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Conformational flexibility of the di(1,3-diaminopropane)copper(II) cation Part 2⁻¹. Structure determination for aqua-di(1,3-diaminopropane-*N*,*N'*)copper(II) dichloride and chlorodi(1,3-diaminopropane-*N*,*N'*)copper(II) chloride methanol solvate and DFT calculations for aqua-di(1,3-diaminopropane-*N*,*N'*)copper(II) cation

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Abstract

The structures of aqua-di(1,3-diaminopropane-*N*,*N'*) copper(II) dichloride (1) and chloro-di(1,3-diaminopropane-*N*,*N'*) copper(II) chloride methanol solvate (2) were determined by single crystal X-ray methods. $[Cu(tn)_2H_2O]Cl_2$ (1) (tn = 1,3-diaminopropane), C_6H_22Cl_2CuN_4O, $M_r = 300.72$, tetragonal, space group $P4_2nm$ (No. 102), a = 9.3146(5), c = 7.591(1) Å, V = 658.63(9) Å³, Z = 2, $D_c = 1.516$ g cm⁻³. $[Cu(tn)_2Cl]Cl \cdot$ MeOH (2), $C_7H_{24}Cl_2CuN_4O$, $M_r = 314.74$, monoclinic, space group $P2_1/c$ (No. 14), a = 8.598(2), b = 16.176(2), c = 10.418(4) Å, $\beta = 107.11(3)^\circ$, V = 1384.7(7) Å³, Z = 4, $D_c = 1.510$ g cm⁻³. Compound 1 is formed in aqueous solution, whereas 2 was obtained in methanol. The coordination polyhedron in 1 is square pyramid with exceptionally high site symmetry of 4mm (C_{4v}) around the copper(II) cation. The distances from the central copper(II) cation to the two nearest chloride ions are different in 2, 2.736(2) and 3.322(2) Å. If the remote chloride is not taken into consideration, the coordination polyhedron could be described as distorted square pyramid. In both compounds the chelate rings display chair conformation. In 1 the two th ligands are coordinated to copper in syn-like fashion, whereas in 2 the rings are in normal anti-like conformation. The rare syn-like conformation is a stable conformation, since the overall geometry was not changed during optimization carried out at the LDA/DNP level of theory. The optimized syn-like conformation is favoured by 16.38 kJ mol⁻¹ over the optimized anti-like conformation of the [Cu(tn)_2(H_2O)]²⁺ cation.

Keywords: Crystal structures; Copper complexes; Bidentate amine complexes

1. Introduction

The complexity of the stererochemistry of Cu(II) complexes is well known [2]. The flexibility of the coordination sphere containing a tn ligand (tn = 1,3-diaminopropane) can tead into excessive difficulties as stated by Kennedy and Lever: 'Complexes of 1,3-diaminopropane are all badly behaved. – Possibly this reflects the greater conformational freedom of the six-membered rings in these complexes.' The authors studied the electronic, vibrational and thermodynamic properties in a series of bis(diamine)copper(II) complexes [3]. The conformational freedom of a tn chelate ring manifests itself especially in Cr(III), Co(III) and Ni(II) compounds. In the majority of the chelates, the six-membered ring displays chair conformation. In tris(1,3-diaminopropane-N,N) chromium(III) pentacyanonickelate(II) dihydrate one of the three tn chelate rings displays skew-boat conformation while the other two have the common chair conformation [4]. In bis(1,3-diaminopropane-N,N') dicyanocobalt(III) monohydrate one of the two chelate rings is in chair and the other in skew-boat conformation. In the corresponding trihydrate derivative both of the rings display chair conformation, however [5]. In a ¹H NMR study the chair conformation was found to be the most stable. However, the skew-boat conformer lies relatively low in energy with respect to the

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¹ For Part 1 see Ref. [1].

chair, $\Delta G = 5.9 \text{ kJ mol}^{-1}$ in tetraaqua(1,3-diaminopropane-N,N')nickel(II) chelate [6].

There is no review published so far about the tn complexes. When only the copper(II) complexes are concerned, the vast majority of them are bis complexes. No tris complexes have been characterized structurally and there are only two monocomplexes: bis(μ -malonato-O,O',O'')-(1,3-diaminopropane-N,N')copper(II) [7] and diaqua-[μ -1,3-propanediyl-bis(oxamato-O,O',O''',O'''',N,N')](1,3-diaminopropane-N,N')dicopper(II) dihydrate [8].

Fig. 1 illustrates the found structures for $Cu(tn)_2A_2$. xH_2O (x=0, 1, 2) compounds, where A is an anion. There are totally 14 structurally characterized compounds belonging to the category I with a substituted benzoate anion as a counter ion [9]. A water molecule can replace a benzoate anion from the coordination sphere of a six-coordinated copper(II) cation, as is the case in categories II and III. Fivecoordinated structures have been found with a coordinated anion (IV) or with a coordinated water (V). In the categories I-V the tn rings are mutually coordinated in *anti*-like fashion. Moreover, all of the chelate rings have chair conformation. In our earlier paper we discussed the conformational flexibility of 1,3-diaminopropane in chelate rings in six-coordinated complexes [1]. This paper deals with the chelate rings in five-coordinated copper(II) complexes.

The very simple compound, $Cu(tn)_2Cl_2$, is difficult to prepare without a coordinated solvent. Similar difficulties were met with $Cu(en)_2Cl_2$ (en = ethylenediamine), which was found to be aquachlorobis(ethylenediamine)copper(II) chloride [10]. Our attempts to synthesize $Cu(tn)_2Cl_2$ crystals



Fig. 1. The coordination types observed for di (1,3-diaminopropane-N,N')-copper(II) cation. The omission of the hydrogen atoms in II and V is due to unavailability of the respective coordinates.

have resulted in two different derivatives. We report here the syntheses and crystal structures of aqua-di(1,3-diaminopropane)copper(II) dichloride (1) and chloro-di(1,3diaminopropane)copper(II) chloride methanol solvate (2). The mutual *syn*-conformation of the chelate rings in 1 is novel in the series depicted in Fig. 1.

2. Experimental

2.1. Syntheses

2.1.1. Synthesis of aqua-di(1,3-diaminopropane-N,N')copper(II) dichloride (1)

Compound 1 was synthesized by adding 2.00 mmol of tn (Fluka) into a hot aqueous solution containing 1.00 mmol $CuCl_2 \cdot 2H_2O$ (Merck, p.a.). The solution was allowed to cool to ambient temperature. The deep blue crystals were separated by filtration and washed with Et₂O. Recrystallization was carried out by dissolving 240 mg of the raw product in 20 ml of hot abs. EtOH after which the hot solution was filtered. The filtrate was allowed to evaporate in an open dish to 4 ml at ambient temperature. After that it was kept in a freezer $(-18 \text{ }^{\circ}\text{C})$ for four weeks. During that period blue crystals formed (totally 140 mg), which were separated by decantation and then washed with Et₂O. Anal. Calc. for C₆H₂₂Cl₂CuN₄O: C, 24.0; N, 18.6; H, 7.4. Found: C, 24.0; N, 18.5; H, 7.5%. The same product (164 mg) was also obtained by dissolving 245 mg of the raw product in 2 ml H₂O and adding 6 ml isopropanol and 6 ml THF and storing the solution for two weeks in the freezer.

2.1.2. Synthesis of chloro-di(1,3-diaminopropane-N,N')copper(II) chloride methanol solvate (2)

Compound 2 was prepared by dissolving $CuCl_2$ (20 mmol) into a solution containing 50 ml THF and 30 ml EtOH. To this solution was added 42 mmol tn in 10 ml EtOH. The immediately formed violet precipitate was filtered and washed with Et₂O. Yield for $Cu(tn)_2Cl_2$ powder was 80%. Suitable single crystals of the title compound for the X-ray analysis were obtained by crystallizing the raw product from MeOH. The recrystallization was carried out by dissolving 230 mg of the raw product in 10 ml of MeOH at room temperature. The insolubles were filtered out. The filtrate (6 ml) was kept in a freezer (-18 °C) for two weeks. The blue crystals formed (63 mg) were separated by decantation and were washed with Et₂O. Anal. Calc. for $C_7H_{24}Cl_2CuN_4O$: C, 26.7; N, 17.8; H, 7.7. Found: C, 26.4; N 17.9; H, 7.8%.

2.2. X-ray structure determination

2.2.1. Crystal data

Compound 1: $C_6H_{22}Cl_2CuN_4O$, $M_r = 300.72$, tetragonal, space group $P4_2nm$ (No. 102), a = 9.3146(5), c = 7.591(1)Å, V = 658.63(9) Å³ (by least-squares refinement of diffractometer angles for 25 independent well-centred reflections in 2 θ range 47.3-49.8°, $\lambda = 0.71069$ Å), Z = 2, $D_c = 1.516$ g cm⁻³, F(000) = 314. Dark violet prisms. Crystal dimensions $0.22 \times 0.32 \times 0.38$ mm, $\mu = 20.52$ cm⁻¹.

Compound 2: $C_7H_{23}Cl_2CuN_4O$, $M_r = 314.74$, monoclinic, space group $P2_1/c$ (No. 14), a = 8.598(2), b = 16.176(2), c = 10.418(4) Å, $\beta = 107.11(3)^\circ$, V = 1384.7(7) Å³ (by least-squares refinement of diffractometer angles for 25 independent well-centred reflections in 2θ range $28.2-39.1^\circ$, $\lambda = 0.71069$ Å), Z = 4, $D_c = 1.51$ g cm⁻³, F(000) = 660. Dark blue prisms. Crystal dimensions $0.15 \times 0.25 \times 0.35$ mm, $\mu = 19.56$ cm⁻¹.

2.2.2. Data collection and processing

Compound 1: Rigaku AFC5S diffractometer, $\omega - 2\theta$ scan mode, scan speed 4.0° min⁻¹, weak reflections with $I < 10.0\sigma(I)$ twice rescanned, graphite monochromated Mo K α radiation, 616 unique reflections mesured ($5 \le 2\theta \le 60^{\circ}$), absorption correction (transmission factors 0.84–1.00), giving 481 independent reflections with $I > 3\sigma(I_o)$. No decay, but Lorentz and polarization corrections were made: correction for secondary extinction, coeff. = 0.71×10^{-5} .

Compound 2: Rigaku AFC5S diffractometer, $\omega - 2\theta$ scan mode, scan speed 8.0° min⁻¹, weak reflections with $I < 10.0\sigma(I)$ twice rescanned, graphite monochromated Mo K α radiation, 2541 unique reflections mesured $(3 \le 2\theta \le 50^{\circ})$. Totally 1559 in calculations with $I > 2\sigma(I_{o})$. Decay correction (-26.00%), experimental absorption correction (transmission factors 0.84–1.00); Lorentz and polarization corrections.

2.2.3. Structure analysis and refinement

Compound 1: Direct methods followed by difference Fourier techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and the hydrogen atoms with isotropic fixed temperature parameters (1.2 times B_{eq} of the carrying atom). The weighting scheme $w = 1/[\sigma^2(F_o)]$ with F_o from counting statistics gave satisfactory agreement analyses. Final R and R' values are 0.021 and 0.027, respectively.

Compound 2: The structure was solved by direct methods and refined by full-matrix least-squares techniques to an Rvalue of 0.046 ($R_w = 0.049$). The heavy atoms were refined anisotropically, and the hydrogen atoms (methyl hydrogens were included in calculated positions) with fixed isotropic temperature factors (1.2 times B_{eq} of the carrying atom).

Neutral atomic scattering and dispersion factors were taken from International Tables for X-Ray Crystallography [11]. All calculations were performed using the TEXSAN crystallographic software [12]. Figures were drawn with ORTEP [13].

The coordinates for both compounds are listed in Table 1. Geometric data including bond lengths and angles are listed in Tables 2 and 3 for compound 1 and 2, respectively. The numbering scheme and thermal ellipsoids for the atoms of the structures are shown in Figs. 2 and 3 for 1 and 2, respectively. Table 1

Atomic positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms of $[Cu(tn)_2H_2O]Cl_2$ and $[Cu(tn)_2Cl]Cl$ ·MeOH with their standard deviations in parentheses ^a

Atom	x/a	y/b	z/ c	$B_{\rm eq}({\rm \AA}^2)$		
$[Cu(tn)_2 F \cdot O]Cl_2$						
Cu(1)	1/2	1/2	0.4830	1.77(3)		
Cl(1)	0.67488(6)	0.67488(6)	0.0605(2)	2.98(2)		
0(1)	1/2	1/2	0.7828(6)	3.35(8)		
N(1)	0.5049(2)	0.7175(2)	0.4562(3)	2.41(8)		
C(1)	0.6060(3)	0.7995(3)	0.5711(5)	2.8(1)		
C(2)	0.7618(3)	0.7618(3)	0.5325(5)	2.92(8)		
$[Cu(tn)_2C]$	[1]Cl · MeOH					
Cu(1)	1.0064(1)	0.12766(5)	0.76894(7)	2.38(3)		
Cl(1)	1.1275(2)	0.1131(1)	0.5548(2)	3.18(7)		
Cl(2)	0.9289(2)	0.1303(1)	1.0630(2)	3.63(7)		
0(1)	0.7764(7)	0.1656(4)	0.3779(6)	4.5(3)		
N(1)	1.1889(8)	0.0716(4)	0.9115(6)	2.8(2)		
N(2)	1.1216(8)	0.2370(4)	0.8171(6)	3.0(3)		
N(3)	0.7974(7)	0.1904(4)	0.6855(7)	3.2(2)		
N(4)	0.8944(6)	0.0180(3)	0.7136(6)	2.7(2)		
C(1)	1.3579(9)	0.0950(5)	0.9295(8)	3.3(3)		
C(2)	1.388(1)	0.1857(5)	0.9568(8)	3.4(3)		
C(3)	1.298(1)	0.2425(5)	0.8429(8)	3.3(3)		
C(4)	0.6451(8)	0.1557(4)	0.7001(8)	3,3(3)		
C(5)	0.6108(9)	0.0710(5)	0.6392(8)	3.4(3)		
C(6)	0.725(1)	0.0054(5)	0.7144(8)	3.8(3)		
C(7)	0.6874(9)	0.1031(4)	0.2955(7)	4.1(3)		

^a The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{eq} = 4/3\Sigma_i \Sigma_j \beta_{ij} a_i a_j$.

Table 2

The bond lengths (Å) and angles (°) for 1 and the optimized $[Cu(tn)_2H_2O]^{2+}$ cation in the *syn*-like (optsyn) and in *anti*-like (optant) conformations

	1	optsyn	optant
Bond distances			
Cu(1)-O(1)	2.276(4)	2.188	2.280
Cu(1) - N(1,2)	2.037(2)	2.046	2.013, 2.022
Cu(1) - N(3,4)			2.018, 2.038
N(1,2)-C(1,3)	1.493(3)	1.476	1.482, 1.479
N(3,4)-C(4,6)		1.478, 1.484	
C(1,3)-C(2)	1.522(3)	1.496	1.507, 1.508
C(4,6)-C(5)			1.505, 1.508
Bond angles			
$N(1)-Cu(1)-N(1^{1})$	168.5(1)	166.3	175.4, 146.3
$N(1)-Cu(1)-N(1^{II})$	86.9(1)	89.0	89.8, 87.8
(bite angle)			
$N(1)-Cu(1)-N(1^{III})$	92.0(1)	89.4	92.7, 92.3
(interring)			
Cu(1)-N(1,2)-C(1,3)	117.7(2)	120.6	117.4, 119.0
Cu(1)-N(3,4)-C(4,6)			115.7, 112.9
N(1,2)-C(1,3)-C(2)	111.8(2)	112.1	111.8, 111.6
C(1)-C(2)-C(1,3)	113.8(3)	113.8	113.9
C(4)-C(5)-C(6)			114.9
Cu(1)-O(1)-H(7)	136(4)	127.8	
H(7)–O(1)–H(7)	88(8)	104.4	

 $^{I} = -x + 1, -y + 1, z; ^{II} = y, x, z; ^{III} = -y + 1, -x + 1, z.$

Cu(1) - N(1)	2.030(6)	N(2)-C(3)	1.467(9)
Cu(1) - N(2)	2.018(6)	N(3)-C(4)	1.473(9)
Cu(1) - N(3)	2.024(6)	N(4)-C(6)	1.474(9)
Cu(1) - N(4)	2.020(5)	C(1)-C(2)	1.50(1)
Cu(1)-Cl(1)	2.735(2)	C(2)-C(3)	1.52(1)
Cu(1)– $Cl(2)$	3.322(2)	C(4) - C(5)	1.50(1)
O(1)-C(7)	1.399(9)	C(5)-C(6)	1.50(1)
N(1)-C(1)	1.46(1)		
N(1)-Cu(1)-N(2)	89.6(2)	N(4)Cu(1)Cl(2)	93.8(2)
N(1)-Cu(1)-N(3)	159.4(3)	Cu(1)-N(1)-C(1)	120.2(5)
N(1)-Cu(1)-N(4)	91.0(2)	Cu(1)-N(2)-C(3)	120.3(5)
N(1)-Cu(1)-Cl(1)	99.2(2)	Cu(1)-N(3)-C(4)	118.0(4)
N(1)-Cu(1)-Cl(2)	69.6(2)	Cu(1) - N(4) - C(6)	120.6(4)
N(2)-Cu(1)-N(3)	88.6(2)	N(1)-C(1)-C(2)	112.7(6)
N(2)-Cu(1)-N(4)	177.6(3)	C(1)-C(2)-C(3)	115.0(6)
N(2)-Cu(1)-Cl(1)	90.1(2)	N(2)-C(3)-C(2)	111.4(6)
N(2)-Cu(1)-Cl(2)	88.6(2)	N(3)-C(4)-C(5)	111.9(6)
N(3)-Cu(1)-N(4)	91.7(2)	C(4) - C(5) - C(6)	114.1(6)
N(3)-Cu(1)-Cl(1)	101.3(2)	N(4)-C(6)-C(5)	113.3(6)
N(3)-Cu(1)-Cl(2)	89.8(2)	Cl(1)-Cu(1)-Cl(2)	168.81(5)
N(4)-Cu(1)-Cl(1)	87.5(2)		

Table 3 Bond distances (Å) and angles (°) in [Cu(tn)₂Cl]Cl·MeOH



Fig. 2. ORTEP drawing of 1 displaying the numbering scheme for the complex unit. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.



Fig. 3. ORTEP drawing of 2 displaying the numbering scheme. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

2.2.4. Physical measurements

Elemental analyses were carried out with Perkin-Elmer 2400 series II CHNS/O Analyzer. UV-Vis and NIR spectra were recorded on a Cary 5E UV-Vis-NIR Spectrometer in Nujol mulls. Solid-state IR spectra were run on a Mattson Galaxy FT infrared instrument using the Nujol mull technique.

2.2.5. Optimizations

Optimizations were carried out by DMol Version 2.2 program package at the LDA/DNP level of theory [14]. The calculations were run on CRAY X-MP and CONVEX C3840 computers of the Computer Center of the Finnish State.

3. Results and discussion

3.1. Compound 1

The copper(II) cation is five-coordinated displaying distorted square pyramidal coordination polyhedron. The copper(II) cation is displaced 0.22(6) Å from the N₄ plane towards the apical water molecule. The observed electronic d-d transitions at 544 and shoulders at 617, 660 and 820 nm are in accord with a slightly distorted square pyramidal coordination polyhedron [2b]. The two shortest Cu-Cl distances are 3.949(1) Å, which is clearly longer than the sum of the corresponding van der Waals radii of 3.30 Å [15].

The chelate rings display chair conformation. Exceptionally the site symmetry around the central copper(II) cation is rather high, $4\text{mm}(C_{4v})$. The total symmetry in the complex unit is $\text{mm}(C_{2v})$. Consequently the middle carbon C(2) lies in both rings on the same side of the N₄ plane due to a mirror plane. This is the first example of the $[\text{Cu}(\text{tn})_2]^{2+}$ complexes, where the ligands are mutually situated in *syn*-fashion. The absence of this conformation in the Cu(tn)₂A₂ complexes is due to the fact that most of them are centrosymmetric. The principle presented by Porai-Koshits says that when a structure with a centre of symmetry is one of several differing little in energy, it is usually found that the centrosymmetric structure is favoured by the crystal packing [16].

The related compounds aqua-di(1,3-diaminopropane-N,N') copper(II) sulfate and aqua-di(1,3-diaminopropane-N,N') copper(II) selenate differ considerably from compound 1 [17]. The ligands display *anti*-fashion coordination. Moreover, in the two compounds the copper(II) cation is situated almost on the coordination plane² and there are relatively long Cu-O distances: 2.57(1) and 2.52(1) Å for sulfate and selenate, respectively. In 1 the Cu-O distance is 2.276(4) Å.

To study the supposed correlation [17] between the Cu– O bond length and displacement of the copper(II) cation from the coordination plane, a survey was made among the compounds available in CSD [18]. Fig. 4. shows the values for the monomeric five-coordinated CuN₄O compounds with

² Morosin and Howatson [17] state that the copper(II) cations would lie on the N_4 plane. However, the deviations from the plane are 0.060(1) and 0.063(1) Å for aqua-di(1,3-diaminopropane)copper(II) sulfate and aquadi(1,3-diaminopropane)copper(II) selenate, respectively.



Fig. 4. Scatter graph of the bond length Cu–O and deviation of the copper(II) cation from the coordination plane in five-coordinated copper(II) compounds with a coordinated apical water molecule. The abbreviations in the Figure are the same than those used in CSD (see Section 5). The dark square refers to 1.

a coordinated water molecule. For a listing of the compounds with their CSD abbreviations see Section 5. The Cu–O bond length shows great variation: the range is 2.22–2.59 Å. The respective displacements are found in the range 0.073–0.372 Å. The calculated correlation of -0.901 corroborates the suggestion made in Ref. [17]. It is noteworthy that the correlation in this case seems to be linear. In a review article the correlation for the square-based pyramidal CuL₅ chromophore is represented by a parabolic curve [19].

The geometrical parameters for the hydrogen bonding system are given in Table 4. It should be remembered, that the X-ray methods do not produce accurate values for the hydrogen atom positions [20]. The values for the X-H bond lengths in Table 4 are obviously too short. Due to symmetry, both of the hydrogen atoms of the coordinated water are hydrogen bonded to a neighbouring chlorine atom. The $H \cdots Cl$ distances suggest hydrogen bonding. Similar situation was found for diaqua-bis(1,3-diaminopropane-N,N')-

copper(II) difluoride, where the axial water molecules are strongly hydrogen bonded [21]. Such a hydrogen bonding is expected to have an effect on the wag angle of the water molecule with respect to the axial bond. Since the O-H···Cl angle is practically 180°, the wag angle is not changed, but is 0°, as calculated theoretically for a series of metal hydrates [22]. However, there are only two other compounds in the data set obtained from CSD, where the wag angle is 0° [23,24].

According to the values shown in Table 4, both of the amine hydrogen atoms seem to be hydrogen bonded. The equatorial hydrogen atoms are pulled out, whereas the axial hydrogen atoms are drawn inwards with respect to the bite angle N-Cu-N of $86.9(1)^\circ$. Thus the net effect is very likely negligible and the angle can be expected to be near to its optimum value.

In the IR spectrum of 1 there is a broad absorption band with three maxima at 3349(m), 3226(m) and 3129(w) cm⁻¹ with weak shoulders at 3273 and 3179 cm⁻¹. The broadening is likely due to hydrogen bonding. The first band in 1 may be assigned to $\nu(H_2O)$ [21]. Usually the bands due to $\nu(N-H)$ stretching appear at and below 3300 cm⁻¹ [25]. In *trans*-di(3-iodobenzoato-*O*)bis(1,3-diaminopropane-*N,N'*)copper(II) the bands are seen at 3293, 3223, 3140 and 3100 cm⁻¹ [9], in *trans*-ditosylatobis(1,3-diaminopropane)copper(II) at 3302, 3273, 3254, 3223 and 3171 cm⁻¹ [26] and in di(1,3-diaminopropane)-3,5-dinitrobenzoatocopper(II) 3,5-dinitrobenzoate at 3298, 3280, 3180, 3104 and 3090 cm⁻¹ [27].

The structurally characterized compounds containing a water molecule coordinated to copper(II) atom and a hydrogen bond to a chloride anion are rare. Only three compounds were found from CSD: tetra-aqua-bis(9-methyladenine)-copper(II) dichloride dihydrate [28], aqua-chloro-(2,6-di-acetylpyridinedisemicarbazone-N,N',N'',O,O') copper(II) chloride dihydrate [29] and diaqua-tetrakis(N-methyl-imidazole-N') copper(II) chloride monohydrate [30]. The average values for $O \cdots Cl$ and $O-H \cdots Cl$ are 3.12(3) Å and 160(7)° in these compounds, respectively. The values for the interaction between a water molecule and a chloride anion in Table 4 are in accord with these values.

3.2. Compound 2

The coordination sphere of compound 2 can be described as a very distorted sp (sp = square pyramid). The distortion

Table 4

The distances (Å) and angles (°) for the hydrogen bonds of compound 1

	Х-Н	H···Y	X···Y	Х–Н · · · Y
$N(1)-H(1)\cdots Cl(1)$	0.91(4)	2.60(3)	3.418(3)	151(3)
$N(1)-H(2)\cdots Cl(1^{IV})$	0.81(2)	2.54(3)	3.329(2)	165(3)
$O(1)-H(9)\cdots Cl(1^{v})$	0.74(5)	2.39(5)	3.123(3)	175(5)

Symmetry codes: $^{1V} = -1/2 + x$, 3/2 - y, 1/2 + z; $^{V} = -x + 1$, -y + 1, z + 1.

1	abl	e	С	

Distances (Å) and angles (°) related to hydrogen bond formation in 2 with their standard deviations in parentheses

	X-H	$H \cdots Y$	N···Y	X–H···Y
$N(1)-H(1)\cdots Cl(2)$	0.66(6)	2.71(7)	3.234(6)	138(8)
$N(1)-H(2)\cdots Cl(2^{i})$	0.88(6)	2.59(7)	3.452(6)	164(4)
$N(2)-H(3)\cdots Cl(1)$	0.79(6)	2.72(7)	3.402(7)	155(7)
$N(2)-H(4)\cdots Cl(2^{ii})$	0.68(6)	2.75(7)	3.432(6)	172(8)
$N(3)-H(5)\cdots O(1)$	0.84(6)	2.51(6)	3.18(1)	138(6)
$N(3)-H(6)\cdots O(1^{iii})$	0.76(7)	2.45(7)	3.114(9)	147(7)
$N(4)-H(7)\cdots Cl(1^{i\nu})$	0.89(6)	2.69(7)	3.470(6)	147(5)
$N(4)-H(8)\cdots Cl(2^{\nu})$	0.98(6)	2.44(6)	3.375(6)	160(5)
$O(1)-H(21)\cdots Cl(1)$	0.64(8)	2.53(8)	3.155(6)	166(11)

Symmetry codes: i = 2 - x, -y, 2 - z; ii = x, 1/2 - y, z - 1/2; iii = x, 1/2 - y, z; iv = 2 - x, -y, 1 - z.

can be evaluated by comparison of the observed dihedral angles formed by the normal to adjacent polytopal faces with the ones of the ideal tbp (tbp = trigonal bipyramid) [31]. In 2 the distortion is 34.6% from sp to tbp. The site symmetry around the central copper(II) cation is clearly C_1 . All of the four-coordinated nitrogen atoms deviate clearly from the least squares plane calculated via them. The average deviation is 0.20(3) Å. The copper(II) cation is displaced 0.148 Å from this plane towards the chloride anion, which lies 2.735(2) Å from the copper(II) cation.

It has been argued that the displacement of the copper(II) cation should be dependent on the axial bond length in fivecoordinated complexes [17]. When the axial bond gets elongated in the complexes displaying distorted sp coordination, the copper(II) atom approaches the equatorial N₄ plane. In chlorobis(*cis*-1,3-cyclohexanediamine-*N*,*N'*)copper(II) perchlorate the axial Cu–Cl distance is shorter, 2.710(4) Å, and yet the displacement is smaller, 0.045 Å [32]. However, when the axial Cu–Cl bond length is short, the deviations from the coordination plane are also markedly greater. This is seen in three similar compounds, for which the Cu–Cl distances are in the range 2.367–2.430 Å and the respective displacements 0.55–0.546 Å [33]. Obviously also the amount of distortion (tbp \leftrightarrow sp) must play a role.

Both of the chelate rings display chair conformation. The chairs are bent to opposite sites with regard to the CuN₄ plane, as is usual in the series of *trans*-di(benzoato-O)bis(1,3-diaminopropane-N,N')copper(II) complexes.

The interring angles N1–Cu–N3 and N2–Cu–N4 are 159.7(2) and 177.4(2)°, respectively. A similar kind of structure has been found for bis(1,3-diaminopropane-N,N') isothiocyanatocopper(II) perchlorate [34], and the structure was described as distorted trigonal bipyramid. The respective angles have the values of 134.2(7) and 178.7(7)°. However, the observed electronic transitions of **2** are located as a maximum at 558 and shoulders at 620 and 658 nm and transitions should occur in the range 700–1050 nm, if the coordination sphere is a trigonal bipyramid [2b]. Now the observed values match well with the range given for distorted square pyramid or distorted elongated pseudo-octahedron. The 4 + 1 or 4 + 1 + 1 (or $4 + 1 + 1^*$) are the preferred coordination sphere is a trigonal bipyramid preferred coordination.

dination modes if the concept of d-s mixing is applied [35]. Obviously compound 2 belongs to the category IV, because the other chloride ion is relatively far away form the copper(II) cation (Cu(1)-Cl(2) = 3.322(2) Å). The interaction cannot be excluded with certainty, however, since the sum of the corresponding van der Waals radii is 3.30 Å.

The two bite angles N-Cu-N are clearly different: the N(1)-Cu(1)-N(2) angle is $89.6(2)^{\circ}$ while the N(3)-Cu(1)-N(4) angle is $91.7(2)^{\circ}$. Based upon semi-empirical MMX calculations the optimized angle was found to be 87.5° for *trans*-di(tosylato-O)-bis(1,3-diaminopropane-N,N')-copper(II) [26]. Usually the bite angle is smaller than 90° as found for *trans*-di(benzoato-O)bis(1,3-diaminopropane-N,N')copper(II) complexes [9].

The geometrical parameters for the hydrogen bonding system are presented in Table 5. The structure is stabilized by extensive inter and intramolecular hydrogen bonds with all the eight hydrogen atoms of the amino groups hydrogen bonded. Usually in the complexes depicted in Fig. 1 only six of the eight hydrogen atoms of the amino groups are hydrogen bonded. In compound 2 the remaining two hydrogen form hydrogen bonded to the coordinated Cl(1) (Fig. 3). The hydrogen bonding manifests itself also in the IR bands at 3349, 3227 and 3128 cm⁻¹ with shoulders at 3279 and 3179 cm⁻¹.

4. Flexibility of the chelate rings

Since the structure of 1 is the first example of *syn*-like conformation, we decided to optimize also the *anti*-like conformation of the $[Cu(H_2O)(tn)_2]^{2+}$ complex cation. The complex units were optimized at the LDF/DNP level of theory. The bond lengths and angles for the optimized structures are shown in Tables 2 and 3.

The overall structure of the syn-like conformation obtained by the optimization is close to the observed one. The chelate rings have still the syn-like conformation. The copper atom is out-of-plane, which is seen from the angle N(1)-Cu(1)- $N(1^1)$. The plane containing the axial water molecule is still



Fig. 5. The optimized structures of the syn- and anti-like conformations of the $[Cu(tn)_2(H_2O]^{2+}$ cation.

perpendicular to the N_4 plane. The biggest difference is seen in the axial Cu-O bond length, which is only 2.188 A. The value is shorter than found in CuN₄O complexes with an apical coordinated water, but is comparable to 2.226(5) Å found for $bis(N^1$ -isopropyl-2-methyl-1,2-propanediamine)aquacopper(II) bishydrogen carbonate hemihydrate [36]. The short value may well reflect the accuracy of calculation. However, it must be remembered that an optimized structure refers to a gas phase with no intermolecular interactions. We suggest that the relatively wide range for the Cu-O bond lengths shown in Fig. 4 is due to variation in the hydrogen bonding network. Thus the short Cu-O bond length in the optimized structure would represent the minimum value to be expected in CuN₄O type complexes with an apical water. This topic will be dealt with in more detail in a future paper concerning the diaquabis(1,3-diaminopropane)copper(II)

cation. There are also differences in the N-Cu-N and Cu-N-C angles. The same reasoning can be applied also here: hydrogen bonding is not involved in the optimized structure, although it is the most probable reason for the variation in these angles [1].

The optimized structures are shown in Fig. 5. Selected bonding parameters are given in Tables 2 and 6. The optimization of the *anti*-like conformation of a $[Cu(tn)_2H_2O]^{2+}$ cation resulted in a structure, where both chelate rings display ring conformation. However, the overall structure resembles now the structure of 2. The distortion is 37.0% from sp to tbp, while for 2 it is 34.6%. No doubt, the result corroborates nicely the assumption of intra strain generated by the two sixmembered chelate rings. According to House and co-workers, the strain would be released on going from sp to tbp [37]. Obviously the coordination is not dependent on the apical moiety. The difference between the self consistent total energies of the optimized syn and anti conformations is 16.38 kJ mol^{-1} in favour of the syn conformation. The apical Cu–O distance is now 2.280 Å and the average equatorial Cu-N bond length 2.023(9) A. The plasticity of the coordination sphere of a copper(II) cation is well seen in these values. Moreover, the easiness of a tn chelate ring to get deformed is seen in the the Cu-N-C angles ranging from 112.9 to 119.0°.

The flexibility of the chelate rings can be described by the characterizing parameters shown in Table 6. The z_i values describe the distance of a carbon C_i from a respective CuN_2 plane [38]. The parameters Θ , φ and Q characterize overall conformation, twisting and the total puckering of a ring, respectively [39]. The six-membered chelate ring in compound 1 is clearly very near to an ideal chair, for which the Θ and φ values are both 0°. However, the ring is more puckered than an optimized ring, which is seen in the respective z_i and Q values. In compound 2 both of the rings are clearly closer to the optimized ring of 1, although there is more twisting of the rings involved. The twisting is also seen in the optimized structure of the *anti*-like conformation of 1. Generally, the slight twisting of rings and other ring forms does not need much energy as seen from Ref. [6].

The chair-to-chair interconversion has also been studied by semi-empirical force-field methods [38]. The lowest-

	1	2 ring 1	2 ring 2	syn opt. ^a	anti opt. ^a ring 1	anti opt. ^b ring 2
Z1	1.04(11)	0.824(14)	0.826(14)	0.793	0.934	1.093
7 ₂	0.85(14)	0.53(2)	0.42(2)	0.429	0.632	0.990
23	1.04(11)	0.847(14)	0.743(14)	0.799	0.905	1.116
<u>o</u>	4.84	5.69	12.1	9.10	3.61	9.30
φ	0.00	13.2	25.8	0.02	30.0	8.38
0	0.658	0.565	0.561	0.562	0.607	0.689
ba ^c	86.8(1)	89.6(1)	91.7(2)	88.9	89.8	87.8

The characteristic deformational values describing the puckering of the chelate rings

* Optimized structure of the syn-like conformation of a $Cu(tn)_2(H_2O)$]²⁺ cation.

^b Optimized structure of the *anti*-like conformation of a $Cu(tn)_2(H_2O)$ ²⁺ cation.

^c Bite angle N-Cu-N.

Table 6

energy pathway in a chair-to-chair interconversion would proceed via a skew-boat intermediate and involve twisting the ring atoms about a N-C axis. The energy threshold as ring strain energy would be approximately 29 kJ mol⁻¹. The energy cost may be considerably lower, since for tetraaqua(1,3-diaminopropane)nickel(II) ΔG for chair-toskew-boat conversion is only 5.9 kJ mol⁻¹ measured by NMR techniques [6]. The optimized structure of the *anti*like conformation of **1** does not exclude either a skew-boat or trigonal bipyramid intermediate.

5. Supplementary material

A listing of the compounds with their CSD abbreviations is available from the authors on request.

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