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### NITROSO GROUP COORDINATION IN THALLIUM(I) OXIMATE COMPLEXES WITH 18-CROWN-6

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## NITROSO GROUP COORDINATION IN THALLIUM(I) OXIMATE COMPLEXES WITH 18-CROWN-6

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Crystal and molecular structures of the macrocyclic complexes  $[\text{Tl}(18\text{-crown-6})\{\text{L}\}]$ , where  $\{\text{L}\} = \{\text{ONC}(\text{CN})\text{C}(\text{S})\text{N}(\text{CH}_3)_2\}^-$  ( $P2_1/n$ , monoclinic,  $a = 14.471(3)$ ,  $b = 8.447(2)$ ,  $c = 18.920(4)$  Å,  $\beta = 92.69^\circ$ ,  $Z = 4$ ;  $R = 0.027$ ) and  $\{\text{ONC}(\text{CN})\text{-}(4\text{-methylthiazolyl-2})\}^-$  ( $P\bar{1}$ , triclinic,  $a = 8.836(4)$ ,  $b = 11.908(5)$ ,  $c = 14.131(4)$  Å,  $\alpha = 62.84(3)$ ,  $\beta = 74.03(3)$ ,  $\gamma = 66.72^\circ$ ,  $Z = 2$ ;  $R = 0.047$ ) have been determined from X-ray diffraction data. The structures are made up of isolated  $\text{Tl}(18\text{-crown-6})\{\text{L}\}$  molecules with irregular eight-coordination about Tl. In both structures the thallium atom forms close contacts (2.73–3.14 Å) with both the nitrogen and oxygen atoms of the nitroso group.

KEYWORDS: thallium(I), oximes, 18-crown-6, X-ray structure

### INTRODUCTION

The coordination chemistry of ambidentate ligands is rich and versatile<sup>1,2</sup> and led to approaches towards ligand design for selective complexation of metal ions.<sup>3</sup> Ambidentate oximic ligands adopt two main bond types:  $\text{M}-\text{ON}=(\text{M} - \text{hard, p-metals})$  and  $\text{M}-\text{N}(\text{O})-$  ( $\text{M} - \text{soft, usually 3d-metals}$ ). They can be considered as test ligands for the relative hardness/softness<sup>4</sup> of a Lewis acid bonding site.<sup>1</sup> In order to characterize the mode of nitroso group binding, X-ray crystal studies of metal oximates are of special interest. Previous work on structural investigations of a thallium benzoylcyanoximate complex with 18-crown-6 ( $[\text{Tl}(18\text{-crown-6})\{\text{BCO}\}]$ ) has shown that the metal atom forms close contacts with the nitroso group ( $\text{Tl}-\text{O}$  2.75,  $\text{Tl}-\text{N}$  3.02 Å,  $\text{Tl}-\text{O}-\text{N}$  89.3°).<sup>5</sup> This fact suggests a tendency to coordination of thallium with both oxygen and nitrogen atoms of the nitroso group. Therefore, in conjunction with other studies on p-metal cyanoximates, it was of considerable interest to investigate the structure of  $\text{Tl}(18\text{-crown-6})$  complexes with oxime ligands. Complexes of the kind  $[\text{Tl}(18\text{-crown-6})\{\text{L}\}]$ , where L is *N,N*-dimethyl-2-nitroso-2-cyanothioacetamide  $\{\text{ONC}(\text{CN})\text{C}(\text{S})\text{N}(\text{CH}_3)_2\}^-$  (TDCO) and 2-(nitrosocyanomethyl)-4-methylthiazole  $\{\text{ONC}(\text{CN})\text{-C}_4\text{H}_4\text{NS}\}^-$  (TLCO) were isolated and structurally characterized.

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## EXPERIMENTAL

Preparations of starting compounds for the present study, Tl{L} were as described previously.<sup>6</sup> Complexes [Tl(18-crown-6){L}] were made by reacting the appropriate thallium cyanoximate in aqueous solution with 18-crown-6. Clear, pale-yellow solutions obtained, on standing, yielded suitable crystals for diffraction.

Anal.: calcd. for [Tl(18-crown-6){TDCO}] (1): C, 32.7; H, 4.8; N, 6.7; Tl 32.7%. Found: C, 32.5; H, 4.8; N, 6.8; Tl, 32.4%. Calcd. for [Tl(18-crown-6){TLCO}](2): C, 34.1; H, 4.4; N 6.6; Tl 32.2%. Found: C, 33.9; H, 4.5; N 6.5; Tl 32.0%.

Crystallographic measurements were made using an Enraf Nonius CAD-4 diffractometer operating in the  $\omega/2\theta$  scan mode. Accurate unit cell parameters and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections in the range  $13 < \theta < 15^\circ$ . Structures were solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. The positions of the hydrogen atoms were idealized and included in the calculations with B(iso) = 5 Å<sup>2</sup>. Table 1 lists details of cell parameters, data acquisition and structure solution. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption

**Table 1** Experimental data for [Tl(18-crown-6){TDCO}] (1) and [Tl(18-crown-6){TLCO}](2).

	1	2
Formula	C <sub>17</sub> H <sub>30</sub> N <sub>3</sub> O <sub>7</sub> STl	C <sub>18</sub> H <sub>28</sub> N <sub>3</sub> O <sub>7</sub> STl
Colour	orange	pale-yellow
Formula weight	624.8	634.8
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.471(3)	8.836(4)
<i>b</i> (Å)	8.447(2)	11.908(5)
<i>c</i> (Å)	18.930(4)	14.131(4)
$\alpha$ (°)	90	62.84(3)
$\beta$ (°)	92.69(2)	74.03(3)
$\gamma$ (°)	90	66.72(4)
<i>V</i> (Å <sup>3</sup> )	2311.36	1207.12
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.796	1.644
<i>F</i> (000)	1224	554
$\mu$ (Mo-K $\alpha$ ) (cm <sup>-1</sup> )	71.8	71.6
Data collection		
T (K)	296	296
Radiation	MoK $\alpha$	MoK $\alpha$
Wavelength (Å)	0.71073	0.71073
2 $\theta$ <sub>max</sub> (deg)	52.0	48.0
Unique data	4542	4061
Structure refinement		
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0016F^2$	
Parameters refined	262	271
<i>R</i> <sup>a</sup>	0.027	0.047
<i>R</i> <sub>w</sub> <sup>b</sup>	0.028	0.061
Data used	2451	3202
Discrimination	3 $\sigma$	3 $\sigma$
Goodness of fit	1.27	2.12

<sup>a</sup> $R = [\sum |F_o| - |F_c|] / \sum |F_o|$ . <sup>b</sup> $R_w = [(\sum w |F_o| - |F_c|)^2 / \sum w |F_o|^2]^{0.5}$ .

using the DIFABS program<sup>7</sup> were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS package.<sup>8</sup>

Final fractional atomic coordinates and equivalent thermal parameters for all non-hydrogen atoms are given in Tables 2 and 3. Selected bond distances and angles are listed in Tables 4 and 5. Tables of observed and calculated structure factors, H atom positions and thermal parameters are available from the authors upon request.

## RESULTS AND DISCUSSION

In both structures under consideration, the crystal lattice comprises monomeric molecular species [Tl(18-crown-6){L}] (Figures 1 and 2). There are no close contacts between neighbouring complexes. The complexes have irregular eight-coordination about Tl comprising oxygen and nitrogen atoms from both L and 18-crown-6 ligands (Figures 1 and 2) with little or no indication of stereoactivity of the lone electron pair of thallium.

The crown ligands are bound to the metal centres and the thallium-oxygen (crown ether) separations are 2.84–3.08 Å (Table 4). These values agree well with results obtained for [Tl(18-crown-6){BCO}],<sup>5</sup> and are practically equal<sup>9</sup> to the sum of the formal ionic radii. The macrocyclic molecules are structurally normal (Tables 4 and 5)

**Table 2** Positional and equivalent isotropic thermal parameters for [Tl(18-crown-6){TDCO}].

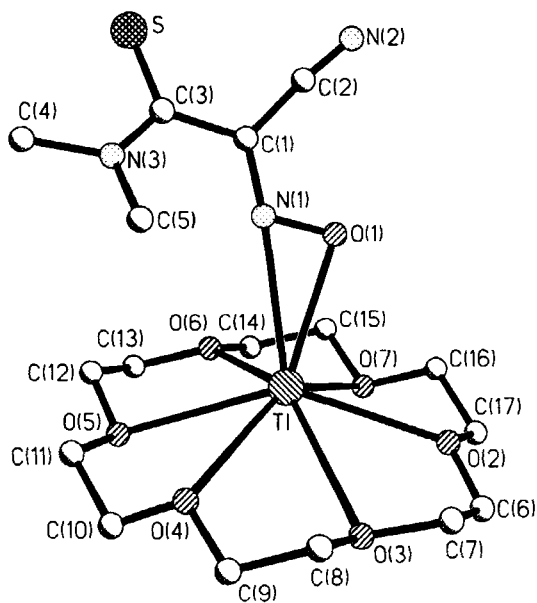
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B<sub>eq</sub></i> , Å <sup>2</sup>
Tl	0.03702(2)	0.49279(3)	0.72107(1)	3.701(4)
S	-0.3539(1)	0.5054(3)	0.5340(1)	5.86(5)
O(1)	-0.0784(3)	0.7092(6)	0.6561(3)	5.3(1)
O(2)	0.1622(4)	0.7422(6)	0.7697(3)	5.9(1)
O(3)	0.1232(4)	0.5127(7)	0.8714(2)	6.2(1)
O(4)	0.0209(4)	0.2418(6)	0.8293(3)	6.9(2)
O(5)	0.0291(4)	0.1421(6)	0.6872(4)	6.9(2)
O(6)	0.0580(4)	0.3703(7)	0.5832(3)	6.7(1)
O(7)	0.1691(3)	0.6343(6)	0.6282(3)	5.7(1)
N(1)	-0.1393(4)	0.5956(6)	0.6533(3)	3.9(1)
N(2)	-0.2453(6)	0.9014(8)	0.5668(4)	7.7(2)
N(3)	-0.2925(4)	0.3833(7)	0.6560(3)	4.5(1)
C(1)	-0.2196(5)	0.6272(7)	0.6210(3)	3.5(1)
C(2)	-0.2370(5)	0.7782(9)	0.5897(4)	4.7(2)
C(3)	-0.2881(4)	0.5014(9)	0.6080(3)	3.9(1)
C(4)	-0.3471(6)	0.243(1)	0.6399(5)	7.2(3)
C(5)	-0.2536(6)	0.3884(9)	0.7278(4)	5.5(2)
C(6)	0.1991(7)	0.746(1)	0.8373(5)	7.5(3)
C(7)	0.1385(7)	0.678(1)	0.8879(4)	7.8(2)
C(8)	0.0655(7)	0.440(1)	0.9154(4)	8.3(3)
C(9)	0.0589(7)	0.271(1)	0.9011(5)	8.3(3)
C(10)	0.0250(6)	0.091(1)	0.8125(6)	8.6(3)
C(11)	-0.0214(6)	0.064(1)	0.7411(7)	9.1(3)
C(12)	-0.0140(7)	0.133(1)	0.6217(6)	9.6(3)
C(13)	0.0468(7)	0.203(1)	0.5697(4)	8.2(2)
C(14)	0.1189(7)	0.444(1)	0.5398(4)	8.2(3)
C(15)	0.1266(6)	0.613(1)	0.5573(4)	6.9(2)
C(16)	0.1744(6)	0.792(1)	0.6464(5)	7.8(3)
C(17)	0.2199(5)	0.8087(9)	0.7190(5)	6.8(2)

**Table 3** Positional and equivalent isotropic thermal parameters for [Tl(18-crown-6){TLCO)].

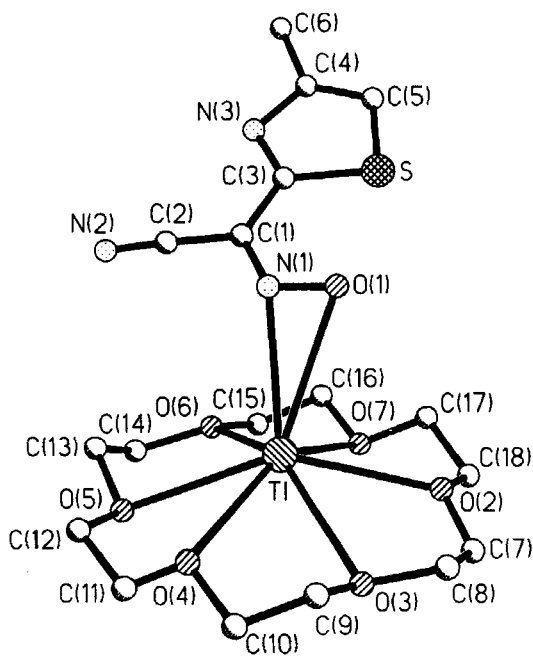
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B<sub>eq</sub></i> , Å <sup>2</sup>
Tl	0.23281(4)	0.16558(3)	0.29795(3)	5.785(9)
S	0.0665(3)	-0.2071(3)	0.2397(2)	7.48(8)
O(1)	0.115(1)	-0.0642(8)	0.3246(7)	10.7(3)
O(2)	-0.0964(9)	0.3308(7)	0.2355(6)	8.2(2)
O(3)	0.022(1)	0.3728(7)	0.3743(6)	9.3(3)
O(4)	0.355(1)	0.2283(7)	0.4327(6)	11.0(2)
O(5)	0.5865(9)	0.1640(8)	0.2669(9)	11.9(3)
O(6)	0.470(1)	0.1282(8)	0.1151(8)	10.9(3)
O(7)	0.1434(9)	0.2614(7)	0.0715(6)	8.7(3)
N(1)	0.265(1)	-0.1056(9)	0.3230(9)	9.0(4)
N(2)	0.664(1)	-0.2567(8)	0.2619(7)	9.2(3)
N(3)	0.3637(8)	-0.3540(6)	0.2118(5)	4.9(2)
C(1)	0.348(1)	-0.1957(7)	0.2801(6)	5.5(2)
C(2)	0.523(1)	-0.2320(8)	0.2707(7)	6.4(2)
C(3)	0.276(1)	-0.2568(7)	0.2439(6)	4.8(2)
C(4)	0.259(1)	-0.3911(7)	0.1825(6)	5.2(2)
C(5)	0.101(1)	-0.3248(9)	0.1919(7)	6.5(3)
C(6)	0.341(1)	-0.5032(8)	0.1435(8)	7.5(3)
C(7)	-0.175(2)	0.427(1)	0.269(1)	10.0(4)
C(8)	-0.152(2)	0.396(1)	0.377(1)	9.4(4)
C(9)	0.077(2)	0.331(1)	0.466(1)	11.5(5)
C(10)	0.233(2)	0.328(1)	0.4731(9)	12.8(4)
C(11)	0.487(2)	0.233(1)	0.423(1)	14.8(5)
C(12)	0.613(1)	0.137(1)	0.383(1)	13.0(4)
C(13)	0.679(2)	0.063(1)	0.224(2)	17(1)
C(14)	0.642(2)	0.116(1)	0.124(1)	13.6(5)
C(15)	0.407(3)	0.179(2)	0.014(1)	15.1(8)
C(16)	0.251(2)	0.169(1)	0.0314(9)	10.4(5)
C(17)	-0.017(2)	0.256(1)	0.092(1)	9.9(4)
C(18)	-0.125(1)	0.361(1)	0.130(1)	10.2(5)

and have slightly distorted  $D_{3d}$  geometry.<sup>10</sup> The puckered, five membered Tl-O-C-C-O rings have *gauche* conformations. Maximum deviations of 18-crown-6 oxygen atoms from their mean plane are *ca* 0.25(2) Å. The metal atom is situated 0.932(1) Å (1) or 0.933(1) Å (2) above this plane toward the anion (Figures 1 and 2). These values are slightly larger than those observed for the benzoylcyanoximate complex<sup>5</sup> (0.86 Å).

The most important observation in these structures is that the thallium atom forms close contacts with both the nitrogen and oxygen atoms of the anion (Figures 1 and 2). Similar modes of nitroso group coordination were also found for a number of uranium complexes with oximes and hydroxylamines,<sup>11,12</sup> but not for p-metals. In (1) the thallium atom and nitroso groups form three-membered chelate rings, Tl-O(1) 2.731(5) and Tl-N(1) 2.933(6) Å. The appropriate angles are Tl-O(1)-N(1), 85.6(3), and O(1)-Tl-N(1), 26.3(1)°. The latter value is less than is observed in  $UO_2^{2+}$ -oximate species<sup>11,12</sup> and reflects relatively long Tl-O and Tl-N distances.<sup>13</sup> Nevertheless, these distances are less than the sum of the appropriate ionic radii,<sup>9</sup> suggesting a certain covalency in Tl – nitroso group bonding. The Tl-O bond length is substantially less than Tl-N, a fact which is consistent with previous structural studies of uranium compounds.<sup>12</sup> Unlike (1) in (2) the Tl-N interaction is more covalent; moreover, the Tl-O(1) distance, *ca* 3.135(9) Å, is longer than the values for the Tl(18-crown-6) fragment (Tl-N(1)-O(1) 85.4(5) and O(1)-Tl-N(1) 22.8(3)°).



**Figure 1** The structure of [Tl(18-crown-6){TDCO}] showing the atom numbering scheme.



**Figure 2** The structure of [Tl(18-crown-6){TLCO}] showing the atom numbering scheme.

**Table 4** Selected bond lengths (Å) for [Tl(18-crown-6){TDCO}] (1) and [Tl(18-crown-6){TLCO}] (2).

(1)			
Tl-O(1)	2.731(5)	C(1)-C(3)	1.466(9)
Tl-O(2)	2.900(6)	O(2)-C(17)	1.42(1)
Tl-O(3)	3.058(5)	O(3)-C(7)	1.45(2)
Tl-O(4)	2.964(5)	O(4)-C(9)	1.46(1)
Tl-O(5)	3.032(5)	O(5)-C(11)	1.44(1)
Tl-O(6)	2.836(5)	O(6)-C(13)	1.44(2)
Tl-O(7)	2.915(5)	O(6)-C(14)	1.39(1)
Tl-N(1)	2.933(6)	O(7)-C(15)	1.47(2)
O(1)-N(1)	1.301(6)	C(6)-C(7)	1.45(1)
N(1)-C(1)	1.315(8)	C(8)-C(9)	1.45(1)
N(2)-C(2)	1.132(9)	C(10)-C(11)	1.50(2)
N(3)-C(3)	1.353(8)	C(12)-C(13)	1.48(1)
S-C(3)	1.657(6)	C(14)-C(15)	1.47(1)
C(1)-C(2)	1.42(1)	C(16)-C(17)	1.50(1)
(2)			
Tl-O(1)	3.315(9)	C(1)-C(2)	1.43(1)
Tl-O(2)	2.901(6)	C(1)-C(3)	1.442(9)
Tl-O(3)	2.901(7)	C(4)-C(5)	1.31(1)
Tl-O(4)	2.898(7)	C(4)-C(6)	1.52(1)
Tl-O(5)	3.027(6)	O(2)-C(18)	1.43(1)
Tl-O(6)	2.934(7)	O(3)-C(8)	1.44(1)
Tl-O(7)	3.084(7)	O(4)-C(10)	1.48(2)
Tl-N(1)	2.987(8)	O(5)-C(13)	1.45(2)
O(1)-N(1)	1.22(2)	O(6)-C(14)	1.49(2)
N(1)-C(1)	1.34(1)	O(6)-C(15)	1.45(3)
N(2)-C(2)	1.15(2)	O(7)-C(17)	1.39(1)
N(3)-C(3)	1.312(7)	C(7)-C(8)	1.45(2)
N(3)-C(4)	1.386(9)	C(11)-C(12)	1.45(2)
S-C(3)	1.716(7)	C(17)-C(18)	1.47(2)
S-C(5)	1.710(8)		

Consideration of the TDCO anion geometry suggests that  $\pi$ -electron delocalization involving cyano and nitroso groups is present. The distances N(1)-O(1) and N(1)-C(1) are practically equal, at 1.301(6) and 1.315(8) Å, respectively. There are two, almost planar, fragments in the TDCO anion with the dihedral angle between O(1)-N(1)-C(1)-C(2)-N(2) and S-C(3)-N(3) mean planes being *ca* 31.1(3)° (torsion angle N(1)-C(1)-C(3)-S is found to be -144.2(6)°), consistent with the structural study of the T1{TDCO} complex.<sup>6</sup> In spite of the non-planar structure of the TDCO anion, it was possible to determine the *trans-anti* orientation of the nitroso group relative to the thiocarbonyl group (Figure 1).

It should be noted that, in contrast to TDCO, the TLCO anion is practically planar and has a *trans-syn* configuration of the NO-group relative to the heterocyclic nitrogen atom (Figure 2). The dihedral angle between mean planes containing cyanoxime and thiazole fragments is 5.8(9)° (torsion angle N(1)-C(1)-C(3)-S 6.7(1.2)°). The N(1)-O(1) bond length of 1.22(2) Å and N(1)-C(1) bond length of 1.34(1) Å indicate that the cyanoxime ligand exists in the nitroso form.<sup>6</sup> The oxygen atom O(1) has a considerably shortened van der Waals contact with the thiazole sulphur atom, O(1)-S *ca.* 2.69(1) Å ( $r(\text{O} < \text{van der Waals})$  1.5;  $r(\text{S} < \text{van der Waals})$  1.85 Å<sup>14</sup>). This observation suggests conjugation of the nitroso and

**Table 5** Selected bond angles (°) for [Tl(18-crown-6){TDCO}] (1) and [Tl(18-crown-6){TLCO}] (2).

(1)			
O(1)-Tl-O(2)	90.9(1)	O(3)-Tl-O(6)	145.1(2)
O(1)-Tl-O(3)	126.6(2)	O(4)-Tl-O(7)	141.8(1)
O(1)-Tl-O(4)	136.4(2)	Tl-N(1)-O(1)	68.1(3)
O(1)-Tl-O(5)	122.9(2)	Tl-O(1)-N(1)	85.6(3)
O(1)-Tl-O(6)	85.4(2)	O(1)-N(1)-C(1)	116.9(6)
O(1)-Tl-O(7)	81.9(1)	N(1)-C(1)-C(2)	120.6(6)
O(1)-Tl-N(1)	26.3(1)	N(1)-C(1)-C(3)	120.5(6)
O(2)-Tl-O(7)	58.4(2)	C(1)-C(2)-N(2)	175.5(9)
O(2)-Tl-O(3)	56.2(2)	S-C(3)-N(3)	122.7(6)
O(3)-Tl-O(4)	55.8(2)	S-C(3)-C(1)	118.9(5)
O(4)-Tl-O(5)	56.2(2)	C(3)-N(3)-C(5)	114.0(7)
O(5)-Tl-O(6)	56.9(2)	O(4)-C(10)-C(11)	110.1(9)
O(6)-Tl-O(7)	59.5(2)	O(5)-C(12)-C(13)	108.9(9)
O(2)-Tl-O(5)	142.5(1)	O(6)-C(14)-C(15)	110.4(9)
(2)			
N(1)-Tl-O(2)	105.4(2)	O(4)-Tl-O(7)	144.7(2)
N(1)-Tl-O(3)	141.1(2)	Tl-N(1)-O(1)	85.4(5)
N(1)-Tl-O(4)	126.5(3)	Tl-O(1)-N(1)	71.8(4)
N(1)-Tl-O(5)	104.6(2)	O(1)-N(1)-C(1)	117(1)
N(1)-Tl-O(6)	75.9(2)	N(1)-C(1)-C(2)	114.8(7)
N(1)-Tl-O(7)	85.8(2)	N(1)-C(1)-C(3)	126.3(7)
O(1)-Tl-N(1)	22.8(3)	C(1)-C(2)-N(2)	177.6(9)
O(2)-Tl-O(7)	57.1(2)	S-C(3)-N(3)	114.7(5)
O(2)-Tl-O(3)	56.8(2)	S-C(3)-C(1)	122.0(5)
O(3)-Tl-O(4)	59.7(3)	C(3)-N(3)-C(4)	109.5(5)
O(4)-Tl-O(5)	57.1(4)	S-C(5)-C(4)	111.1(5)
O(5)-Tl-O(6)	57.5(3)	N(3)-C(4)-C(5)	116.0(6)
O(6)-Tl-O(7)	54.9(2)	N(3)-C(4)-C(6)	116.4(6)
O(2)-Tl-O(5)	143.7(2)	O(5)-C(12)-C(11)	111.8(9)
O(3)-Tl-O(6)	140.9(2)	O(6)-C(15)-C(16)	110(2)

thiazole groups. This system may be considered as a model for the 'special role' of sulphur in thiazole chemistry and biochemistry.<sup>15</sup>

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#### References

1. J.L. Burmeister, *Coord. Chem. Reviews*, **105**, 77 (1990).
2. A.M. Golub, H. Kohler and V.V. Skopenko (Eds.), "Chemistry of Pseudohalides", (Elsevier, Amsterdam, 1986).
3. R.D. Hancock and A.E. Martell, *Chem. Reviews*, **89**, 1875 (1989).
4. R.G. Pearson, *Inorg. Chem.*, **27**, 734 (1988).
5. K. Domasevitch, V. Ponomareva and E. Rusanov, *J. Coord. Chem.*, **34**, 259 (1995).
6. N.N. Gerasimchuk, K.V. Domasevitch, A.A. Kapshuk and A.N. Tchernega, *Zh. Neorg. Khim.*, **38**, 1837 (1993).



7. N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
8. B.A. Frenz, in "Computing in Crystallography", Ed. H. Schenk, R. Olthof-Hasekamp, H. van Koningsveld, G.B. Bassi *et al.*, (Delft University Press, Delft, 1976).
9. R.D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).
10. A. Yu. Tsivadze, A.A. Varnek and V.E. Khutorsky, "Coordination Compounds of Metals with Crown-Ligands", (Nauka, Moscow, 1991).
11. R. Graziani, U. Casellato and A. Vigato, *J. Chem. Soc., Dalton Trans.*, 697 (1983).
12. A.G. Beykharov, I.M. Orlova, Yu. N. Mikhaylov and R.N. Shchokolov in "Uranium chemistry", (Nauka, Moscow, 1989), p. 55.
13. A.J. Blake, J.A. Greig and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 529 (1991).
14. S.S. Batsanov, *Zh. Neorg. Khim.*, **36**, 3015 (1991).
15. "Comprehensive Organic Chemistry", Ed. D. Barton and W.D. Ollis, Vol. 4, "Heterocyclic Compounds", (Pergamon Oxford, 1979).