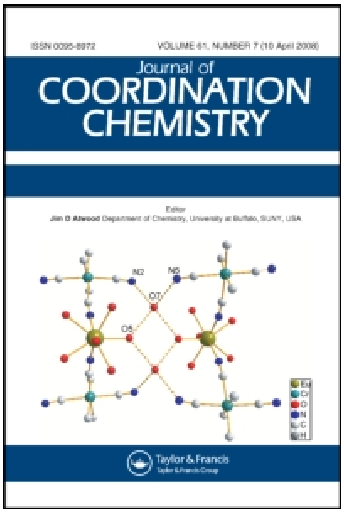

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CRYSTAL AND MOLECULAR STRUCTURE OF A THALLIUM(I) (4-METHYLTHIAZOLYL-2)-CYANOXIMATE COMPLEX WITH *CIS-ANTI-CIS*-DICYCLOHEXANO-18-CROWN-6

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CRYSTAL AND MOLECULAR STRUCTURE OF A THALLIUM(I) (4-METHYLTHIAZOLYL-2)-CYANOXIMATE COMPLEX WITH *CIS-ANTI-CIS*-DICYCLOHEXANO-18-CROWN-6

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The crystal and molecular structure of a macrocyclic complex [T1(DCH-18C6){X}], where X = (4-methylthiazolyl-2)-cyanoxime, DCH-18C6 = *cis-anti-cis*-dicyclohexano-18-crown-6 (*P1*, triclinic, a = 8.354(1), b = 8.729(1), c = 10.724(2)Å, α 87.78(1), β = 74.24(1), γ = 75.46(1)°, Z = 1; R = 0.026; Rw = 0.032; G.O.F. = 1.30 for 2741 unique reflections with $I>3\sigma(I)$) has been determined from X-ray diffraction data. The structure is made up of isolated [T1(DCH-18C6){X}] molecules with seven-coordination about T1 of distorted hexagonal pyramidal geometry. The thallium atom forms close contacts with the six oxygen atoms of the crown-ether (2.823(7)-3.121(6)Å) and the oxygen atom of the oxime group (2.82(2), 2.49(2)Å). The oxygen atom of the oxime group is disordered about two positions each with population 0.5.

Keywords: thallium(I); oximes; thiazoles; X-ray structure

INTRODUCTION

Thiazole derivatives are of considerable interest due to the broad occurrence of the thiazole fragment in Nature. Thus, this heterocycle is a part of numerous antibiotics (althiomycin, penicillin)^{1} and is an active centre in thiamine.$^{1-2}$ In order to characterize the factors influencing the structure of these species, X-ray crystal studies of compounds containing isolated fragments are of special interest.

Recent studies have shown that thiazolyloximes are appropriate models for investigation of the structural peculiarities of thiamine and especially althiomycin with respect to their thiazole-containing part.$^{3-5}$ The free oximes in their different

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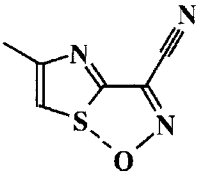
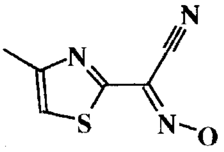
forms (HL, L$^-$) have the unusual sterically unfavourable *syn*-configuration relative to the thiazole fragment;[3] this has not been observed for other hetaryloxime previously.[6] This configuration remains under complex formation only in the case of Tl(18C6){X}[4] (where 18C6 = 18-crown-6, X = (4-methylthiazolyl-2)-cyanoxime) and changes in the cases of Tl(phen){X}[5] and Tl{X}.[7] Therefore, in conjunction with the study of the Tl(18C6){X} structure, it was of interest to investigate the structure of other crown-ether complexes of thallium(I) with thiazolylcyanoxime. Herein we describe the synthesis and X-ray structure of Tl(DCH-18C6){X}, where DCH-18C6 = *cis-anti-cis*-dicyclohexano-18-crown-6.



observed structure



sterically favorable structure

EXPERIMENTAL

Preparation of the starting compound for the present study, Tl{X} was as described previously.[7] DCH-18C6 (Moscow Institute of Chemical Technology, Russia, 98% purity) was used without further purification.

Synthesis of Tl(DCH-18C6){X}

To 20 cm^3 of a hot aqueous solution of 0.221 g (0.570 mmol) of Tl{X} (60°C), a solution of 0.212 g (0.570 mmol) of DCH-18C6 in 2-propanol and water (1:1) was added at once. The yellow crystalline compound was obtained by slow isothermal evaporation of this solution. Yield: 0.321 g (74%). Suitable crystals were obtained by recrystallization of Tl(DCH-18C6){X} from aqueous solution. *Anal.* Calcd. for [Tl(DCH-18C6){X}](%): C, 41.05; H, 5.26; N, 5.53; Tl, 26.84. Found: C, 41.16; H, 5.03; N, 5.41; Tl, 27.00.

Crystallographic measurements were made at 296 K 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 $13<\theta<15°$. The intensity data for 2746 unique reflections were collected within the range $1<2\theta<52°$ using graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement 2741 reflections with $I>3\sigma(I)$ were used. Lorentz and polarization corrections as well as an empirical correction for absorption using the DIFABS program were applied.[8] All structural calculations were carried out using the SDP-PLUS program package.[9] The oxygen atom of the NO-group was found to be disordered about two positions each with population 0.5. The positions of the hydrogen atoms were idealized and included in the calculations with $B_{iso} = 5Å^2$. Refinement was terminated with all non-hydrogen parameter shifts $<0.15\sigma$; a weighting scheme of the form $w = [\sigma^2(F_o)+n*10^{-4}(F_o^2)]^{-1}$ was found appropriate for $n = 16$. Convergence was obtained at $R = 0.026$ and $R_w = 0.032$, G.O.F. = 1.30. For the inverted structure $R = 0.038$, $R_w = 0.050$, G.O.F. = 2.01 (349 refined parameters, largest peak in the final difference map = 1.5(1) e/Å^3).

Crystal data for $C_{26}N_3O_7H_{40}Tl$: $FW = 760$, triclinic, space group $P1$ with $a = 8.354(1)$, $b = 8.729(1)$, $c = 10.724(2)$ Å $\alpha = 87.78(1)$, $\beta = 74.24(1)$, $\gamma = 75.46(1)°$, $V = 728.1(2)$ Å^3, $Z = 1$, $D_{calc} = 1.685$ g cm^{-3}, $\mu(MoK_\alpha) = 71.8$ cm^{-1}, $F(000) = 366$.

Final fractional atomic coordinates and equivalent thermal parameters are given in Table I. Selected bond distances and angles are listed in Tables II and III. Tables of observed and calculated structural factors and anisotropic thermal parameters are available from the authors upon request.

TABLE I Fractional positional parameters of non-hydrogen atoms and their standard deviations

Atom	*x/a*	*y/b*	*z/c*	B_{eq}, Å^2
Tl	0.000	0.000	0.000	3.710(4)
S	0.3889(3)	-0.2093(3)	-0.4039(2)	4.57(5)
O(1)	0.2013(7)	-0.2731(8)	0.1238(5)	4.4(1)
O(2)	0.1007(7)	-0.3160(7)	-0.0966(6)	4.5(1)
O(3)	-0.2044(7)	-0.1456(7)	-0.1440(5)	4.1(1)
O(4)	-0.3511(7)	0.1503(8)	0.0045(5)	4.5(1)
O(5)	0.2338(7)	0.1964(7)	0.2144(5)	4.5(1)
O(6)	0.0605(7)	0.0217(7)	0.2728(5)	3.9(1)
O(7)a	0.194(2)	0.195(2)	-0.154(2)	6.1(4)
O(7)b	0.206(3)	-0.005(2)	-0.217(2)	8.1(4)
N(1)	0.5419(9)	-0.0284(8)	-0.5581(6)	3.8(1)
N(2)	0.260(1)	0.103(2)	-0.2440(8)	7.5(3)
N(3)	0.461(2)	0.363(1)	-0.418(1)	7.9(3)
C(1)	0.321(1)	-0.343(1)	0.0066(9)	4.5(2)
C(2)	0.240(1)	-0.428(1)	-0.0637(9)	5.1(2)
C(3)	0.124(1)	-0.378(1)	-0.1796(7)	3.9(2)
C(4)	-0.070(1)	-0.243(1)	-0.2452(7)	3.8(2)
C(5)	-0.295(1)	-0.005(1)	-0.1873(8)	5.4(2)
C(6)	-0.427(1)	0.086(1)	-0.0763(9)	5.7(2)
C(7)	-0.466(1)	0.216(1)	0.1215(8)	4.4(2)
C(8)	-0.380(1)	0.299(1)	0.1926(9)	5.0(2)
C(9)	-0.162(1)	0.256(1)	0.3026(7)	3.9(2)
C(10)	-0.078(1)	0.118(1)	0.3709(7)	3.9(2)

TABLE I *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	B_{eq}, Å^2
C(11)	0.143(1)	-0.125(1)	0.3197(8)	5.3(2)
C(12)	0.277(1)	-0.216(1)	0.2088(9)	5.3(2)
C(13)	-0.091(1)	-0.481(1)	-0.1092(8)	4.7(2)
C(14)	-0.166(1)	-0.549(1)	-0.2047(9)	5.2(2)
C(15)	-0.256(1)	-0.419(1)	-0.2772(9)	5.1(2)
C(16)	-0.141(1)	-0.309(1)	-0.3416(7)	4.7(2)
C(17)	-0.139(1)	0.357(1)	0.2384(8)	4.8(2)
C(18)	0.030(1)	0.417(1)	0.3387(9)	5.1(2)
C(19)	0.111(1)	0.283(1)	0.4144(9)	5.3(2)
C(20)	-0.012(1)	0.183(1)	0.4744(8)	4.6(2)
C(21)	0.4372(9)	-0.0297(9)	-0.4440(7)	3.4(1)
C(22)	0.714(1)	-0.200(1)	-0.753(1)	5.2(2)
C(23)	0.5959(9)	-0.1747(8)	-0.6184(7)	3.5(1)
C(24)	0.523(1)	-0.288(1)	-0.5493(9)	4.4(2)
C(25)	0.366(1)	0.107(1)	-0.3568(7)	3.9(2)
C(26)	0.423(1)	0.248(1)	-0.3928(9)	4.5(2)

TABLE II Selected Bond Lenghts (Å) for [Tl(DCH-18C6) {X}]

Tl—O(1)	3.038(6)	O(7)a—N(2)	1.19(2)
T1—O(2)	2.823(7)	O(7)b—N(2)	1.14(2)
T1—O(3)	3.096(7)	N(1)—C(21)	1.298(9)
T1—O(4)	2.885(6)	N(1)—C(23)	1.37(1)
T1—O(5)	2.868(6)	N(2)—C(25)	1.30(1)
T1—O(6)	3.121(6)	N(3)—C(26)	1.13(1)
T1—O(7)a	2.82(2)	C(1)—C(2)	1.47(2)
T1—O(7)b	2.49(2)	C(3)—C(13)	1.52(1)
S—C(21)	1.725(9)	C(10)—C(20)	1.55(1)
S—C(24)	1.704(8)	C(21)—C(25)	1.44(2)
O(1)—C(1)	1.421(9)	C(22)—C(23)	1.50(1)
O(1)—C(12)	1.41(1)	C(23)—C(24)	1.38(1)
O(2)—C(2)	1.44(1)	C(25)—C(26)	1.43(1)

TABLE III Selected Bond Angles (°) for [T1(DCH-18C6) {X}]

O(1)—T1—O(2)	56.5(2)	C(21)—N(1)—C(23)	111.4(7)
O(1)—T1—O(3)	106.4(2)	O(7)a—N(2)—C(25)	134(2)
O(1)—Tl—O(4)	139.5(2)	O(7)b—N(2)—C(25)	120(1)
O(1)—T1—O(5)	104.7(2)	C(14)—C(15)—C(16)	111.9(9)
O(1)—T1—O(6)	55.9(2)	C(10)—O(6)—C(11)	113.5(6)
O(1)—T1—O(7)a	115.5(3)	O(1)—C(1)—C(2)	110.2(7)
O(1)—T1—O(7)b	100.5(4)	O(2)—C(2)—C(1)	108.2(8)
S—C(24)—C(23)	110.1(6)	O(2)—C(3)—C(13)	112.5(6)
S—C(21)—N(1)	114.6(6)	C(22)—C(23)—C(24)	125.0(7)
S—C(21)—C(25)	122.2(5)	N(2)—C(25)—C(21)	122(1)
C(21)—S—C(24)	89.4(4)	N(2)—C(25)—C(26)	119.1(9)
N(1)—C(21)—C(25)	123.2(8)	C(21)—C(25)—C(26)	118.8(6)
N(1)—C(23)—C(22)	120.5(7)	N(3)—C(26)—C(25)	176.7(9)
N(1)—C(23)—C(24)	114.4(6)		

RESULTS AND DISCUSSION

The lattice consists of discrete [T1(DCH-18C6){X}] molecules (Figure 1). There are no close contacts between the neighboring molecules in the crystal.

The coordination polyhedron of the central atom is a significantly distorted hexagonal pyramid (Figure 1). The crown-ether coordinates the thallium atom by the six oxygen atoms with Tl—O separations in the range 2.823(7)–3.121(6) Å (Table II), which are consistent with previous structural studies of thallium(I) complexes with macrocyclic polyethers.[10] The C—C, C—O distances and C—C—O, C—O—C angles are typical for crown ether complexes (Table II, III).[10–11] The five-membered Tl—O—C—C—O rings have the *gauche* conformation. Substitutents of C—O bonds are situated in *trans* positions with respect to each other (Figure 1). The crown ether has slightly distorted D_{3d} geometry, which is the most stable in its complex compounds.[11] The cyclohexane rings have the chair conformation. Maximum deviation of the oxygen atoms of DCH-18C6 from their mean plane is 0.12(1) Å. This is some lower then that in lead(II) DCH-18C6 complexes with thiocyanate ion.[12] The thallium atom lies 1.00(1) Å above this plane toward the anion (Figure 1); that is consistent with previous studies of thallium(I) complexes with crown ethers.[4, 10, 12–13]

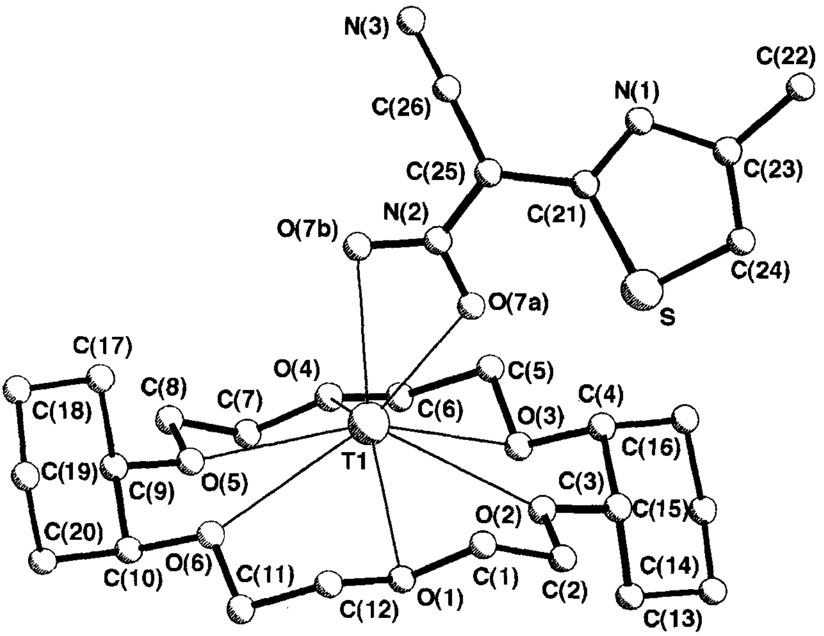


FIGURE 1 Molecular structure of the [T1(DCH-18C6){X}] complex, showing the atom labelling scheme.

The oxygen atom of the oxime group was found to be disordered about two positions (Figure 1). This disorder affects accuracy in bond lengths and angles in the CNO fragment (Table II, III). Analogous to Tl(phen){X},[5] in the title compound the thallium atom is coordinated by the oxygen atom of the NO-group (Figure 1). Change of coordination mode of the X-anion from Tl—N(NO) to Tl—O(NO) by comparison with Tl(18C6){X}[4] may be explained in term of increasing steric hindrance between the anionic and neutral ligands in the Tl(A)(X) compounds upon substituting 18C6 by DCH-18C6.[10–11]

Geometric parameters of the thiazole fragment have typical values (Table III).[1] The N(3)—C(26) distance, 1.13(1) Å, together with the N(3)—C(26)—C(25) angle, 176.7(9)°, is evidence of the *sp*-hybrid character of the C(26) atom. The X-anion has a practically planar structure (torsion angles S—C(21)—C(25)—C(26) 175.7(1)°, O(7)a—N(2)-C(25) -1(2)°. The bonds C(25)—C(26), 1.43(1), and C(21)—C(25), 1.44(2) Å, are substantially shortened relative to a typical C(sp^2)-C(sp^2)[14] bond; this indicates considerable π-electron delocalization in the X-anion.

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