Synthesis and Crystal Structure of 1,4,7-Tris(2-mercaptoethyl)-1,4,7-triazacyclononane

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The title compound, 1,4,7-tris(2-mercaptoethyl)-1,4,7-triazacyclononane ($H_3tmtacn$), was synthesized and the crystal structure was determined by the single-crystal X-ray diffraction method at 293 K. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.9553(13)\text{\AA}$, $b = 13.7164(19)\text{\AA}$, $c = 14.724(2)\text{\AA}$, $\beta = 102.528(2)^\circ$, $V = 1962.7(5)\text{\AA}^3$, $D_x = 1.355\text{ g/cm}^3$, and $Z = 4$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0538 and 0.1436, respectively, for all 4528 independent reflections. The triazacyclononane moiety is protonated at the two nitrogen atoms with hydrogen-bonded chloride ions and water molecules as $H_3tmtacn \cdot 2HCl \cdot H_2O$.

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There has been considerable interest in the coordination chemistry of tacn-based macrocyclic ligands (tacn = 1,4,7-triazacyclononane).¹ Recently, we reported on an octahedral nickel(II) complex with a hexadenetate ligand based on tacn, 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane, where three 2-aminoethyl-pendant groups bind a nickel(II) ion in an octahedral geometry with the basal three tacn-nitrogen atoms.² Concerning this study, 1,4,7-tris(2-mercaptoethyl)-1,4,7-triazacyclononane ($H_3tmtacn$) is an interesting hexadentate ligand, having three thiolic-sulfur and three amino-nitrogen donor atoms to give an octahedral mononuclear gallium(III),³ indium(III)^{4,5} and iron(III)⁶ complexes with three bidentate *S,N*-chelates. However, there is no report on the crystal structure of the ligand, itself. In this study, we successfully prepared single-crystals of the hexadentate ligand as dihydrochloric acid salt (Fig. 1), and determined the crystal structure in order to elucidate the molecular structure of the hexadentate ligand.

The ligand was synthesized by a method described by Moore *et al.*³ 1,4,7-Triazacyclononane (0.4802 g, 3.7 mmol) was dissolved in benzene (25 cm³) under argon. To this solution was added ethylene sulfide (2.280 g, 37 mmol); the mixture was heated under reflux for 5 h. The solution was concentrated to

dryness by using a rotary evaporator. A mixed solution of 60% hydrochloric acid (6 cm³) and ethanol (40 cm³) was added, and the mixture was left at 4°C to precipitate. The resulting white precipitate was filtered off, washed by ethanol, and dried under a vacuum. Yield, 1.285 g (81%). *Anal.* Found: C, 35.81; H, 7.97; N, 10.14%. Calcd for $C_{12}H_{31}Cl_2N_3OS_3$ ($H_3tmtacn \cdot 2HCl \cdot H_2O$): C, 35.99; H, 7.80; N, 10.49%. IR (KBr,

Table 1 Crystal and experimental data

Chemical formula: $C_{12}H_{31}Cl_2N_3OS_3$
Formula weight = 400.48
$T = 293\text{ K}$
Crystal system: monoclinic
Space group: $P2_1/n$
$a = 9.9553(13)\text{\AA}$
$b = 13.7164(19)\text{\AA}$
$c = 14.724(2)\text{\AA}$
$\beta = 102.528(2)^\circ$
$V = 1962.7(5)\text{\AA}^3$
$Z = 4$
$D_x = 1.355\text{ g/cm}^3$
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)
$\mu(\text{Mo } K_\alpha) = 0.652\text{ mm}^{-1}$
$F(0\ 0\ 0) = 856$
Crystal size = $0.42 \times 0.25 \times 0.08\text{ mm}^3$
No. of reflections collected = 11908
No. of independent reflections = 4528
θ range for data collection: 2.05 to 28.69°
Data/Restraints/Parameters = 4528/0/200
Goodness-of-fit on $F^2 = 1.165$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0538$, $wR2 = 0.1394$
R indices (all data): $R1 = 0.0619$, $wR2 = 0.1436$
$(\Delta/\sigma)_{\max} = 0.000$
$(\Delta\rho)_{\max} = 0.383\text{ e\AA}^{-3}$
$(\Delta\rho)_{\min} = -0.306\text{ e\AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer
Program system: SHELXTL
Structure determination: Direct methods (SHELXS-97)
Refinement: full matrix least-squares (SHELXL-2014/7)
CCDC deposition number: 1432788

Fig. 1 Chemical structure.

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Fig. 2 ORTEP view of the title compound, showing the labeling scheme of the non-H atoms. The thermal ellipsoids are shown at the 50% probability level.

Table 2 Selected bond distances (Å) and angles (°)

S1-C8	1.807(3)	N2-C4	1.502(3)
S2-C10	1.797(3)	N2-C5	1.515(3)
S3-C12	1.807(3)	N2-C9	1.503(3)
N1-C2	1.514(3)	N3-C1	1.461(3)
N1-C3	1.514(3)	N3-C6	1.461(3)
N1-C7	1.518(3)	N3-C11	1.463(3)
C2-N1-C3	113.3(2)	C5-N2-C9	112.8(2)
C2-N1-C7	108.2(2)	C1-N3-C6	113.8(2)
C3-N1-C7	113.5(2)	C1-N3-C11	115.2(2)
C4-N2-C5	114.1(2)	C6-N3-C11	114.1(2)
C4-N2-C9	111.2(2)		

cm⁻¹): 2965 ($\nu_{\text{as}}\text{CH}_2$), 2869 ($\nu_{\text{s}}\text{CH}_2$), 2531 (νSH), 702 (νCS). X-ray quality crystals were obtained by recrystallization from ethanol.

A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- K_{α} radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares methods. All of the hydrogen atoms on C, N1, N2, S1 and S3 atoms were placed in calculated positions, guided by difference Fourier maps. However, the hydrogen atom on the S2 atom could not be located. Hydrogen atoms of the water molecule were located from the difference Fourier maps and refined. All of the calculations were carried out on a Windows 7 Core i5 computer utilizing the SHELXTL software package and SHELXL-2014/7. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-1432788. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

The molecular structure drawn by ORTEP is shown in Fig. 2. Selected bond distances and angles are given in Table 2. The hydrogen-bonding parameters are summarized in Table 3. Among the three nitrogen atoms of the tacn moiety, two amino nitrogen atoms, N1 and N2, are protonated, forming hydrogen bonds with the chloride ion and the unprotonated nitrogen atom, N3 (Table 3). All of the bond lengths are within the normal ranges as N-C, S-C, and C-C single-bonds, although the C-N bond distances around the N3 atom (1.461(3) – 1.463(3) Å) are a

Table 3 Hydrogen-bonding geometry (Å, °)

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(°)
S1-H1C...Cl2	1.20	2.57	3.7404(13)	165.3
N1-H1D...Cl1	0.98	2.20	3.150(2)	164.1
N2-H2D...Cl1	0.98	2.40	3.214(2)	139.8
N2-H2D...N3	0.98	2.14	2.719(3)	116.2
O1-H1E...Cl2 ⁱ	1.02(7)	2.25(7)	3.233(4)	162(5)
O1-H1F...Cl1	0.93(5)	2.36(7)	3.287(4)	172(4)

Symmetry code: (i) 1-x, 1-y, -z.

Fig. 3 Packing diagram of the title compound, showing hydrogen bondings (dashed lines).

little shorter than those of the N1 and N2 atoms (1.502(3) – 1.518(3) Å). The elongations in the C-N distances around the N1 and N2 atoms reflect the protonated nitrogen atoms. Three 2-mercaptoethyl pendant groups are oriented in the same direction to the tacn-ring moiety with an extended form compared with those of the metal complexes.³⁻⁶ This structural feature is in harmony with an octahedral coordination fashion of this ligand in metal complexes.³⁻⁶ In the crystal, the ligand molecules are connected by hydrogen bonds with chloride ions and water molecules, forming a polymeric structure (Fig. 3).

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