Crystal Structure of 9-Aza-3,6,12,15-tetrathiaheptadecane Hydrochloride

Mari Toyama,† Takumi Isono, Atushi Ichiyama, and Kenji Chayama

Department of Chemistry of Functional Molecules, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan

The crystal structure of the title compound, 9-aza-3,6,12,15-tetrathiaheptadecane hydrochloride (N-H-ATH·HCl), was determined by X-ray crystallography. The crystal structure revealed that the substitution from an S atom in a polythioether to an NH group to form a monoaza polythioether does not have any influence on the structural features of acyclic polythioethers. The compound crystallized in an orthorhombic system, and was characterized as: \(P2_12_12_1\), \(a = 4.84742(17), b = 10.3753(3), c = 36.4017(18)\AA, Z = 4, V = 1830.77(12)\AA^3\). The \(R_1\) and \(wR_2\) values were 0.0706 and 0.1959, respectively, for 2929 reflections.

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On the basis of the HSAB rule,† polythioethers have been used as good extractants and for the separations of Ahrland’s class-b metal ions including noble metal ions. We have reported on solvent extractions of class-b metal ions with cyclic and acyclic polythioethers, and showed that acyclic polythioethers were more extractable for class-b metal ions compared to cyclic analogs. Moreover, the extraction behavior of cyclic and acyclic monoaza polythioethers were similar to those of the corresponding polythioethers without only NH group, respectively. This indicated that it was possible to introduce the substituted group into the N atom of the monoaza polythioether while maintaining the extraction abilities of polythioethers. N-substituted-9-aza-3,6,12,15-tetrathiaheptadecanes (N-R-ATH), in which the R was benzyl, 4-nitrobenzyl, or diphenylmethyl groups, were synthesized from 9-aza-3,6,12,15-tetrathiaheptadecane (N-H-ATH), and we investigated the extraction and detection of Ag⁺. The introduction of an N-substituent enhanced the hydrophobicity of the monoaza polythioether than the original N-H-ATH, and reduced more the proton affinity of the N-donor atom than the N-H-ATH. Similarly, in the case of complexes \([\text{Ag}(N-R-ATH)]^+, \) which were monomeric tetra-S-coordinated species without \(N\)-coordination, the Ph group in the \(N\)-substituent in the coordinated \(N\)-R-ATH acted as a “hydrophobic cover” of the Ag⁺ ion to enhance the hydrophobicity of \([\text{Ag}(N-R-ATH)]^+\). Thus, the hydrophilicities of the extractant N-R-ATH and the complexes \([\text{Ag}(N-R-ATH)]^+\) are able to control by a kind of \(N\)-substituent. The N-H-ATH and its derivatives are very fascinating compounds.

There are many reports about the crystal structures of cyclic and acyclic polythioethers or monoaza polythioethers that include one or more metal ions. On the other hand, there is only one report on the crystal structures of two acyclic polythioethers, 1,9-bis(p-toly1)-2,5,8-trithianonane and 1,12-bis(p-toly1)-2,5,8,11-tetra thia decane, in the absence of complexes of metal ions, written by Desper and his co-workers in 1990. The structural features of these polythioethers are all CS-CC bonds that adopt gauche torsion angles, and all SC-CS bonds to exist in anti-conformations. These characteristic con Formations matched with estimated conformations obtained by Raman and IR analysis, and computational studies. Here, we report on the crystal structure of N-H-ATH hydrochloride (N-H-ATH·HCl, Fig. 1), which is analogous to acyclic polythioethers and the first report concerning a crystal structure for acyclic monoaza polythioethers.

The preparation of the title compound was based on a method from the literature. Colorless and plate crystals of N-H-ATH·HCl suitable for X-ray crystallography were obtained by the vapor diffusion of diethyl ether into an ethanol solution of N-H-ATH·HCl. X-ray crystallography was performed at 173 K on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu Kα radiation. The structure was solved by direct methods (SIR2011), and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. The C-H and N-H hydrogen atoms were located at theoretically calculated positions with a riding model. The crystal data are summarized in Table 1.

An ORTEP view of N-H-ATH·HCl is shown in Fig. 2; selected bond lengths and angles are summarized in Table 2. The title compound consists of two parts: a protonated N-H-ATH cation, (N-H₂-ATH)⁺, and a Cl⁻ anion. The N1 atom has two hydrogen atoms, and one of them comes from HCl. One of hydrogen atoms on the N1 atom connects with the counter ion, Cl⁻, and the other H atom associates with another Cl⁻, which is a Cl⁻ anion in a neighboring unit, through hydrogen bonds (2.323 and 2.226 Å, respectively), i.e. an \((N-H₂-ATH)⁺\) cation has two hydrogen bonds with two Cl⁻ anions (Table S1 and Fig. S1).

† To whom correspondence should be addressed.
E-mail: mari@center.konan-u.ac.jp

Fig. 1 Chemical diagram of the title complex.
Such Cl–H···N–Cl \(^+\) hydrogen-bonding networks extend along with the \( b \) axis to form a zig-zag 1D-chain (Fig. S2).

Two N–C bond lengths (1.494(11) and 1.504(10)Å) are longer than those in [Ag(N–R-ATH)\(^+\)] \((R = \text{benzyl or diphenylmethyl}, 1.461(5) - 1.475(5)\text{Å})\), but comparable with those in a diethylammonium salt, \([(\text{C}_2\text{H}_5)\text{NH}_2\]3BiCl6 (1.478(7) and 1.536(8)Å), in which two independent hydrogen bonds of the NH hydrogens and Cl atoms in two (BiCl6)\(^3-\) anions as observed in the title compound (vide supra). All S–C bond lengths (1.788(15) – 1.820(8)Å) and C–C bonds (1.46(2) – 1.54(2)Å) in the title compound are similar to those in 1,9-bis-(p-tolyl)-2,5,8,11-tetrathiadodecane (1.802(2) – 1.817(2)Å and 1.48(5) – 1.51(9)Å, respectively), which have a polythioether backbone.\(^6\)

The CS–CC bonds adopt gauche torsion angles, and SC–CS bonds exist in anti-conformations (Table 2 and Fig. 2). Such structural features are also observed in the crystal structure of two acyclic polythioethers.\(^6\) The torsion angle for the N1–C6–C5–S2 (168.5(5)\(^\circ\)) is similar to those for two SC–CS bonds (S1-C3-C4-S2, –171.6(5) and S3-C9-C10-S4, –178.3(5)\(^\circ\)), suggesting that the substitution from an S atom in a polythioether to an N–H group to form a monoazathioether does not have any influence on the SC–CS conformation. However, another N1-C7-C8-S3 torsion angle (–75.5(7)\(^\circ\)) is significantly smaller than the N1-C6-CS-S2 and two SC-CS bonds. It might be caused by a weak attractive interaction between the S3 atom and an H atom of the NH group (S3–H–N1–H = 2.912 Å), which has I-D hydrogen bonds, Cl–H···N–Cl \(^+\) (Fig. S1). The weak S3–H–N1 interaction could be observed only in a crystal, not in a solution. The \(^1\)H NMR spectrum of this compound showed that two thioether chains were equivalent in a solution (Fig. S3).

In the \(^1\)H NMR spectrum of the title compound in DMSO-\(_d_6\), a broad singlet with intensities of 2H was observed at \( \delta = 9.00 \). Moreover, an aqueous solution of the title compound was neutral. Both indicated that the title compound maintained the protonated NH\(^+\) form in solutions. When the neutral N-H-ATH was dissolved in an acidic solution or neutral water, it would become the protonated NH\(^+\) form or the hydration form, such as H-O-H···NH, respectively. Therefore, this crystal structure of the protonated N-H-ATH might help to consider the behavior of the extractant, N-H-ATH, in solutions.

**Supporting Information**

A CIF format file and Figs. S1, S2, and S3, and Table S1. These materials are available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

**References**

1. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, 85, 3533.
2. D. Sevdić and H. Meider, *J. Inorg. Nucl. Chem.*, 1981, 43, 153.
3. K. Chayama, C. Kurihara, H. Tsuji, and E. Sekido, *Bunseki Kagaku*, 1993, 42, 47.
4. K. Chayama, N. Awano, Y. Tamari, H. Tsuji, and E. Sekido, *Bunseki Kagaku*, 1993, 42, 687.
5. S. Iwatsuki, A. Ichiyama, S. Tanooka, M. Toyama, K. Katagiri, M. Kawahata, K. Yamaguchi, H. Danjo, and K. Chayama, *Dalton Trans.*, 2016, 45, 12548.
6. J. M. Darer, D. R. Powell, and S. H. Gellman, *J. Am. Chem. Soc.*, 1990, 112, 4321.
7. S. Rothammel and H. Burzlaff, *Acta Cryst.*, 1993, C49, 1594.
8. Data Collection and Processing Software, Rigaku Corporation, Japan, 2015.
9. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, and R. Spagna, *J. Appl. Cryst.*, 2012, 45, 357.
10. G. M. Sheldrick, *Acta Cryst.*, 2008, A64, 112.