Synthesis and Structural Characterisation of Cyclohexylamine Hemihydrochloride

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The first structural characterization of a simple aliphatic amine 'hemi' salt is reported: cyclohexylamine hemihydrochloride. An X-ray structure determination reveals that a cyclohexylammonium cation and a cyclohexylamine molecule are linked by a hydrogen bond N^+–H···N. Further H bonds N–H···Cl lead to a layer structure.

A *'hemi'* salt of a base B with an acid HX is usually understood to be an ionic compound in which the overall composition corresponds to 2 B·HX. As far as we are aware, such compounds were previously unknown for cases with simple aliphatic amines (B = RNH_2) and simple counteranions X. We here report the serendipitous isolation and subsequent characterization of the compound with B = cyclohexylamine and X = Cl.

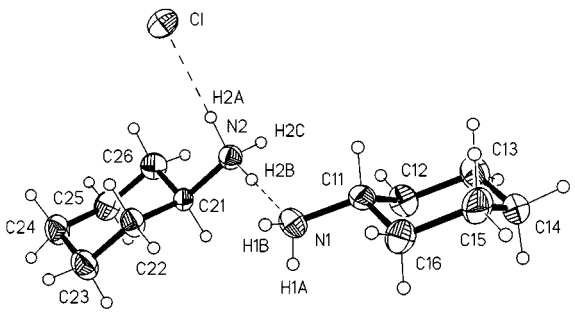
During our investigations of (amine)chlorogold(I) species[1] we attempted to grow crystals of the reaction product of cyclohexylamine and (tht)AuCl (tht: tetrahydrothiophene) by liquid-liquid diffusion of cyclohexylamine into a solution of (tht)AuCl in dichloromethane. We obtained two kinds of crystals: Very small needles, later to be characterized as bis(cyclohexylamine)gold(I) chloride[2], and larger blocks that floated on the solution. An X-ray crystal structure determination showed the latter product to be cyclohexylamine hemihydrochloride, containing one protonated and one neutral amine molecule linked via $N^+-H\cdots N$ hydrogen bonds. We have since obtained the compound by less fortuitous methods (see Experimental Section).

A search of the Cambridge Crystallographic Data Base[3] for structures with an NH_2 group and an NH_3^+ group in different residues revealed only one comparable structure, also with cyclohexylamine: bis(cyclohexylammonium) heptasulfide cyclohexylamine[4], in which two of the amines were apparently linked via $N^+-H\cdots N$ hydrogen bonds although the H atoms could not be reliably located. Additionally, there were several structures where two amine or amide molecules bearing other functional groups are linked together via O–H···O hydrogen bonds, viz. anthranilic acid[5], diglycine hydrochloride[6], di-L-leucine hydrochloride[7], L-phenylalanine L-phenylalaninium formate[8], bis(acetamide) hydrochloride[9] and bis(benzamide)hydrogen triiodide[10]. However, none of these cases corresponds to a simple aliphatic amine *'hemi'* salt.

A referee drew our attention to an important recent publication[11] (previously unknown to us) in which several species containing the moiety $N^+-H\cdots N$ were the subject of structure determinations and PM3 calculations, and many structures from the literature were discussed. However, none of the structures contains a species $[RNH_3\cdots H_2NR]^+$.

The asymmetric unit of cyclohexylamine hemihydrochloride (Figure 1) contains a cyclohexylamine molecule (N1, C11–16), a cyclohexylammonium cation (N2, C21–26), and a chloride anion. All five hydrogen atoms bonded to nitrogens are involved in hydrogen bonds, forming layers perpendicular to the *z* axis (Figure 2, Table 1). The two amine moieties are connected via N2–H2B···N1, with N1···N2 2.805(3) A; in the heptasulfide derivative[4] the N···N distance was 2.782(1) A. A database analysis[11] found frequency maxima at 2.68 and 2.93 A respectively for $N^+-H\cdots N$ and N–H···N systems. The other four hydrogen atoms form hydrogen bonds to chloride anions, with the shortest N···Cl distance 3.202(2) A; note that the N–H bond lengths involving the ammonium nitrogen N2 are longer, but the N···Cl and H···Cl contacts shorter, than those with N1. In the 1:1 salt cyclohexylamine hydrochloride the shortest N···Cl contact is 3.162(3) A[12].

Figure 1. The formula unit of cyclohexylamine hemihydrochloride in the crystal, showing the atom labelling scheme. Ellipsoids represent 50% probability levels. H atom radii are arbitrary



Both amine moieties show the expected chair conformations of the cyclohexyl ring [av. absolute torsion angle: 55.6° (ring 1), 55.8° (ring 2)], with equatorial N and C–N

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Figure 2. Packing diagram of cyclohexylamine hemihydrochloride, showing one layer at z ca. 1/4. Projection down the z axis. H atoms of the cyclohexyls are omitted for clarity; radii are arbitrary. Dashed lines indicate H bonds. Symmetry operators are given in Table 1

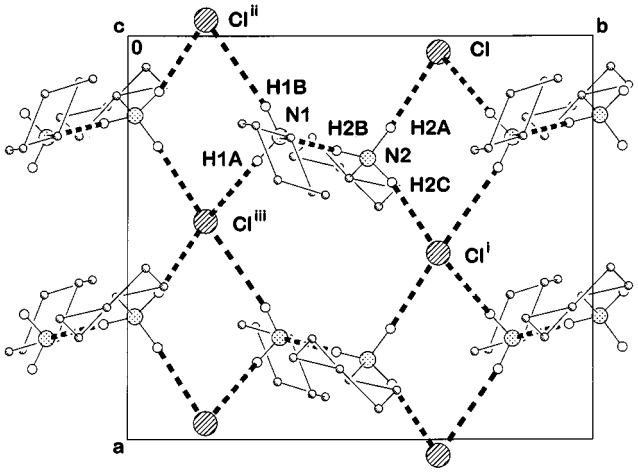

Table 1. Hydrogen bonds

N−H···X	N−H [A]	N···X [A]	H···X [A]	N−H···X [°]
N1−H1A···Cl[iii]	0.866(15)	3.433(2)	2.619(17)	157(2)
N1−H1B···Cl[ii]	0.876(16)	3.484(2)	2.631(17)	165(2)
N2−H2A···Cl	0.962(14)	3.202(2)	2.242(15)	176(2)
N2−H2C···Cl[i]	0.952(14)	3.178(2)	2.244(15)	167(2)
N2−H2B···N1	0.992(15)	2.805(3)	1.812(15)	180(2)

Symmetry operators: [i] $1/2 + x, y, 1/2 - z$. − [ii] $-x, -1/2 + y, 1/2 - z$. − [iii] $1/2 - x, -1/2 + y, z$.

bond lengths of 1.466(3) A (N1−C11) and 1.489(3) A (N2−C21); cf. 1.510(5) A in the 1:1 hydrochloride structure[12].

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Experimental Section

Cyclohexylamine Hemihydrochloride: 1) Cyclohexylamine (3 ml) was layered over dichloromethane (2 ml) at room temperature. Within two weeks large colourless crystals had grown; they lose cyclohexylamine to the air (rapidly under vacuum) and are thus not stable except in the presence of mother liquor. 2) Two drops of conc. HCl were added to cyclohexylamine (ca. 10 ml) at room temperature. Within two weeks small colourless crystals had formed. $C_{12}H_{27}ClN_2$ (234.81): calcd. C 61.38, H 11.59, N 11.93; found C 61.14, H 10.84, N 11.94. − ^{1}H NMR (D_2O): δ = 1.17 (m), (2 H, 2-H, 2′-H); ca. 1.2 (m), (1 H, 4′-H); 1.25 (m), (2 H, 3-H, 3′-H); 1.61 (m), (1 H, 4-H); 1.72 (m), (2 H, 3-H, 3′-H); 1.85 (m), (2 H, 2-H, 2′-H); 2.83 (m), (1 H, 1-H). − ^{13}C NMR (D_2O): δ = 25.16 (3-C), 25.74 (4-C), 33.81 (2-C), 50.77 (1-C).

The proton signals were correlated via ($^{1\,H,\ 13}$C)-COSY experiments. The NMR data in solution consist of only one set of signals, with proton signals shifted downfield compared to cyclohexylamine and upfield compared to cyclohexylamine hydrochloride [cf. ^{1}H NMR (D_2O), shift for (1-H): δ = 2.60 (m) for cyclohexylamine, δ = 3.12 (m) for cyclohexylamine hydrochloride].

Crystal Structure Determination of Cyclohexylamine Hemihydrochloride: Crystal data: $C_{12}H_{27}ClN_2$, M_r = 234.81, orthorhombic, space group *Pbca*, a = 10.0690(10), b = 11.6575(14), c = 24.584(3) A, V = 2885.7(6)A^3, Z = 8, D_c = 1.081 Mg/m^3, μ = 0.242 mm^{-1}, F(000) = 1040, T = −100°C. Colourless prism 0.40 × 0.38 × 0.24 mm. − *Data collection and reduction*: The crystal was mounted in inert oil on a glass fibre. Data were collected to $2\theta_{max}$ = 50° using monochromated Mo-K_α radiation (λ = 0.71073A) on a Siemens P4 diffractometer fitted with an LT-2 low temperature attachment. A total of 3654 intensities were collected, of which 2523 (R_{int} = 0.0344) were independent. Cell constants were refined from setting angles of 62 reflections in the 2θ range 7−25°. − *Structure Solution and Refinement:* The structure was solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-93)[13]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at N were refined freely, other H using a riding model. The final $wR(F^2)$ was 0.0764 for all data, 156 parameters and 121 restraints, conventional $R(F)$ = 0.0406, S = 0.78, maximum Δρ = 0.22eA^{-3}.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-101021. Copies may be obtained without charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. +44(0)1223/336033; E-mail: deposit@chemcrys.cam.ac.uk].

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