordinates for the general eightfold position: $\pm(x,y,z;\ \frac{1}{2}-x,y,\frac{1}{2}+z;x,\frac{1}{2}+y,\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$. From data obtained from a powder film taken in a camera of Guinier-Hägg type, the following cell parameters were refined: $a=10.198(1)$ Å, $b=18.769(1)$ Å and $c=7.043(1)$ Å. The density is 2.04(1) g cm^{-3}; calc. for $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ 2.03 g cm^{-3}. The crystals were analyzed for copper and chlorine. Found Cu 30.62 (electrolytically): Cl 33.3 (gravimetrically). Calc. for $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ Cu 30.92; Cl 34.5. IR-spectra indicated that water was present in the structure.

The intensity measurements were made using the automatic linear diffractometer PAILRED and graphite monochromated MoKα-radiation. Both crystals were sealed in glass capillaries during the data collection. The dimensions of the crystals were 0.09 × 0.10 × 0.25 mm and 0.21 × 0.25 × 0.50 mm for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ and they were rotated around their *b*- and *c*-axes, respectively. The omega-scan technique was used with scan speed 1°/min and weak reflexions (< 4000 counts) were measured twice. The half scan intervals were 1.5 − 1.6° (1.5 − 1.6°) for Ω_1 and 1.9 − 2.4° (2.3 − 2.5°) for Ω_2. The values in parentheses refer to those used for the crystal of $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ and Ω_1 was used for $\theta > 20°$ and Ω_2 for $\theta \leq 20°$. For the crystal of $[CuCl_2(C_2H_6O_2)]$ 2616 reflexions from $h0l - h15l$ were measured and for that of $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ 6634 from $hk0 - hk11$. From these 1739 ($\sin\theta_{max} = 0.55$) and 4385 ($\sin\theta_{max} = 0.60$), respectively, had $\Delta I/I \leq 0.5$.[1] Absorption correction was applied; $\mu_{MoK\alpha} = 44.7$ and 40.9 cm^{-1} for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$, respectively. For $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ the *hkl* and $\bar{h}kl$ reflexions were averaged, leaving 2388 independent reflexions. As a final check, structure amplitudes were calculated for the unobserved reflexions. They all had values lower than or equal to the corresponding threshold values. The data programs used are described earlier.[5]

STRUCTURE ANALYSIS

The structures were solved by routine heavy-atom Patterson and Fourier methods and refined by full-matrix least-squares techniques to *R*-values of 0.042 ($R_w = 0.051$) and 0.047 ($R_w = 0.058$) for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$, respectively. Anisotropic temperature factors were applied to the non-hydrogen atoms while for the hydrogen atoms the thermal vibrations were assumed to be isotropic. The function $\sum w(||F_o| - |F_c||)^2$ was minimized using weights calculated according to the function $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ [6] using the constants $a = 400$, $c = -0.015$ and $d = 0.003$ for $[CuCl_2(C_2H_6O_2)]$ and 450, 0.005 and 0.003 for $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$. The scattering curves for Cu, Cl, O, and C were those proposed by Cromer and Waber [7] and dispersion correction ($\Delta f'$, $\Delta f''$) was applied for Cu and Cl.[8] For the hydrogen atoms the scattering curve proposed by Stewart *et al.*[9] was used. As a final check a difference Fourier synthesis was calculated, from which nothing abnormal could be detected. The highest peak was found in the vicinity of copper. The final positional and thermal parameters are given in Tables 1 and 2. The list of observed and calculated structure amplitudes will be supplied by the author on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

The structures are built from near planar discrete molecules $CuCl_2(C_2H_6O_2)$ which are arranged in different ways in the two struc-

Table 1. Atomic positional and thermal parameters for $[CuCl_2(_2H_6O_2)]$. For the non-hydrogen atoms all parameters have been multiplied by 10^4. The anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. For the hydrogen atoms the positional parameters have been multiplied by 10^3. The labelling of atoms is shown in Fig. 3. (Standard deviations in parentheses.)

	x/a	y/b	z/c	$\beta_{11}(B)$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	73(1)	1208(0.5)	3282(1)	105(1)	62(0.4)	169(1)	−6(0.4)	30(1)	−20(0.5)
Cl(1)	−2108(1)	−197(1)	3288(1)	109(1)	63(1)	194(2)	−7(1)	23(1)	−7(1)
Cl(2)	−1292(1)	2609(1)	4847(1)	160(2)	68(1)	126(2)	12(1)	21(1)	−9(1)
O(1)	1528(5)	152(4)	1881(6)	139(6)	90(3)	287(9)	−14(3)	62(6)	−68(4)
O(2)	2329(4)	2200(3)	3269(4)	124(5)	66(2)	166(5)	−5(3)	6(4)	12(3)
C(1)	3405(6)	333(5)	2182(9)	104(6)	108(5)	278(13)	5(5)	50(7)	−33(7)
C(2)	3756(6)	1649(5)	2364(8)	127(7)	99(5)	242(11)	−6(5)	47(7)	10(6)
H(1)	142(9)	−49(8)	164(9)	6(2)					
H(2)	235(8)	290(6)	291(8)	4(1)					
H(3)	376(9)	−22(8)	341(10)	7(2)					
H(4)	403(8)	−10(6)	137(9)	5(1)					
H(5)	389(9)	213(7)	114(9)	6(2)					
H(6)	487(8)	197(6)	281(8)	4(1)					

Table 2. Atomic positional and thermal parameters for $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$. For the labelling of atoms see Fig. 4.

	x/a	y/b	z/c	$\beta_{11}(B)$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	1773(0.4)	1274(0.2)	239(1)	52(0.3)	17(0.1)	126(1)	2(0.1)	6(0.4)	−6(0.2)
Cl(1)	2852(1)	2073(0.4)	2078(1)	64(1)	19(0.2)	98(1)	−1(0.3)	5(1)	1(0.3)
Cl(2)	3461(1)	553(0.5)	−400(1)	75(1)	28(0.3)	164(2)	19(0.4)	−6(1)	−18(0.5)
O(1)	565(2)	641(1)	−1241(4)	68(2)	19(1)	163(5)	−3(1)	16(3)	−8(1)
O(2)	68(2)	1675(1)	995(4)	61(2)	25(1)	180(5)	3(1)	10(3)	−20(2)
O(3)	0	25	4081(5)	81(4)	43(2)	119(6)	28(2)	0	0
C(1)	4244(4)	4067(2)	3633(7)	66(3)	26(1)	237(10)	2(1)	−21(4)	18(3)
C(2)	1037(4)	3776(2)	568(8)	58(3)	27(1)	263(10)	0.4(1)	−30(4)	17(3)
H(1)	424(6)	60(4)	276(12)	6(2)					
H(2)	−14(5)	184(3)	218(9)	4(1)					
H(3)	63(6)	229(3)	486(12)	7(2)					
H(4)	418(4)	370(2)	267(7)	3(1)					
H(5)	366(5)	448(3)	335(8)	4(1)					
H(6)	98(5)	420(3)	147(8)	4(1)					
H(7)	186(5)	345(3)	41(9)	5(1)					

tures. In $[CuCl_2(C_2H_6O_2)]$ each molecule has Cu almost at $x=0$ and the packing of the molecules makes possible two longer contacts from each Cu to chlorines of adjacent molecules. These longer Cu---Cl contacts connect the near planar molecules in infinite layers parallel to (100) as is indicated in Fig. 1. In $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ the longer Cu---Cl contacts connect the molecules in infinite chains along [001]. These chains are further connected in pairs *via* the water molecules by means of hydrogen bonds in infinite layers extending parallel to (010). This arrangement is shown in Fig. 2.

The arrangement around the Cu-atoms. Around each copper atom there is a near planar arrangement with the two glycol oxygens and the two chlorine atoms from the formula unit as coordinated ligands (Figs. 3 and 4). The deviations from the calculated least-squares plane, defined by the coordinated ligands, are −0.007(2) [0.008(1)], 0.006(1) [−0.015(1)], 0.129(5) [0.159(3)], −0.069(4) [−0.159(3)] and 0.057(1) [0.113(1)] Å for Cl(1), Cl(2), O(1), O(2), and Cu, respectively. (The values in square brackets refer to those found in $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$.) The Cu−O distances ranging between 1.958(4) and 2.004(3) Å agree well with other reported

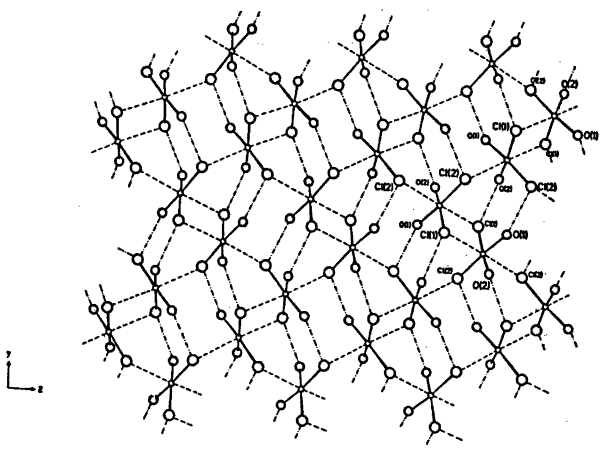

Fig. 1. The molecular packing in $[CuCl_2(C_2H_6O_2)]$. The carbon and hydrogen atoms are omitted. The dashed lines indicate the 'nonbonded' Cu---Cl contacts and the ··· lines the hydrogen bond contacts.

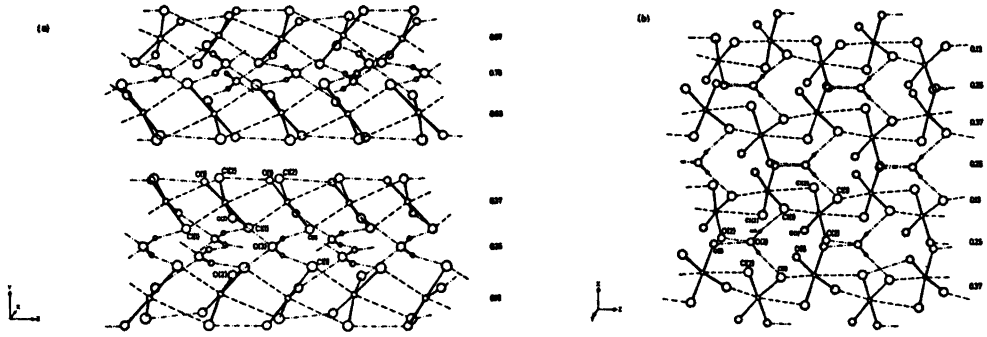

Fig. 2. The molecular packing in $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$. Viewed along (a) the x-axis and (b) the y-axis. The numerals at the right correspond to the y-value of the Cu and O(3) atoms respectively. Legend as for Fig 1.

Cu – O bond lengths.[10]

The near planar $CuCl_2(C_2H_6O_2)$ molecules are connected *via* longer 'nonbonded' Cu---Cl contacts, in order to achieve the favoured tetragonally distorted, octahedral (4+2) arrangement around each Cu(II) (Figs. 1 and 2). Thus in the structure of $[CuCl_2(C_2H_6O_2)]$ planar four-membered rings $Cu<^{Cl(1)}_{Cl(1)}>Cu$ centered around a crystallographic inversion center are formed. The Cu – Cl(1)---Cu angle is 87.29(4)°, the Cl – Cl distance 3.875(2) Å and the Cu – Cu distance 3.704(1) Å. Furthermore, there is another type of connecting arrangement Cu-Cl(2)---Cu with a corresponding angle of 128.45(5)° and a Cu – Cu distance of 4.704(1) Å.

In $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ the four-membered ring arrangement $Cu<^{Cl(1)}_{Cl(2)}>Cu'$ is not planar and the deviations from the calculated least-squares plane are 0.062(1), 0.077(1), −0.305(1), and −0.394(1) Å for Cu, Cu′, Cl(1), and Cl(2), respectively. The Cu – Cu′ contact is 3.821(1) Å, well in excess of the value corresponding to Cu – Cu bonding (2.63 – 2.99 Å).[11,12] The Cl(1) – Cl(2) separation of 3.618(1) Å is in good agreement with the sum of the van der Waals radii for Cl (3.60 Å).[13]

The bonded Cu – Cl distances in the two structures as well as the longer Cu---Cl contacts in $[CuCl_2(C_2H_6O_2)]$ are in agreement with those reported by Willett and Rundle [14] for some copper chloride complexes. The great inequality in the 'nonbonded' Cu---Cl contacts in the hydrated compound $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$ must be due to the insertion of half a water molecule per unit cell as in the water-free analogue the two 'nonbonded' Cu---Cl contacts

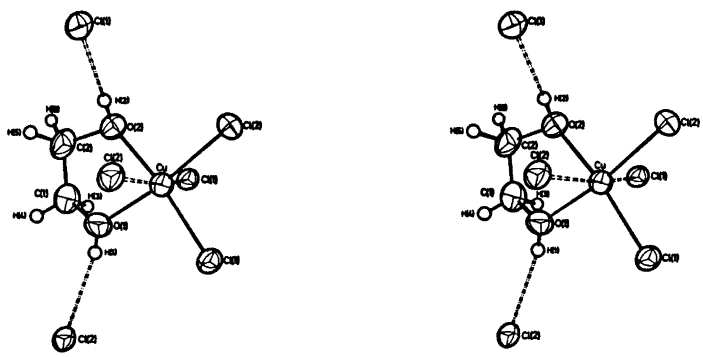

Fig. 3. A stereoscopic view of the coordination around Cu(II) in $[CuCl_2(C_2H_6O_2)]$. The ellipsoids are scaled to enclose 50 % probability. (Dashed lines indicate 'nonbonded' Cu---Cl contacts and the hydrogen bond directions are shown with -·- lines.)

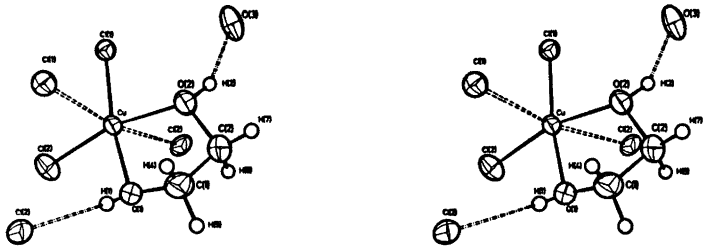

Fig. 4. A stereoscopic view of the coordination around Cu(II) in $[CuCl_2(C_2H_6O_2)]\cdot\frac{1}{2}H_2O$. Legend as for Fig. 3.

are almost equal (mean value 3.020 Å). Distances and angles in the two compounds are given in Table 3.

The glycol ligand. As in the earlier reported glycol complexes [1–5] the glycol ligand acts as a bidentate chelating agent and has *gauche* conformation in relation to the C–C bond. The dihedral angle is 35.7 and 51.6° for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$, respectively, the former value being much smaller than those found earlier (45.9–56.1°).[1–5] The dihedral angles seem to be correlated to the deviations of the carbon atoms from the O–Cu–O plane. They are 0.510(7) [0.365(5)] for C(1) and 0.043(6) [−0.351(5)] Å for C(2). (The values in square brackets refer to $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$.) This difference in ring symmetry might account for the greater stability

Table 3. Distances (Å) and angles (°) in $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$. Standard deviations in parentheses.

	$[CuCl_2(C_2H_6O_2)]$	$[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$
Cu–O(1)	1.958(4)	2.004(3)
Cu–O(2)	1.996(3)	1.968(3)
Cu–Cl(1)	2.232(1)	2.267(1)
Cu–Cl(2)	2.235(1)	2.235(1)
Cu···Cl(1)	3.064(1)	2.712(1)
Cu···Cl(2)	2.976(1)	3.365(1)
Cl(1)–Cl(2)	3.320(2)	3.402(1)
O(1)–O(2)	2.518(5)	2.551(4)
O(1)–C(1)	1.404(6)	1.457(5)
O(2)–C(2)	1.446(6)	1.442(5)
C(1)–C(2)	1.468(8)	1.497(7)
O(1)–H(1)	0.73(8)	0.74(9)
O(2)–H(2)	0.81(7)	0.91(6)
C(1)–H(3)	1.11(8)	0.96(5)
C(1)–H(4)	0.93(6)	0.99(5)
C(2)–H(5)	1.07(7)	1.02(6)
C(2)–H(6)	0.93(6)	1.05(6)
O(1)–C(1)–C(2)	108.5(4)	105.0(3)
O(2)–C(2)–C(1)	108.7(4)	104.8(3)
Cu–O(1)–C(1)	115.0(4)	112.1(2)
Cu–O(2)–C(2)	115.5(3)	114.2(2)
Cl(1)–Cu–Cl(2)	95.97(5)	98.14(3)
Cl(1)···Cu···Cl(2)	170.03(3)	169.07(3)
Cl(1)–Cu–O(1)	92.0(1)	171.1(1)
Cl(1)–Cu–O(2)	169.4(1)	91.2(1)
Cl(2)–Cu–O(1)	172.1(1)	90.5(1)
Cl(2)–Cu–O(2)	93.1(1)	165.1(1)
O(1)–Cu–O(2)	79.1(1)	79.9(1)

found for the hydrated compound compared to the water-free analogue. The intraring dimensions agree with those previously found for this kind of complex. The angles around oxygen and carbon involving hydrogen atoms agree fairly well with the tetrahedral angle; they range between 88 – 130 and 102 – 125° for $[CuCl_2(C_2H_6O_2)]$ and $[CuCl_2(C_2H_6O_2)].\frac{1}{2}H_2O$, respectively.

Hydrogen bond contacts. Within the infinite layers, from which $[CuCl_2(C_2H_6O_2)]$ is comprised, there is a pattern of hydrogen bond contacts between different molecules as indicated in Fig. 1. Each of the two chlorine atoms accepts one hydrogen bond from a glycol hydroxyl and the Cl··O distances are 3.077(4) and 3.068 (4) Å for Cl(1) and Cl(2), respectively. The corresponding O – H··Cl angles of 173(6) and 165(7)° indicate that the bonds do not deviate significantly from linearity.

In the hydrated compound both inter- and intrachain hydrogen bonds are found. The interchain contacts, which give rise to the layer formation, are formed *via* the water molecules. Each water oxygen shows four hydrogen bonds, tetrahedrally arranged; two as hydrogen bond donor to chlorine atoms, 3.146(3) Å, and two as hydrogen bond acceptor from the glycol hydroxyls, 2.669(4) Å. This arrangement is shown in Fig. 2. The bond O – H··Cl does not deviate significantly from linearity (∠O – H··O 164(6)°) and the acceptor Cl lies approximately in the plane of the water molecule. On the other hand, the O – H··O bond seems to be bent; the O – H··O angle is 152(5)°. Within the chains there are also hydrogen bond contacts between different molecules. They are of the O – H··Cl type with the glycol hydroxyls as donors. The Cl··O distance of 3.098(3) Å is in good agreement with other reported Cl··O distances and the O – H··Cl bond shows no significant deviation from linearity (∠O – H··Cl 175(7)°).

This increase of hydrogen bond contacts in the hydrated compound compared to the water-free compound will, in addition to the release of strain in the chelate ring, be of significant importance when the stability of the compounds is considered.

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