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SYNTHESIS AND STRUCTURE OF TRIS(8-MERCAPTOQUINOLINATO)-THALLIUM AND TRIS(8-HYDROXY-QUINOLINATO)THALLIUM MONOHYDRATE

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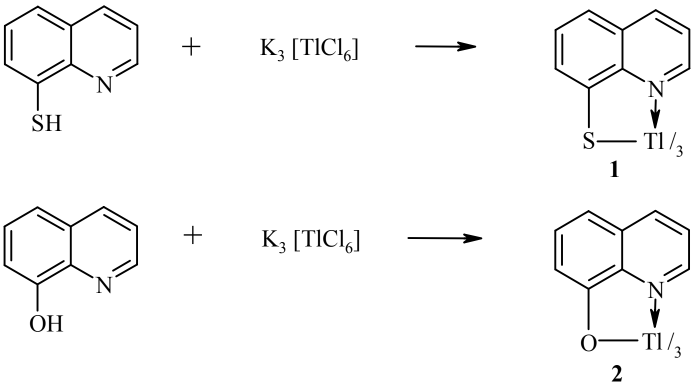
Tris(8-mercaptoquinolinato)thallium $Tl(C_9H_6NS)_3$ *and tris(8-hydroxyquinolinato)thallium monohydrate* $Tl(C_9H_6NO)_3{\cdot}H_2O$ *have been synthesized. Their structures have been confirmed by X-ray crystallographic analysis.*

Keywords: 8-mercapto- and 8-hydroxyquinolinates, intramolecular thallium compounds, molecular structure.

Thallium (III) in ethanol–water medium in the presence of acetate buffer reacts with both 8-mercaptoquinoline and with 8-hydroxyquinoline to give the yellow, intracomplex compounds **1** and **2**.



In spite of the structural similarity of the 8-hydroxyquinoline and 8-mercaptoquinoline, large differences are observed in the properties of these reagents and their intracomplex compounds [1]. In particular, by contrast with 8-hydroxyquinoline, the 8-mercaptoquinoline and its derivatives react with metal ions which form stable sulfides in water. A comparison of the structure of the metal complexes of 8-mercaptoquinoline and 8-hydroxyquinoline and their derivatives is of great interest since it allows a correlation of steric structure as a function of the nature of the S or O ligand atom.

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The aim of the current investigation is a determination and comparison of the molecular and crystal structures of compounds **1** and **2**. Preliminary data concerning the structure of the complex **2** has been given in the reports [2, 3].

The structure of the molecules **1** and **2** with the atomic numbering is given in Figs. 1 and 2. The crystal structure of **1** is formed by the $Tl(C_9H_6NS)_3$ neutral complexes and that of **2** by the $Tl(C_9H_6NO)_3$ neutral complexes with crystallization water molecules.

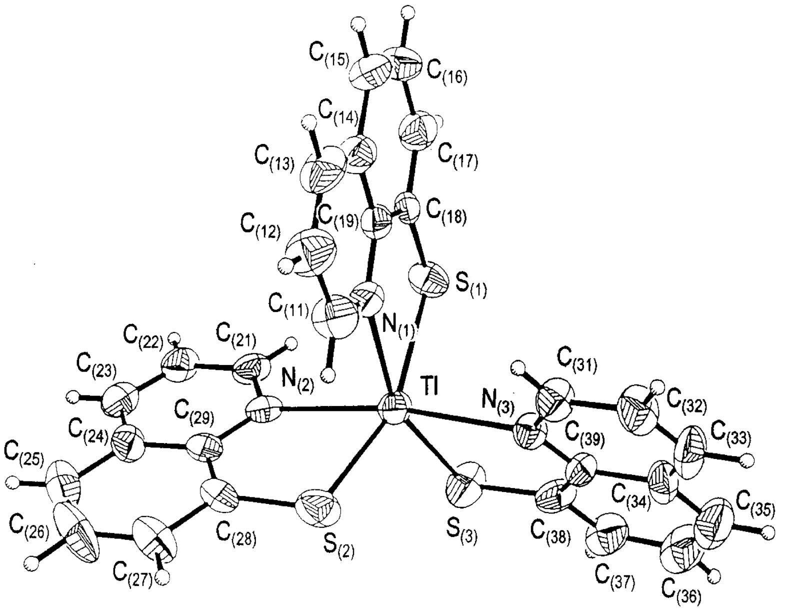

Fig. 1. Spatial model of the molecule of compound **1** with atomic numbering.

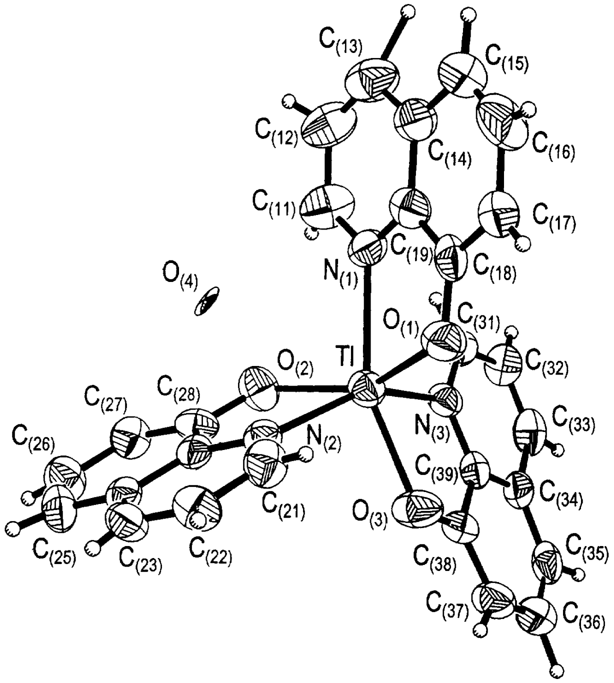

Fig. 2. Spatial model of the molecule of compound **2** with atomic numbering.

The thallium complexes are three ring, intracomplex compounds in which the three mercaptoquinoline or hydroxyquinoline ligands coordinate to the central thallium atom bidentately *via* the S(O) and N atoms. The coordination polyhedra of the Tl atom in the complexes **1** and **2** are distorted octrahedra formed by the three nitrogen atoms and three sulfur atoms (in **1**) or three oxygen atoms (in **2**). The distortion of these octahedra in the coordination sphere of the thallium atoms is reflected in the valence angles, values of which are given in Tables 1 and 2, together with bond lengths.

The octahedral environment of the thallium atoms, according to the scheme proposed in [4], corresponds to an asymmetric isomer. This isomer is characterized by different diagonal angles S(O)–Tl–S(O), S(O)–Tl–N, and N–Tl–N. A similar environment for the central atom is found in the structures of the 8-mercaptoquinolinates of the transition (Co, Rh, Ir) and non-transition elements (Ga, In). These differences in the asymmetric octahedral environment of the central atom in the transition and non-transition element complexes result in a different pattern of M–S and M–N bond lengths [5]. The interatomic distances Tl–S 2.468(3)-2.578(4) Å and Tl–O 2.193(7)-2.226(6) Å point to a stable bond between the Tl and S or Tl and O atoms (the sum of the covalent radii being 2.734 and 2.444 Å respectively [6]). The thallium atom and the nitrogen atoms form three coordinated bonds of length 2.490(9)-2.661(11) in **1** and 2.327(8)-2.345(8) Å in **2** (sum of the covalent radii of the Tl and N atoms 2.43 Å).

The Tl–S bond in the complex **1** has a covalent character since the mean bond length (2.511 Å) is markedly less than the sum of the covalent radii of the corresponding atoms. The mean Tl–N bond length (2.547 Å) exceeds the corresponding sum and the bond is coordinative. Substitution of the ligand sulfur atom for

TABLE 1. Valence Angles for the Tl Atoms in Compounds **1** and **2**

Compound **1**	ω, deg	Compound **2**	ω, deg
S(1)–Tl–S(2)	156.7(1)	O(1)–Tl–O(2)	151.5(3)
S(1)–Tl–S(3)	97.5(1)	O(1)–Tl–O(3)	93.6(3)
S(2)–Tl–S(3)	104.9(1)	O(2)–Tl–O(3)	110.8(3)
N(1)–Tl–N(2)	97.6(3)	N(1)–Tl–N(2)	112.8(3)
N(1)–Tl–N(3)	87.7(3)	N(1)–Tl–N(3)	91.7(3)
N(2)–Tl–N(3)	170.1(3)	N(2)–Tl–N(3)	151.3(3)
S(1)–Tl–N(1)	74.2(2)	O(1)–Tl–N(1)	73.1(3)
S(1)–Tl–N(2)	93.1(2)	O(1)–Tl–N(2)	93.6(3)
S(1)–Tl–N(3)	96.4(2)	O(1)–Tl–N(3)	108.1(3)
S(2)–Tl–N(1)	86.2(2)	O(2)–Tl–N(1)	87.9(3)
S(2)–Tl–N(2)	76.9(2)	O(2)–Tl–N(2)	74.1(3)
S(2)–Tl–N(3)	95.2(3)	O(2)–Tl–N(3)	93.2(3)
S(3)–Tl–N(1)	161.0(2)	O(3)–Tl–N(1)	156.6(3)
S(3)–Tl–N(2)	100.0(2)	O(3)–Tl–N(2)	86.6(3)
S(3)–Tl–N(3)	76.0(2)	O(3)–Tl–N(3)	73.8(3)

TABLE 2. Bond Lengths for the Tl Atoms in Compounds **1** and **2**

Compound **1**	*l*, Å	Compound **2**	*l*, Å
Tl–S(1)	2.468(3)	Tl–O(1)	2.226(7)
Tl–S(2)	2.487(4)	Tl–O(2)	2.213(7)
Tl–S(3)	2.578(4)	Tl–O(3)	2.193(7)
Tl–N(1)	2.661(11)	Tl–N(1)	2.345(8)
Tl–N(2)	2.494(10)	Tl–N(2)	2.327(8)
Tl–N(3)	2.490(9)	Tl–N(3)	2.343(7)

oxygen in the analogous complex **2** causes a change in the nature of the Tl–N bond. The mean Tl–N bond length of 2.345 Å points to its covalent character. The angular distortion of the normal coordinated thallium polyhedron points to a contribution of the ionic nature of the Tl–O bond.

The octahedral environment of the central atom in the complexes **1** and **2** is characterized by a spread of bond lengths which depends on the nature of the *trans* partners. In complex **1** the shortest Tl–S and Tl–N bonds are found in a *trans* position and form amongst themselves the valence angles $S_{(1)}$–Tl–$S_{(2)}$, (156.7 °) and $N_{(2)}$–Tl–$N_{(3)}$ (170.1°), The *trans* angle $S_{(3)}$–Tl–$N_{(1)}$ contains the longest Tl–S and Tl–N bonds. The spread of bond lengths in the complex **2** is similar to that in 8-mercaptoquinolinate transition elements: the *trans* angle $O_{(1)}$–Tl–$O_{(2)}$ contains lengthened Tl–O bonds and the *trans* angle $N_{(2)}$–Tl–$N_{(3)}$ the shortest Tl–N bonds. The shortest Tl–O bond and the longest Tl–N bond form the *trans* angle $O_{(3)}$–Tl–$N_{(1)}$.

The intracyclic chelate angles S–Tl–N and O–Tl–N are less than 90° and occur in the ranges 74.2(2) to 76.9(2)° in **1** and 73.1(3) to 74.1(3)° in **2**. The deviation of the octahedral environment of the thallium atoms is also characterized by the S(O)–Tl–S(O), S(O)–Tl–N, and N–Tl–N diagonal angles which differ significantly from 180°. In compound **1** these values are, respectively, 156.7(1), 161.0(2), and 170.1(3)° and in **2** the diagonal angles are 151.5(3), 156.6(3), and 151.3(3)°. The interligand angles in the coordinated polyhedron of the Tl atoms vary from 86.6 to 104.9° in **1** and from 86.3 to 112.8° in **2**.

The dihedral angles between the coordinated planes $S_{(1)}TlN_{(1)}/S_{(2)}TlN_{(2)}$, $S_{(1)}TlN_{(1)}/S_{(3)}TlN_{(3)}$, and $S_{(2)}TlN_{(2)}/S_{(3)}TlN_{(3)}$ in **1** are 82.4(7), 96.8(5), and 75.5(3)° respectively. In compound **2** the angles between the analogous planes $O_{(1)}TlN_{(1)}/O_{(2)}TlN_{(2)}$, $O_{(1)}TlN_{(1)}/O_{(3)}TlN_{(3)}$, and $O_{(2)}TlN_{(2)}/O_{(3)}TlN_{(3)}$ are respectively 68(2), 108(2), and 70(4)°. These values also point to extreme distortion of the octahedral coordination of the central Tl atom both in the thallium 8-mercaptoquinolinate and, particularly, in the thallium 8-hydroxyquinolinate.

The planarity of the three, five-membered metallocycles in the complexes **1** and **2** differ little. Within the limits of error, two of the metallocycles in the complexes are planar. The third metallocycle is twisted along the line $S_{(2)}\cdots N_{(2)}$ and $O_{(2)}\cdots N_{(2)}$ by 11(2) and 10(2)° respectively. The deviation of the $O_{(2)}$ atom from the plane of the metallocycle of this ligand can, apparently, be explained by the formation of a weak $O_{(2)}\cdots HO_{(4)}$ hydrogen bond. The $O_{(2)}\cdots O_{(4)}$ distance is 3.12 Å. A stronger hydrogen bond is evidently formed between the molecules of crystallization water with an $O_{(4)}\cdots O_{(4)}$ distance (0.5-*x*, 0.5-*y*, 1-*z*) of 2.85 Å

TABLE 3. Crystallographic Data for Compounds **1** and **2**

	Compound **1**	Compound **2**
Formula	$C_{27}H_{18}N_3S_3Tl$	$C_{27}H_{20}N_3O_4Tl$
Molecular weight	684.99	654.83
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C* 2/*c*
Lattice parameters:		
a, Å	9.094(2)	23.896(5)
b, Å	10.422(3)	15.480(3)
c, Å	13.658(2)	13.843(3)
α, deg.	108.69(2)	90
β, deg.	99.07(2)	118.50(3)
γ, deg.	91.45(3)	90
Cell volume, *V*, $Å^3$	1206.9(5)	4500.1(16)
Number of molecules in the cell, *Z*	2	8
Density, *d*, g/cm^3	1.885	1.933
Difference factor, *R*	0.0608	0.0305

EXPERIMENTAL

Synthesis of Tris(8-mercaptoquinolinato)thallium $Tl(C_9H_6NS)_3$ (1). The sodium salt of 8-mercaptoquinoline (2 g) was dissolved with heating in ethanol (50 ml) and water (20 ml) and saturated sodium acetate trihydrate solution (1 ml) and glacial acetic acid (0.1 ml) were added. $K_3[TlCl_6]\cdot 2H_2O$ (1.6 g) in water (25 ml) was then added to the solution obtained. The precipitated yellow solid was filtered off and washed with water and then ethanol and dried in air. Yield 1.85 g (96.4%). Found, %: C 48.17; H 2.52; N 5.87; S 14.38; Tl 29.21. $C_{27}H_{18}N_3S_3Tl$. Calculated, %: C 47.34; H 2.65; N 6.13; S 14.04; Tl 29.84.

Monocrystals were grown by slow cooling of a heated, saturated solution of the complex in chloroform.

Synthesis of Tris(8-hydroxyquinolinato)thallium Monohydrate $Tl(C_9H_6NO)_3\cdot H_2O$ (2). 8-Hydroxyquinoline (2 g) and sodium acetate trihydrate (2 g) were dissolved with heating in ethanol (20 ml), glacial acetic acid (0.1 ml) and a solution of $K_3[TlCl_6]\cdot 2H_2O$ (2.3 g) in water (20 ml) were added, and the whole was diluted to 100 ml with water. The precipitated yellow solid was washed with water and dried in air. Yield 2.3 g (76.4%). Found, %: C 49.23; H 3.21; N 6.08; Tl 30.89; H_2O 2.86. $C_{27}H_{18}N_3O_3Tl\cdot H_2O$. Calculated, %: C 49.52; H 3.08; N 6.42; Tl 29.84; H_2O 2.75.

Monocrystals were grown by slow cooling of a heated, saturated solution of the complex in chloroform–ethanol (1:2).

X-ray Investigation of the monocrystals was carried out at 25°C with $\omega/2\theta$ scanning (MoKα radiation, graphite monochromator, $2\theta_{max}$ 50°) using an automatic, four circle diffractometer (Syntex $P2_1$ for compound **1** and Nicolet P3 for compound **2)**. The basic crystallographic parameters for the compounds investigated are given in Table 3.

The structure was solved by direct (compound **1**) and Patterson (compound **2**) methods and refined in a full matrix least squares analysis in the anisotropic approximation for the non-hydrogen atoms with hydrogen atom coordinates based on geometrical considerations for compound **1** and in compound **2** the hydrogen atom coordinates were refined in the isotropic approximation. The hydrogen atoms in the water molecules were not localized. Calculations were performed using the programs [7, 8]. Crystallographic parameters, atomic coordinates, and their temperature factors, bond lengths, and valence angles in the molecules of compounds **1** and **2** have been deposited in the Cambridge Crystallographic Database (CCD) under the numbers CCDC 156862 and CCDC 156863 respectively. This information is available at the following address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (international) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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