1,3-Diaxial Repulsion *vs.* π-Delocalization in the 7-Amino-2,4-diazabicyclo[3.3.1]nonan-3-one Skeleton

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(1*R*,5*S*,6*S*,8*R*)-6,8,9-Trihydroxy-3-oxo-2,4-diazabicyclo[3.3.1]nonan-7-ammonium chloride hydrate (**3**Cl·H_2O) and (1*R*,5*S*,6*S*,8*R*)-7-amino-6,8,9-trihydroxy-2,4-diazabicyclo[3.3.1]nonan-3-one (**4**) have been prepared, and their crystal structures have been determined from single-crystal X-ray diffraction data. Both compounds consist of a bicyclic skeleton with the three N-atoms in an all-*cis*-1,3,5-triaxial arrangement. Considerable repulsion between these axial N-atoms is indicated by a significant distortion of the two cyclohexane chairs and by increased N···N distances. The lone pair of the free amino group of **4** is involved in intermolecular H-bonding and is turned away from the adjacent carbonyl C-atom of the urea moiety. The structural properties together with the observed reactivity do not provide any evidence for an intramolecular donor-acceptor interaction between the carbonyl C- and the amine N-atom.

1. Introduction. – In contrast to the well-known and very stable 1,3,5,7-tetraazaadamantane (urotropine), 2,4,10-triazaadamantane has been reported to be a rather reactive and unstable compound [1]. Although the 2,4,10-triazaadamantane skeleton is expected to have a low-strain geometry, it reacts readily to form the ring-opened amidine, where 1,3-diaxial repulsion induces considerable strain. Obviously, the formation of the adamantane structure would require a loss of π-delocalization in the amidine fragment, and this effect seems to outweigh the favorable, low-strain properties of the adamantane geometry. This is different for the urotropine molecule where no π-stabilization would be possible in an open form. For metal complexes, the 2,4,10-adamantane structure is, however, well-known and has been elucidated for a variety of complexes of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (**1a**) and related ligands with transition-metal cations such as Co^{III}, Ni^{II}, or Cu^{II} [2]. The question arises though, whether such a structure would also be possible with a C-atom in place of a metal cation as shown in the *Scheme* for the tetrol **6**. Inspection of the geometry of the amine **4** in terms of a simple ball-and-stick model indicated that at least a weak attraction between the electrophilic C-atom of the C=O group and the lone pair of the amino N-atom could be expected. *Dunitz* and co-workers have shown for a series of 1,8-disubstituted naphthalenes with a C=O substituent at C(1) and a nucleophilic substituent at C(8) that weak attractive interactions between these two groups are indeed indicated by systematic structural distortions [3]. We report here the synthesis and crystal structures of the free amine **4** and the protonated ammonium cation $\mathbf{3}^+$

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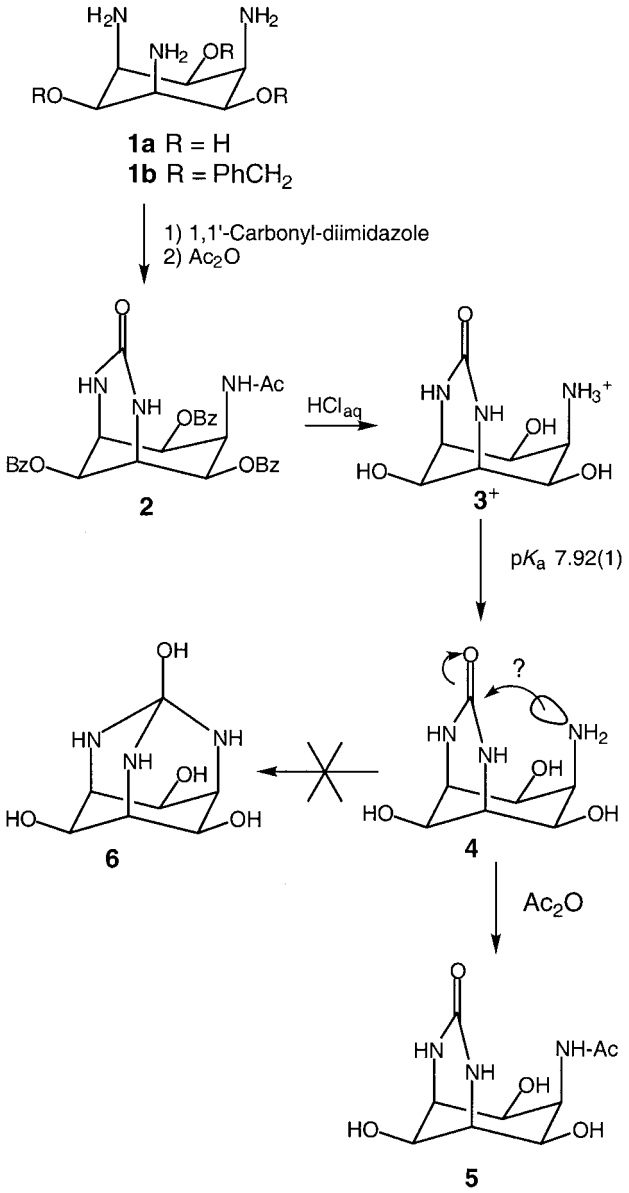
Scheme



isolated as the hydrated hydrochloride **3**Cl · H_2O and analyze the geometric parameters of **4** for such possible donor-acceptor interactions.

2. Results and Discussion. – To achieve better solubility in organic solvents, the parent 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (**1a**) was transformed into the tris-*O*-

benzylated triamine **1b** (*Scheme*). Subsequent reaction with 1,1′-carbonyldiimidazole resulted in the formation of a corresponding urea derivative. This reaction was followed by ^{1}H-NMR spectroscopy, which indicated additional conversion (probably of the remaining amino group); and the resulting complex mixture of compounds could not be resolved. This problem could, however, be circumvented by adding Ac_2O to the mixture a few minutes after the start of the reaction, and the product could then be isolated in good yield as the acetamide **2**. Further treatment with aqueous HCl allowed removal of the Bz groups, and hydrolysis of the acetamide in one single step. Hydrolysis of the urea moiety was not observed under the conditions applied. The bicyclic triol was then isolated in the form of the weakly acidic ammonium salt **3**Cl · H_2O (pK_a 7.92), and the free amine **4** was liberated by deprotonation on an anion-exchange resin. Both compounds, the ammonium salt **3**Cl · H_2O and the free amine **4**, proved to be stable and were fully characterized in the solid state and in solution. A subsequent transformation to the adamantane cage **6** could not be observed at all.

To better understand the steric properties of **3**Cl · H_2O and **4**, a single-crystal X-ray analysis was performed for these two compounds. The ammonium salt **3**Cl · H_2O crystallizes in the monoclinic space group *Cc*; however, its anion-cation packing is closely related to the hexagonal NiAs structure: the positions of the Cl^- anions correspond roughly to a hexagonal closest packing (with axis *c* as the pseudo $6_3/m$ axis), whereas the cations are approximately located in the octahedral holes of this packing. Consequently, each cation is surrounded by six Cl^- anions forming a slightly distorted octahedron, and each Cl^- anion is surrounded by six cations located in the vertices of an almost regular trigonal prism. Four of the six surrounding cations form one H-bond each to the central Cl^- anion involving alicyclic OH groups, the ammonium group, and one of the urea NH groups as H donors. The Cl^- anion is further H-bonded to a disordered H_2O molecule. Additional H-bonds are formed between neighboring cations. These involve the ammonium group and one of the urea NH groups as H donors and the carbonyl O-atom as well as alicyclic OH groups as H acceptors. The H-bonding network is completed by interactions between the cations and the H_2O molecules. Although the cation itself has no crystallographic symmetry, there is only minor deviation of the non-H-atomic positions from C_s symmetry with a pseudo mirror plane running through C(1), N(1), C(4), O(4), C(53), O(53) (*Fig. 1*), and, according to the NMR data, the cation adopts fully C_s symmetry in solution. An analysis of the puckering parameters for the two six-membered rings revealed a considerably distorted chair for the cyclohexane ring with puckering parameters $Q = 0.598(2)$ Å, $\theta = 161.2(2)^\circ$, and $\phi = 9.0(5)^\circ$, indicating a significant twist towards an envelope conformation [4]. This distortion is obviously a consequence of the severe repulsion between the axial ammonium group and the two axial N-atoms of the urea moiety. The corresponding intramolecular distances are N(1)···N(3): 3.228(2) Å and N(1)···N(5): 3.055(2) Å (to be compared with N(3)···N(5): 2.3041(18) Å). This strain can also be recognized by the considerable displacement of the three axial C–N vectors from a parallel arrangement. In agreement with extensive delocalization of the lone pairs at the two urea N-atoms, there is no indication of any intramolecular N–H···N H-bonding. The six-membered ring comprising the urea moiety (puckering parameters: $Q = 0.582(2)$ Å, $\theta = 112.5(2)^\circ$, $\phi = 295.6(2)^\circ$) adopts a structure lying in-between an envelope and a boat conformation.

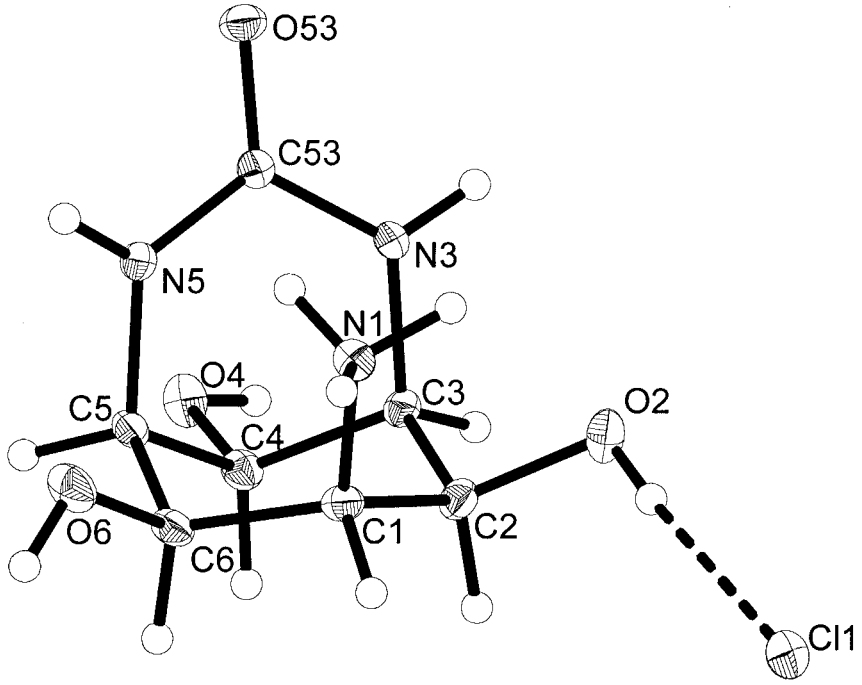


Fig. 1. *View of the ammonium cation* $\mathbf{3}^+$. Displacement ellipsoids are drawn at the 50% probability level, radii of the H-atoms are of arbitrary size.

The crystal structure of the free amine **4** can be described as a stack of slightly wavy layers along axis *b*. The layers have an approximate hexagonal geometry where every molecule is surrounded by six neighbors forming a slightly distorted hexagon. A variety of H-bonds are formed within each layer and also between different layers. The intralayer H-bonds have one of the urea NH group (N3) and an OH group (O4) as H donors. An OH group (O6) and the free amino group (N1) serve as H acceptors. Interlayer H-bonds are formed between the OH groups (O2, O6) as H donors and an OH group (O4) together with the carbonyl O-atom (O53) as acceptors. Similarly to the ammonium cation $\mathbf{3}^+$, the free amine **4** adopts C_s symmetry in solution and approaches this symmetry closely in the crystal structure (*Fig. 2*). In comparison with the cation $\mathbf{3}^+$, the puckering parameters of the cyclohexane ring ($Q = 0.618(1)$ Å, $\theta = 12.7(1)^\circ$, $\phi = 172.7(4)^\circ$) indicate a similar but somewhat less-pronounced distortion of the chair towards an envelope conformation, and the intramolecular N···N distances N(1)···N(3): 3.0996(13) Å, N(1)···N(5): 3.1566(13) Å, N(3)···N(5): 2.3078(13) Å are in agreement with the corresponding values for $\mathbf{3}^+$. The six-membered ring comprising the urea moiety has an almost ideal envelope conformation ($Q = 0.528(1)$ Å, $\theta = 53.8(1)^\circ$, $\phi = 120.6(1)^\circ$). The distance between N(1) (the nucleophilic center of the amino group) and C(53) (the electrophilic center of the C=O group) is 3.0819(14) Å. In the cation $\mathbf{3}^+$, the N(1)···C(53) separation is 3.299(2) Å, and deprotonation of the ammonium group obviously causes a slight decrease of the N(1)···C(53) distance. However, this distance is still considerably longer than the corresponding lengths in the 1,8-disubstituted

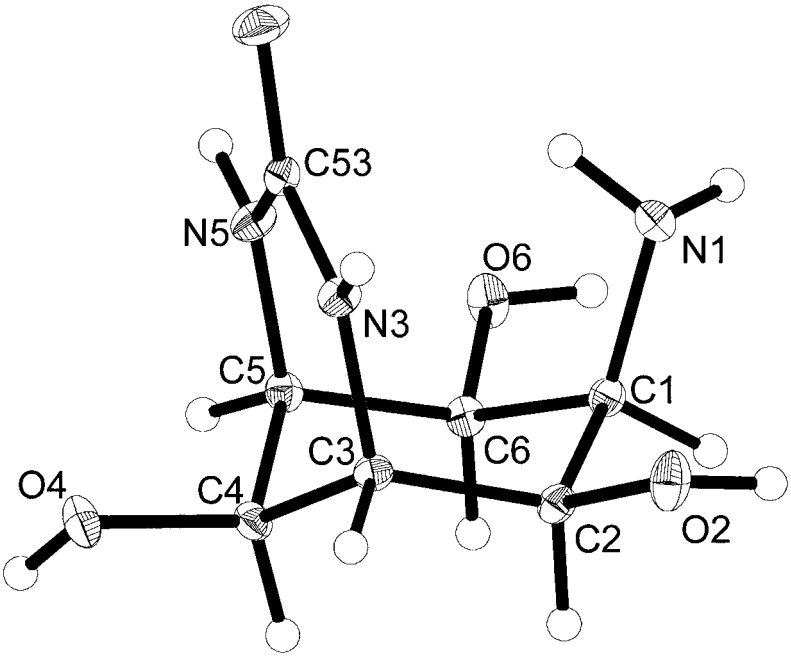


Fig. 2. *View of the free amine* **4**. Displacement ellipsoids are drawn at the 50% probability level, radii of the H-atoms are of arbitrary size.

naphthalene systems, where separations of 2.56–2.62 Å have been observed for such donor-acceptor interactions [3]. It is also noteworthy that, in the structures of $\mathbf{3}^+$ and **4**, the carbonyl C-atoms show no significant deviation from a planar coordination, and it further appears that the lone pair of the free amino group of **4** is involved in an intermolecular H-bond to an OH group of an adjacent molecule. Such N···HO H-bonds between aliphatic amino and OH groups have been recognized as playing an important role in solid-state structures of related compounds [5]. Moreover, the observed pK_a value of 7.92 indicates only slightly increased acidity of the ammonium group compared to the unsubstituted 1,3-diamino-5-ammonio-1,3,5-trihydroxy-*cis*-inositol ($H\mathbf{1a}^+$), which has a pK_a of 8.90 [6]. In addition, the free amino group of **4** retains its reactivity as a nucleophile against external electrophiles, as demonstrated by the ready conversion to the acetamide **5** in the presence of Ac_2O. All these observations indicate no significant donor-acceptor interaction between the nitrogen donor (N1) and the carbonyl acceptor (C53).

3. Conclusions. – The crystal structures of the ammonium cation $\mathbf{3}^+$ and the corresponding amine **4** both exhibit considerably strained geometries due to 1,3- and 1,5-diaxial repulsion between the N-atoms of the urea group, and the ammonium or amino group, respectively. From a steric point of view, the free amino group of compound **4** has an ideal position (angle and distance) to attack the carbonyl C-atom, resulting either in the generation of a full C–N single bond (2,4,10-adamantane

formation) or in weak donor-acceptor interactions as observed in suitably 1,8-disubstituted naphthalene derivatives [3]. In either case, such an interaction would result in a significant release of steric strain. However, the geometric parameters of **4** together with the observed reactivity towards electrophiles such as H^+ or Ac_2O provided no evidence for the presence of any constructive N(1)···C(53) interaction. It appears that the high degree of stabilization obtained from the π-delocalization, which requires a strictly planar geometry at the urea C-atom, prevents any structural move towards tetrahedral coordination. The absence of such interactions and consequently the retained nucleophilic reactivity make the amine **4** an interesting synthon for a selective monoalkylation of the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol.

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Experimental Part

General. all-cis-*2,4,6-Tris(benzyloxy)cyclohexane-1,3,5-triamine* (**1b**) was prepared as described in [7]. $CHCl_3$ was purified by elution on Al_2O_3 (*Brockman*, grade I). All other reagents were commercially available and were used without further purification. The pK_a value ($= -\log K$, $K = [\mathbf{4}] \times [H^+] \times [\mathbf{3}^+]^{-1}$) of $\mathbf{3}NO_3$ was determined by potentiometric titration experiments (25.0°, $\mu = 0.1$M KNO_3, p$K_w = 13.80$) of a soln. of $\mathbf{3}NO_3$ (50 ml, 0.002 M) with 0.1M KOH as described in [7]. A total of 25 points in the range $7.07 \leq pH \leq 8.34$ were evaluated with the computer program SUPERQUAD [8]. The estimated standard deviation in the pK_a is less than 0.01. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX 500* spectrometer (^{1}H: 500.13 MHz, ^{13}C: 125.9 MHz), δ in ppm, sodium (D_4)(trimethylsilyl)propionate or TMS (= 0 ppm) as internal standard. FAB-MS (pos.-ion mode): VG ZAB-VSEQ instrument; the samples dissolved in H_2O or DMSO, and mixed with a glycerol or a 3-nitrobenzyl-alcohol matrix. C,H,N Analyses were performed by *H. Feuerhake* (Anorganische Chemie, Universität des Saarlandes).

N-*[(1*R,*5*S,*6*S,*8*R*)-6,8,9-Tris(benzyloxy)-3-oxo-2,4-diazabicyclo[3.3.1]non-7-yl]acetamide* (**2**). To a soln. of **1b** (4500 mg, 10.05 mmol) in $CHCl_3$ (60 ml) was added 1,1′-Carbonyldiimidazole (10.05 mmol; dissolved in 35 ml of $CHCl_3$, under Ar). The resulting clear soln. was stirred for additional 5 min at r.t. Ac_2O (2.91 ml, 30.16 mmol) was added, and the soln. was stirred for an additional 2 h. Volatile components were then removed by evaporation, and the resulting residue was dissolved in CH_2Cl_2 (50 ml). The soln. was extracted with aq. NaOH (1M) and HCl (1M). The org. phase was evaporated, and the resulting white solid was dried *in vacuo*, redissolved in CH_2Cl_2, and purified by chromatography (silica gel; AcOEt/MeOH 8:1): 4.92 g (9.54 mmol, 95%) of **2**. ^{1}H-NMR ($CDCl_3$, TMS): 7.39–7.22 (*m*, 15 H); 6.06 (*d*, *J* = 10.2, 1 NH); 5.41 (*d*, *J* = 4.1, 2 NH); 5.20 (*m*, 1 H); 4.72 (*d*, *J* = 11.7, 2 H); 4.52 (*s*, 2 H); 4.42 (*d*, *J* = 11.7, 2 H); 3.74 (br. *m*, 2 H); 3.28 (*m*, 3 H); 1.98 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, TMS): 171.3 (C=O); 154.9 (C=O); 137.5 (C_{tert}); 137.0 (C_{tert}); 128.6 (CH); 128.6 (2 CH); 128.1 (CH); 127.9 (CH); 127.8 (2 CH); 127.7 (CH); 75.0 (CH); 70.8 (CH_2); 69.9 (CH_2); 66.6 (CH); 44.9 (CH); 23.7 (Me). FAB$^+$-MS: 516.2 (100 [$M+1$]$^+$). Anal. calc. for $C_{30}H_{33}N_3O_5$ (515.62): C 69.88, H 6.45, N 8.15; found: C 69.82, H 6.65, N 8.02.

*(1*R,*5*S,*6*S,*8*R*)-6,8,9-Trihydroxy-3-oxo-2,4-diazabicyclo[3.3.1]nonan-7-ammonium Chloride Hydrate* (**3**Cl·H_2O). Acetamide **2** (4.90 g, 9.50 mmol) was refluxed under Ar in 200 ml of conc. HCl for 100 min. The resulting clear and colorless soln. was evaporated to a volume of *ca.* 100 ml and extracted with Et_2O. The aq. phase was then evaporated, and the resulting white solid was dried rigorously *in vacuo:* 2.40 g (9.30 mmol, 98%) of **3**Cl·H_2O. ^{1}H-NMR (D_2O, pD < 2): 4.11 (*dd*, *J* = 2.7, 5.9, 2 H); 3.94 (*t*, *J* = 2.4, 1 H); 3.82 (*t*, *J* = 5.9, 1 H); 3.74 (br. *m*, 2 H). ^{13}C-NMR (D_2O, pD < 2): 159.8; 68.8; 61.6; 58.2; 55.4. FAB$^+$-MS: 204.0 (100, **3**$^+$). Anal. calc. for $C_7H_{13}N_3O_4 \cdot HCl \cdot H_2O$ (257.66): C 32.63, H 6.26, N 16.31; found: C 32.70, H 6.09, N 16.19. Single crystals were grown by dissolving the product in aq. HCl and layering this soln. with EtOH.

*(1*R,*5*S,*6*S,*8*R*)-7-Amino-6,8,9-trihydroxy-2,4-diazabicyclo[3.3.1]nonan-3-one* (**4**). The hydrochloride **3**Cl·H_2O was deprotonated with *Dowex 2X8* (OH^- form) anion-exchange resin. Evaporation and recrystallization from H_2O/EtOH/NH_3 10:5:1 yielded quantitatively single crystals of **4**. ^{1}H-NMR (D_2O, pD > 12): 3.73 (*m*, 2 H); 3.68 (br. *s*, 1 H); 3.44 (*t*, *J* = 2.1, 2 H); 3.28 (*t*, *J* = 5.6, 1 H). Anal. calc. for $C_7H_{13}N_3O_4$ (203.2): C 41.38, H 6.45, N 20.68; found: C 41.27, H 6.56, N 20.50.

The nitrate **3**NO_3 was precipitated by adding 3 equiv. of conc. HNO_3 to a soln. of **4** in EtOH. Anal. calc. for $C_7H_{14}N_4O_7$ (266.21): C 31.58, H 5.30, N 21.05, found: C 31.76, H 5.34, N 21.09.

N-*(all*-cis-*6,8,9-Trihydroxy-3-oxo-2,4-diazabicyclo[3.3.1]non-7-yl)acetamide* (**5**). The free amine **4** (5.0 g, 24.5 mmol) was suspended in a mixture of 400 ml of MeOH and 6.9 ml (73.5 mmol) of Ac_2O. The suspension was refluxed for 90 min and filtered. The resulting clear soln. was evaporated to a total volume of a few ml. Solid **5** was then precipitated by adding 150 ml of dry EtOH. Drying *in vacuo* over P_2O_5 yielded 5.65 g (23.04 mmol, 94%) of **5**. White, crystalline solid. ^{1}H-NMR (D_2O): 4.59 (*t*, *J* = 5.8, 1 H); 3.94 (*dd*, *J* = 5.8, 2.1, 2 H); 3.92 (*t*, *J* = 2.1, 1 H); 3.63 (br. *m*, 2 H); 2.05 (*s*, 3 H). ^{13}C-NMR (D_2O): 178.8; 160.2; 71.2; 61.7; 58.6; 54.2; 25.5. FAB$^+$-MS: 204.0 (100, $[M+1]^+$). Anal. calc. for $C_9H_{15}N_3O_5$ (245.24): C 44.08, H 6.17, N 17.13; found: C 44.29, H 6.46, N 17.10.

X-Ray Crystal-Structure Determination of **3***Cl* · H_2O *and* **4**[2]) (see the *Table*, and *Figs. 1* and *2*). Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, λ = 0.71073 Å) at r.t. (295 K) [9]. The measured data were corrected for *Lorentz* and polarization effects. Numerical absorption corrections were applied with seven and eight indexed and measured crystal faces for **3**Cl · H_2O and **4**, respectively [10]. A decay correction was done for **3**Cl · H_2O with the MolEN program system [11]. The structures were solved by direct methods with the SHELXS-97 program system [12]. All non-H-atoms for both structures were refined with anisotropic displacement parameters. A correction for secondary extinction was applied for **3**Cl · H_2O and **4** during refinement on F^2 with the program SHELXL-97 [13]. For compound **3**Cl · H_2O, the H_2O O-atom was disordered over two sites (ratio refined to 0.79 : 0.21). The H_2O H-atoms were

Table. *Crystallographic Data for Compounds* **3***Cl* · H_2O *and* **4**

	3	**4**
Empirical formula	$C_7H_{16}ClN_3O_5$	$C_7H_{13}N_3O_4$
Formula weight	257.68	203.20
Crystal size [mm]	0.52 × 0.37 × 0.15	0.42 × 0.40 × 0.22
Temp. [K]	295(1)	295(1)
Wavelength (MoK_α) [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$
a [Å]	6.800(1)	6.080(1)
b [Å]	11.954(2)	12.049(2)
c [Å]	13.053(3)	10.855(2)
β [°]	95.83(3)	93.95(3)
Volume [Å^3]	2617.6(10)	793.3(2)
Z	4	4
Density (calc.) [mg/m^3]	1.621	1.701
μ(MoK_α) [mm^{-1}]	0.375	0.140
2 θ Range [°]	6.28 to 60.00	5.06 to 59.96
Reflections collected	3258	4907
Independent reflections	1668 [$R_{(int)}$ = 0.0163]	2302 [$R_{(int)}$ = 0.0182]
Max. and min. transmission	0.9459, 0.8288	0.9699, 0.9436
Data/restraints/parameters	1668/8/178	2302/0/139
R[a]), wR[b])	0.0257, 0.0675	0.0325, 0.1013
Final Δ_{max}/σ	0.001	0.000
$\Delta\rho$ (max; min) [e Å^{-3}]	0.323, −0.269	0.381, −0.197

[a]) Based on *F* and reflections with I > 2σ(*I*).
[b]) Based on F^2 and all unique reflections.

[2]) The crystallographic data (excluding structure factors) for **3**Cl · H_2O and **4** have been deposited at the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-150905 and CCDC-150906, respectively. Copies of the data can be obtained, free of charge, on application of the CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

located in a difference *Fourier* map, their positional parameters were refined by using six distance restraints and the PART instructions of SHELXL-97. In compound **4**, all positions of the H-atoms could be located in difference electron-density maps, but only H(11) and H(12), bound at N(1), were refined with isotropic displacement parameters. The three OH H-atoms in **3**Cl · H_2O and **4** were allowed to rotate and were locked at interpretable residual electron densities at the respective O-atoms by means of distance restraints (AFIX 147 option) with SHELXL-97. All other positions of H-atoms in **3**Cl · H_2O and **4** were calculated after each refinement cycle (riding model). It should be noted that the structure of **3**Cl · H_2O crystallized in the non-centrosymmetric space group *Cc*. Structures in this space group could often be described in a higher true symmetry, as reported, *e.g.*, by *Baur* and *Kassner* [14], and *Marsh* [15]. Having in mind the 'Perils of *Cc*', the structure of **3**Cl · H_2O was checked for higher symmetry with MISSYM [16]. Extra symmetry elements could not be detected. The structure is also not merohedrically twinned (*Flack*'s *x*-parameter was 0.00(5) at convergence) [17].

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