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Crystal and Molecular Structure of {1,2-Bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane}-bis(isothiocyanato)calcium

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Abstract—The crystal and molecular structure of {1,2-bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane}bis(isothiocyanato)calcium was studied by single crystal X-ray diffraction. The compound is a host–guest complex. In the molecule of this complex, the podand is “wrapped” around the Ca^{2+} cation (CN 8), which is coordinated with all the six oxygen atoms of the podand and with two nitrogen atoms of two SCN^- ligands. The geometric parameters and crystal packing of the complex were determined. The molecules in the crystal are linked by O–H···S hydrogen bonds to form three-dimensional layers.

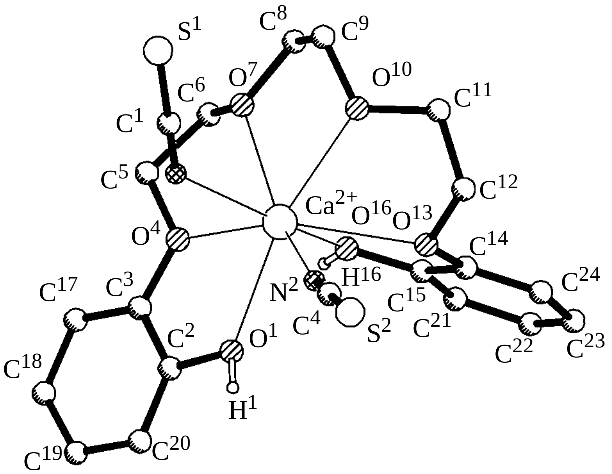
Similar to crown ethers, their acyclic analogs, podands, form host–guest complexes with cations of various metals [1]. However, the crystal and molecular structures of podand complexes are considerably less sudied than the structures of crown ether complexes. In this work we studied by single crystal X-ray diffraction a new complex of 1,2-bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane podand (L) with calcium thiocyanate, $[Ca(NCS)_2L]$ (II). Previously, X-ray structural data were available only for monohydrate of this podand, $L \cdot H_2O$ [2], and for a complex of a related podand, 1,2-bis[2-(*o*-methoxyphenoxy)ethoxy]ethane (L'), with sodium thiocyanate, [Na(NCS)L'] [3].

The molecular structure of **I** in crystal is shown in the figure; the bond lengths and the main bond and torsion angles are listed in Tables 1–3. Complex **I** is a host–guest complex [1]. In its molecule, podand L is “wrapped” around the Ca^{2+} ion, which is coordinated with all the six oxygen atoms of the podand and with two nitrogen atoms of the two SCN^- ligands.

In the structure of **I**, the coordination polyhedron of the Ca^{2+} cation (CN 8) is irregular, and in very rough approximation it can be considered as a strongly distorted hexagonal bipyramid with the base consisting of the N^2 atom of one of the SCN^- ligands and five oxygen atoms (O^1, O^4, O^7, O^{10}, O^{13}) of L, with the N^1 atom of the other SCN^- ligand and O^{16} atom of L occupying the opposite apices. The coordination polyhedron of this Ca^{2+} ion can be described more precisely as follows. The O^1, O^4, O^7, and O^{10} atoms of L are approximately coplanar [within ±0.025(1) Å]; the Ca^{2+} cation and two nitrogen atoms, N^1 and N^2, of the SCN^- ligands deviate from this plane to the same side by 0.101(1), 2.483(2), and 1.031(3) Å, respectively; and the remaining two oxygen atoms of L, O^{13} and O^{16}, deviate from this plane to the opposite side by 1.654(2) and 2.319(2) Å, respectively.

In the structure of **I**, the mean lengths of the Ca–O [2.50(4) Å] and Ca–N [2.44(1) Å] coordination bonds are slightly or significantly shorter than the sums of the effective ionic radius of Ca^{2+} (1.12 Å for CN 8) [4] and the van der Waals radii of the O (1.40–1.52 Å) and N (1.50–1.55 Å) atoms [5, 6].

The conformation of L in the structure of **I** can be characterized in detail by the torsion angles (Table 3).



Molecular structure of **I** in crystal; hydrogen atoms at the carbon atoms are not shown for clarity.

Table 1. Bond lengths (*d*, Å) in the structure of **I**

Bond	*d*	Bond	*d*
Ca–N^1	2.446(2)	O^7–C^8	1.434(2)
Ca–N^2	2.427(2)	C^8–C^9	1.501(3)
Ca–O^1	2.432(1)	C^9–O^{10}	1.433(2)
Ca–O^4	2.519(1)	O^{10}–C^{11}	1.425(2)
Ca–O^7	2.485(1)	C^{11}–C^{12}	1.496(3)
Ca–O^{10}	2.470(1)	C^{12}–O^{13}	1.444(2)
Ca–O^{13}	2.585(1)	O^{13}–C^{14}	1.389(2)
Ca–O^{16}	2.500(1)	C^{14}–C^{15}	1.393(2)
S^1=C^1	1.644(2)	C^{14}–C^{24}	1.380(2)
N1=C1	1.162(3)	C^{15}–O^{16}	1.371(2)
S^2=C^4	1.639(2)	C^{15}–C^{21}	1.388(2)
N^2=C^4	1.156(3)	C^{17}–C^{18}	1.396(3)
O^1–C^2	1.383(2)	C^{18}–C^{19}	1.367(3)
C^2–C^3	1.388(2)	C^{19}–C^{20}	1.390(3)
C^2–C^{20}	1.386(3)	C^{21}–C^{22}	1.381(3)
C^3–O^4	1.376(2)	C^{22}–C^{23}	1.379(3)
C^3–C^{17}	1.392(2)	C^{23}–C^{24}	1.384(3)
O^4–C^5	1.446(2)	H^1–O^1	0.85(2)
C^5–C^6	1.492(3)	H^{16}–O^{16}	0.85(2)
C^6–O^7	1.427(2)		

In the main chain of this podand (consisting of 16 non-hydrogen atoms and H^1 and H^{12} atoms of two OH groups), two torsion angles ($O^1C^2C^3O^4$ and $O^{13}C^{14}C^{15}O^{16}$) are synperiplanar (of the *cis* type), three torsion angles ($O^4C^5C^6O^7$, $O^7C^8C^9O^{10}$, and $O^{10}C^{11}C^{12}O^{13}$) are synclinal (of the *gauche* type), three torsion angles ($C^8C^9O^{10}C^{11}$, $C^{11}C^{12}O^{13}C^{14}$, and $C^{12}O^{13}C^{14}C^{15}$) are anticlinal (partially eclipsed), and the remaining torsion angles are antiperiplanar (of the *trans* type). It should be noted that the conformation of L in the structure of **I** differs significantly from its conformation in the crystal of the monohydrate $L \cdot H_2O$ [2] and somewhat resembles the conformation of the related podand L' in the crystal of [Na(NCS)L'] [3].

In the structure of **I**, four bonds (O^1–O^2, O^{15}–O^{16}, C^3–O^4, O^{13}–C^{14}) are somewhat longer compared to the mean bond lengths in related fragments {C_{ar}–OH, 1.362(15) Å; C_{ar}–O–C(sp^3), 1.370(11) Å [7]}. Two bonds (O^4–C^5, C^{12}–O^{13}) are slightly longer compared to the mean bond length in C–CH_2–O–C_{ar} fragments {1.431(13) Å [7]}. The lengths of four bonds (C^6–O^7, O^7–C^8, C^9–O^{10}, O^{10}–C^{11}) are slightly larger than, or approximately equal to the mean bond length in C–CH_2–O–C(sp^3) fragments {1.426(11) Å [7]}. On the contrary, three bonds (C^5–C^6, C^8–C^9, C^{11}–C^{12}) are appreciably shorter compared to the mean bond length in C(sp^3)–CH_2–CH_2–C(sp^3) fragments {1.542(14) Å [7]}. The shortening of three C–C bonds is typical of O–CH_2–CH_2–O fragments and is well known for crown ethers [8].

Table 2. Selected bond angles (ω, deg) in the structure of **I**

Angle	ω	Angle	ω
N^1CaN^2	80.17(7)	CaN^1C^1	135.2(2)
N^1CaO^1	98.27(6)	CaN^2C^4	166.8(2)
N^1CaO^4	85.35(6)	$S^1C^1N^1$	177.8(2)
N^1CaO^7	78.71(6)	$S^2C^4N^2$	179.5(2)
N^1CaO^{10}	89.26(6)	$H^1O^1C^2$	106(2)
N^1CaO^{13}	140.89(6)	$O^1C^2C^3$	116.8(2)
N^1CaO^{16}	154.94(6)	$O^1C^2C^{20}$	122.6(2)
N^2CaO^1	79.45(6)	$C^3C^2C^{20}$	120.5(2)
N^2CaO^4	137.39(6)	$C^2C^3O^4$	115.1(1)
N^2CaO^7	148.08(6)	$C^2C^3C^{17}$	119.8(2)
N^2CaO^{10}	89.67(6)	$O^4C^3C^{17}$	125.1(2)
N^2CaO^{13}	71.06(5)	$C^3O^4C^5$	118.1(1)
N^2CaO^{16}	124.25(6)	$O^4C^5C^6$	107.9(2)
O^1CaO^4	63.23(4)	$C^5C^6O^7$	108.1(2)
O^1CaO^7	127.13(5)	$C^6O^7C^8$	111.8(2)
O^1CaO^{10}	165.44(5)	$O^7C^8C^9$	106.3(2)
O^1CaO^{13}	101.77(5)	$C^8C^9O^{10}$	109.9(2)
O^1CaO^{16}	82.63(5)	$C^9O^{10}C^{11}$	114.3(2)
O^4CaO^7	63.92(4)	$O^{10}C^{11}C^{12}$	106.9(2)
O^4CaO^{10}	130.20(4)	$C^{11}C^{12}O^{13}$	109.2(1)
O^4CaO^{13}	133.71(4)	$C^{12}O^{13}C^{14}$	117.3(1)
O^4CaO^{16}	72.63(4)	$O^{13}C^{14}C^{15}$	115.6(2)
O^7CaO^{10}	66.47(5)	$O^{13}C^{14}C^{24}$	123.5(2)
O^7CaO^{13}	113.34(5)	$C^{15}C^{14}C^{24}$	120.6(2)
O^7CaO^{16}	80.90(5)	$C^{14}C^{15}O^{16}$	116.8(1)
$O^{10}CaO^{13}$	65.23(5)	$C^{14}C^{15}C^{21}$	119.3(2)
$O^{10}CaO^{16}$	95.82(5)	$O^{16}C^{15}C^{21}$	123.9(2)
$O^{13}CaO^{16}$	61.76(4)	$C^{15}O^{16}H^{16}$	107(2)

Table 3. Selected torsion angles (τ, deg) in the structure of **I**

Angle	τ	Angle	τ
$O^{10}CaN^1C^1$	–8.7(2)	$C^6O^7C^8C^9$	178.7(2)
$O^{13}CaN^1C^1$	38.4(3)	$O^7C^8C^9O^{10}$	56.2(2)
$N^2CaO^{16}C^{15}$	–27.1(2)	$C^8C^9O^{10}C^{11}$	98.3(2)
$O^{10}CaO^{16}C^{15}$	66.4(1)	$C^9O^{10}C^{11}C^{12}$	–179.0(2)
$H^1O^1C^2C^3$	160(2)	$O^{10}C^{11}C^{12}O^{13}$	57.9(2)
$O^1C^2C^3O^4$	3.5(2)	$C^{11}C^{12}O^{13}C^{14}$	91.9(2)
$C^2C^3O^4C^5$	–176.4(2)	$C^{12}O^{13}C^{14}C^{15}$	–135.0(2)
$C^{17}C^3O^4C^5$	4.1(2)	$C^{12}O^{13}C^{14}C^{24}$	50.7(2)
$C^3O^4C^5C^6$	–161.0(2)	$O^{13}C^{14}C^{15}O^{16}$	2.8(2)
$O^4C^5C^6O^7$	–50.4(2)	$C^{14}C^{15}O^{16}H^{16}$	–166(2)
$C^5C^6O^7C^8$	–171.0(2)		

The two phenyl rings in L in the structure of **I** are almost planar: the deviations of the carbon atoms are within ±0.016(2) Å for the first ring and ±0.007(2) Å for the second ring. The angle between the least-squares planes of these two phenyl rings is 79.35(6)°. The least-squares planes of the first and second phenyl rings form with the least-squares plane of the O^1, O^4, O^7, and O^{10} atoms of L the angles of 4.9(1)° and 77.90(5)°, respectively. The mean C⋯C bond length in these phenyl rings is 1.385(6) Å, virtually coinciding with the mean value for substituted benzene rings, 1.384(13) Å [7].

In the structure of **I**, two anionic ligands SCN^- are located on the one side of the least-squares plane of the first five oxygen atoms of L and coordinate the Ca^{2+} ion via nitrogen. These two SCN^- ligands are almost linear, and the lengths of their covalent bonds are close to the mean values for isocyanates: S=C 1.642(17) and N=C 1.149(17) Å [9].

In the crystal structure of **I**, there are two types of intermolecular hydrogen bonds: $O^1–H^1\cdots S^1(i)$ and $O^{16}–H^{16}\cdots S^2(ii)$. The corresponding interatomic distances and angles are as follows: $O^1\cdots S^1(i)$ 3.238(2), $O^{16}\cdots S^2(ii)$ 3.175(1), $H^1\cdots S^1(i)$ 2.39(2), $H^{16}\cdots S^2(ii)$ 2.33(2) Å; $\angle[O^1–H^1\cdots S^1(i)]$ 174(2)°, $\angle[O^{16}–H^{16}\cdots S^2(ii)]$ 172(2)°; symmetry codes: (i) $x - 1$, y, z; (ii) $1/2 - x$, $1 - y$, $z - 1/2$. The molecules of **I** are linked with $O^1–H^1\cdots S^1(i)$ hydrogen bonds in infinite chains running along the x axis and with $O^{16}–H^{16}\cdots S^2(ii)$ hydrogen bonds in infinite chains running along the z-axis. As a result, three-dimensional layers parallel to the xz plane are formed.

The other (except for the above indicated H bonds) short interatomic contacts between molecules of **I** in the crystal are close to, or slightly shorter than, the sums of the corresponding van der Waals atomic radii.

EXPERIMENTAL

Complex **I** was prepared as follows. Podand L and $Ca(NCS)_2$ in a 1 : 1 molar ratio were dissolved in a 5 : 1 acetone–water mixture. Slow evaporation of the solution at room temperature resulted in formation of colorless transparent crystals of **I** of X-ray quality.

The unit cell parameters and the three-dimensional set of reflection intensities were obtained with an Enraf-Nonius CAD-4 automated diffractometer (MoK_α radiation, graphite monochromator. $C_{18}H_{22}O_6 \cdot Ca(NCS)_2$, M 490.60, rhombic system: a 7.719(2), b 16.813(3), c 17.060(3) A; V 2214.0(8) Å^3, Z 4, d_{calc} 1.472 g cm^{-3}, $\mu(MoK_\alpha)$ 5.12 cm^{-1}, space group $P2_12_12_1$.

The intensities of 4137 reflections were measured in the reciprocal space octant ($2\theta \le 63°$) in the $\omega/2\theta$ scanning mode using a 0.25 × 0.46 × 0.47-mm single crystal of **I**. When measuring intensities, we used a special mode in which the final scanning was performed for all (including very weak) reflections. After exclusion of 29 systematically absent reflections, the working set of measured $F^2(hkl)$ and $\sigma(F^2)$ values included 4108 unique reflections.

Structure **I** was solved by the direct method using the SHELXS 97 program [10] and refined by the full-matrix least-squares method (with respect to F^2) using the SHELXL 97 program [10] in the approximation of anisotropic thermal vibrations for non-hydrogen atoms. For the structure refinement, we used almost all the reflections from the working set [including very weak reflections with $I < 2\sigma(I)$], except several reflections for which the measured and calculated F^2 values were poorly consistent.

In the structure of **I**, all hydrogen atoms were localized objectively in the intermediate Fourier differential electron density synthesis. Then the coordinates of the majority of hydrogen atoms were calculated geometrically using the rider model [10], and the individual isotropic thermal parameters U_{iso} of all hydrogen atoms were refined by the least-squares method. The coordinates of the H^1 and H^{16} atoms (belonging to the OH groups of the podand) were refined as for free atoms.

For the exposed crystal of **I**, we also refined by the least-squares method the absolute structure parameter: χ –0.03(3) [11]. In the last cycle of the full-matrix refinement, all the 309 varied parameters of the structure of **I** changed in the absolute value by less than 0.001σ. The final coordinates and thermal parameters of the atoms are listed in Tables 4 and 5.

The final R factors are as follows: $R1$ 0.028 and $wR2$ 0.068 for 3600 observed reflections with $I \ge 2\sigma(I)$; $R1$ 0.038 and $wR2$ 0.100 for all 4108 measured unique reflections; goodness of fit S 1.04 (for the definitions of $wR2$ and S, see [10]). In the final Fourier difference electron density synthesis, $-0.29 < \delta\rho < 0.21$ e Å^{-3}. The f curves and anomalous-dispersion corrections to them ($\Delta f'$ and $\Delta f''$) were taken from the International Tables [12].

Table 4. Coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) of non-hydrogen atoms in the crystal structure of **I**

Atom	x	y	z	U_{eq} [a]
Ca	4535.0(4)	5078.6(2)	2066.8(2)	23.04(7)
S^1	9443.9(8)	5529.2(4)	3794.2(4)	50.6(1)
C^1	7598(3)	5688(1)	3341(1)	35.6(4)
N^1	6321(2)	5815(1)	3003(1)	46.7(4)
S^2	3214.5(8)	3758.6(3)	4748.2(3)	41.1(1)
C^4	3394(3)	4186(1)	3888(1)	31.9(4)
N^2	3533(3)	4487(1)	3282(1)	45.1(4)
O^1	1834(2)	5798.6(8)	2257.0(8)	33.8(3)
C^2	1559(2)	6559(1)	1976(1)	27.9(3)
C^3	2862(2)	6887(1)	1518.3(9)	25.1(3)
O^4	4236(2)	6389.7(7)	1364.5(7)	28.4(2)
C^5	5689(3)	6707(1)	930(1)	36.1(4)
C^6	6690(3)	6024(1)	605(1)	39.3(4)
O^7	7019(2)	5477.9(8)	1228.2(8)	35.1(3)
C^8	8201(3)	4863(1)	997(1)	45.5(5)
C^9	8464(3)	4347(1)	1706(2)	44.7(5)
O^{10}	6828(2)	4057.3(8)	1980.8(8)	35.1(3)
C^{11}	6421(3)	3271(1)	1729(1)	36.0(4)
C^{12}	4675(3)	3074(1)	2056(1)	34.0(4)
O^{13}	3434(2)	3655.0(7)	1783.6(7)	30.7(3)
C^{14}	2542(2)	3482(1)	1097.0(9)	24.2(3)
C^{15}	2416(2)	4104(1)	560.4(9)	25.5(3)
O^{16}	3244(2)	4798.7(7)	751.7(7)	32.6(3)
C^{17}	2706(3)	7665(1)	1247(1)	32.7(4)
C^{18}	1213(3)	8097(1)	1425(1)	40.4(5)
C^{19}	–88(3)	7759(1)	1854(1)	42.4(5)
C^{20}	56(3)	6983(1)	2129(1)	37.2(4)
C^{21}	1438(3)	4000(1)	–115(1)	35.5(4)
C^{22}	574(3)	3291(1)	–236(1)	42.2(5)
C^{23}	690(3)	2679(1)	300(1)	40.3(4)
C^{24}	1689(3)	2773(1)	967(1)	32.4(4)

[a] The U_{eq} values were calculated as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 5. Coordinates (×10^3) and isotropic thermal parameters (Å^2 × 10^3) of hydrogen atoms in the crystal structure of **I**

Atom	x	y	z	U_{eq} [a]
H^1	115(3)	575(2)	264(1)	47(7)
H^{16}	286(3)	516(1)	44(1)	45(7)
H^{5A}	642	702	127	40(6)
H^{5B}	528	704	51	59(8)
H^{6A}	603	576	19	42(6)
H^{6B}	778	621	38	49(7)
H^{8A}	929	509	83	68(9)
H^{8B}	772	455	57	61(9)
H^{9A}	921	390	157	63(8)
H^{9B}	903	465	212	50(7)
H^{11A}	728	290	192	44(7)
H^{11B}	640	324	116	39(6)
H^{12A}	433	255	189	42(6)
H^{12B}	472	308	262	38(6)
H^{17}	359	789	95	36(6)
H^{18}	110	862	125	41(6)
H^{19}	–108	805	196	47(7)
H^{20}	–84	675	241	58(8)
H^{21}	137	441	–48	56(8)
H^{22}	–10	323	–68	75(10)
H^{23}	10	220	21	64(9)
H^{24}	179	236	133	35(6)

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