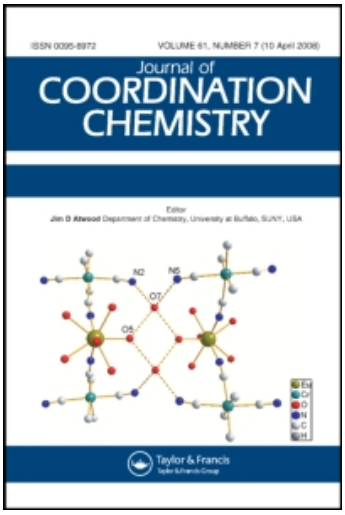

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CRYSTAL AND MOLECULAR STRUCTURE OF A THALLIUM(I) BENZOYLCYANOXIMATE COMPLEX WITH 18-CROWN-6

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The crystal and molecular structure of a macrocyclic complex [Tl(18-crown-6){BCO}], where {BCO} = {ONC(CN)C(O)Ph}$^-$ (space group $P2_12_12_1$, with a = 8.072(2), b = 14.614(4), c = 20.691(4)Å, Z = 4), has been determined. The structure was refined by least-squares methods to a final R of 0.027 for 1890 reflections with $I > 3\sigma(I)$. The structure is made up of isolated Tl(18-crown-6) {BCO} molecules in which the thallium forms seven close contacts with oxygen atoms which surround metal atom in an irregular fashion.

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

INTRODUCTION

A number of cyanoximates of copper, nickel, iron, lead and thallium have been reported.[1,2] These complexes belong to a group of compounds of composition $M\{ONC(CN)\text{-}Z\}_n$ (Z = CN, $CONR_2$, COR, aryl), which is of considerable interest in co-ordination chemistry.[3]

Lately we have investigated a number of structures of the class TlL, where L is a cyanoxime group, and have found that nitroso-oxygens are always coordinated to two or three thallium(I) atoms forming infinite Tl-O-Tl-O chains.[3] However, in thallium(I) benzoylcyanoximate (Tl{BCO}) the linkage pattern was of isolated thallium-oxygen four-membered rings.[4] It was of special interest to investigate the crystal structures of TlL-crown ether complexes with potentially monodentate nitroso-oxygen atoms. No crystal structures of Tl(I)-18-crown-6 complexes were found in the literature.

EXPERIMENTAL

18-Crown-6 (Reakhim, 98% purity) was used without further purification. Preparations of starting compounds, HBCO, Tl{BCO} were as described previously.[5]

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Tl(18-crown-6){BCO} was obtained by reaction of a hot aqueous solution of Tl{BCO} with an appropriate crown ether solution. The solid obtained was dried *in vacuo* at room temperature. It decomposes slowly at about 110°C and melts at 128°C (with decomposition).

Calcd. for Tl(18-crown-6) {BCO}: C, 39.3; H 4.5; N 4.4; Tl 31.8%. Found: C, 39.2; H 4.6; N 4.3; Tl 31.2%

Transparent yellow-orange crystals were obtained by recrystallization from aqueous solution. Preliminary unit cell parameters and intensities of 2514 unique reflections were recorded at 23°C using an Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of scanning rates $\omega/2\theta = 1.2$). Intensity data were collected in the range $1<\theta<26°$ using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (MULTAN) and refined by full-matrix, least-squares techniques in the anisotropic approximation. In the refinement, 1890 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were placed at calculated positions with $B(iso) = 5Å^2$. Convergence was obtained at $R = 0.027$ and $R_w = 0.032$, G.O.F. = 1.05 (289 refined parameters; largest peak in the final difference map = 0.48 e/Å^3). The weighting scheme $w = (\sigma^2F + 0.0016F^2)^{-1}$ was used. Corrections for Lorentz and polarization effects as well as for absorbtion (using DIFABS[6]) were applied. All structural calculations were carried out with a PDP-11/23 + computer using the SDP-PLUS program package.[7]

Crystal data for $C_{21}H_{29}N_2O_8$ Tl: m = 641.8, orthorhombic, space group $P2_12_12_1$, a = 8.072(2), b = 14.614(4), c = 20.691(4)Å, V = 2240.8Å^3, Z = 4, $d(calc)$ = 1.75 g cm^{-3}, μ = 70.1 cm^{-1}, $F(000)$ = 1260.

Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Table 1 Principal interatomic distances and angles are listed in Tables 2 and 3.

RESULTS AND DISCUSSION

The unit cell contains isolated molecules, [Tl(18-crown-6) {BCO}] (Figure 1). There are no close contacts, between neighbouring molecules.

The thallium(I) atom forms seven close contacts with oxygen atoms which surround the metal atom in an irregular way (Figure 1). The Tl-O(crown ether) separations lie between *ca* 2.87–3.06Å (Table 2). The thallium—nitroso-oxygen bond length is 2.747(8)Å. We regard this contact as being mainly covalent.[3,8] In Tl{BCO} the Tl-O (nitroso-group) bond lengths are *ca* 2.57(1)-2.69(1)Å.[4]

The coordinated monodentate benzoylcyanoximate group is structurally normal (Tables 2, 3). Within the limits of error, values in most cases agree satisfactorily with results obtained from crystallographic investigations of $(C_6H_5)_4$Sb{BCO}, Ag{BCO} and Tl{BCO} complexes.[4,5]

C-O and C-C distances (Table 2) in the macrocycle are typical for polyether complexes.[9] The puckered five membered Tl-O-C-C-O rings have a *gauche* conformation and the macrocycle has a slightly distorted D_{3d} geometry. This conformation is the most stable arrangement for 18-crown-6.[9] Each oxygen atom has short van der Waals contacts [*ca* 2.80(1)Å] with two neighbouring oxygen atoms[10], *e.g.*, O(3)-O(4) and O(3)-O(8).

The thallium atom deviation from the mean plane of macrocyclic oxygen atoms

Table 1 Positional and equivalent isotropic thermal parameters for [Tl(18-crown-6){BCO}].

Atom	*x/a*	*y/b*	*z/c*	B_{eq}Å^2
Tl	-0.81654(5)	-0.03867(3)	-0.03130(2)	3.956(6)
O(1)	-1.0167(8)	0.0745(5)	-0.1029(3)	4.8(2)
O(2)	-0.7269(9)	0.2343(5)	-0.2518(3)	5.8(2)
O(3)	-0.6999(9)	-0.0713(5)	-0.1606(3)	5.1(2)
O(4)	-0.9689(8)	-0.1741(5)	-0.1126(3)	4.7(1)
O(5)	-1.0711(9)	-0.1598(4)	0.0188(3)	4.9(1)
O(6)	-0.8310(9)	-0.1064(4)	0.1083(3)	4.9(1)
O(7)	-0.558(1)	-0.0002(5)	0.0654(3)	5.5(2)
O(8)	-0.4594(8)	-0.0263(4)	-0.0685(3)	5.0(2)
N(1)	-0.890(1)	0.1250(5)	-0.1159(3)	4.1(2)
N(2)	-1.132(1)	0.1369(7)	-0.2518(4)	5.9(2)
C(1)	-0.889(1)	0.1650(6)	-0.1739(4)	3.8(2)
C(2)	-1.025(1)	0.1484(6)	-0.2178(4)	4.5(2)
C(3)	-0.746(1)	0.2176(7)	-0.1948(4)	3.9(2)
C(4)	-0.622(1)	0.2483(6)	-0.1457(4)	3.5(2)
C(5)	-0.456(1)	0.2491(6)	-0.1653(4)	4.3(2)
C(6)	-0.333(1)	0.2779(7)	-0.1233(5)	5.6(2)
C(7)	-0.378(1)	0.3098(7)	-0.0618(5)	5.0(2)
C(8)	-0.538(1)	0.3103(7)	-0.0435(4)	5.0(2)
C(9)	-0.663(1)	0.2794(6)	-0.0850(4)	4.3(2)
C(10)	-0.787(1)	-0.1362(7)	-0.1972(4)	5.4(2)
C(11)	-0.961(1)	-0.1381(7)	-0.1779(4)	5.4(2)
C(12)	-1.135(1)	-0.1874(8)	-0.0915(5)	5.3(2)
C(13)	-1.135(1)	-0.2260(7)	-0.0265(5)	4.9(2)
C(14)	-1.078(1)	-0.1915(8)	0.0828(5)	6.1(3)
C(15)	-1.004(1)	-0.1194(9)	0.1249(5)	6.5(3)
C(16)	-0.749(2)	-0.0425(8)	0.1473(4)	6.4(3)
C(17)	-0.573(2)	-0.0352(8)	0.1287(5)	5.8(2)
C(18)	-0.393(1)	-0.0016(8)	0.0407(6)	6.4(3)
C(19)	-0.387(1)	0.0369(7)	-0.0255(6)	6.4(3)
C(20)	-0.452(1)	0.0046(8)	-0.1336(6)	5.9(3)
C(21)	-0.529(1)	-0.0659(7)	-0.1763(5)	5.2(2)

Table 2 Selected bond lengths (Å) for [Tl(18-crown-6){BCO}].

Tl-O(1)	2.747(8)	O(6)-C(16)	1.40(2)
Tl-O(3)	2.875(7)	O(7)-C(17)	1.41(1)
Tl-O(4)	2.874(7)	O(7)-C(18)	1.43(2)
Tl-O(5)	2.904(7)	O(8)-C(19)	1.41(1)
Tl-O(6)	3.057(7)	O(8)-C(20)	1.42(1)
Tl-O(7)	2.947(8)	N(1)-C(1)	1.34(1)
Tl-O(8)	2.989(8)	N(2)-C(2)	1.13(1)
O(1)-N(1)	1.29(2)	C(1)-C(2)	1.44(1)
O(2)-C(3)	1.21(1)	C(1)-C(3)	1.46(2)
O(3)-C(10)	1.40(1)	C(3)-C(4)	1.49(1)
O(3)-C(21)	1.42(1)	C(10)-C(11)	1.47(3)
O(4)-C(11)	1.45(1)	C(12)-C(13)	1.46(2)
O(4)-C(12)	1.42(1)	C(14)-C(15)	1.49(2)
O(5)-C(13)	1.44(1)	C(16)-C(17)	1.48(2)
O(5)-C(14)	1.40(1)	C(18)-C(19)	1.49(2)
O(6)-C(15)	1.45(2)	C(20)-C(21)	1.49(2)

Table 3 Selected bond angles (°) for [Tl(18-crown-6){BCO}].

O(1)-Tl-O(3)	78.0(2)	O(5)-Tl-O(6)	55.9(2)
O(1)-Tl-O(4)	81.3(2)	O(5)-Tl-O(7)	112.1(2)
O(1)-Tl-O(5)	98.2(2)	O(5)-Tl-O(8)	144.2(3)
O(1)-Tl-O(6)	133.1(2)	O(6)-Tl-O(7)	56.4(2)
O(1)-Tl-O(7)	132.0(3)	O(6)-Tl-O(8)	107.4(2)
O(1)-Tl-O(8)	113.1(2)	O(7)-Tl-O(8)	58.6(2)
O(3)-Tl-O(4)	58.8(2)	Tl-O(1)-N(1)	89.3(5)
O(3)-Tl-O(5)	117.6(2)	O(1)-N(1)-C(1)	115.9(9)
O(3)-Tl-O(6)	146.9(2)	N(1)-C(1)-C(2)	119(1)
O(3)-Tl-O(7)	115.5(2)	N(2)-C(2)-C(1)	179(1)
O(3)-Tl-O(8)	57.0(2)	O(2)-C(3)-C(1)	120(1)
O(4)-Tl-O(5)	59.1(2)	O(2)-C(3)-C(4)	121(2)
O(4)-Tl-O(6)	108.3(2)	C(2)-C(1)-C(3)	120.3(8)
O(4)-Tl-O(7)	146.3(2)	C(1)-C(3)-C(4)	119.2(8)
O(4)-Tl-O(8)	107.7(2)		

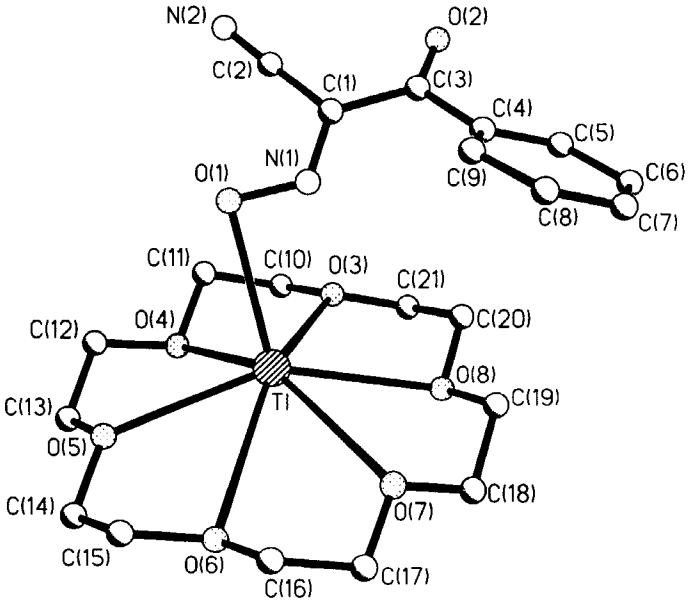

Figure 1 The structure of [Tl(18-crown-6){Benzoyl cyanoximate}], showing the atom labelling scheme.

0.86(1)Å. It is interesting to note the structures of rubidium(I) 18-crown-6 complexes due to the very similar ionic radii of Tl^+ (1.50Å) and Rb^+ (1.52Å).[10] For example, in Rb(18-crown-6)NCS, the metal atom deviation from the least-squares oxygen atom plane is *ca* 1.19Å.[11] Similar deviations was also observed for a number of Rb complexes with benzo- and cyclohexyl-analogues of 18-crown-6. These values are significantly greater than the value observed in titled compound. This suggests a more covalent character for the Tl-(18-crown-6) oxygen bonds.

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Supplementary Data

Full lists of bondlengths and angles, thermal parameter and observed and calculated structure factors are available from the authors upon request.

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