Polymorph of Dibenzo-24-Crown-8 and its Mercury Complex

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Abstract. Dibenzo-24-crown-8 is studied herein as a flexible ligand able to adopt different conformations, as well as for the complexation of mercury. The recrystallization of dibenzo-24-crown-8 (DB24C8) from dry THF gives a new polymorphic structure of this ligand. This new structure is described and compared to the literature compound. Additionally, coordination of this ligand to mercury iodide HgI_2 is studied.

Introduction

Polymorphism[1] – the multiplicity of structures or forms – is a term that is used in many disciplines. For chemists, it refers to the existence of more than one crystal structure for a given chemical compound. The properties of such a substance are determined by (i) its composition and (ii) its structure, influencing e.g. optical properties, solubility, and thus bioavailability, etc.[1–10] Polymorphism can potentially be found in any crystalline material including polymers, minerals, and metals, and is related to allotropy, which refers to elemental solids.[6–8] Over the past 20 years, there has been a sharp increase in the interest in polymorphic systems, both because of it being an intrinsically interesting phenomenon and as an increasingly important component in the development of a variety of materials (e.g. pharmaceuticals, dyes and pigments, explosives, etc.). When polymorphism exists as a result of difference in crystal packing, it is called packing polymorphism.[6] Polymorphism can also result from the existence of different conformers of the same molecule in conformational polymorphism.[6] In pseudo-polymorphism the different crystal types are the result of hydration or solvation.[11] The differences in crystal packing can have considerable differences in solubility, hygroscopicity, bioavaibility, physical stability, etc. Due to these possible changes in property, an understanding the conditions, under which the different polymorphs of a compound can be obtained, which is of great interest in the case of active pharmaceutical compounds or materials molecules. In our group, we were mainly interested in the polymorphism of coordination compounds,[12] especially in the context of antimicrobial silver compounds,[4,13] for which conformational as well as pseudo-polymorphism was observed.

McCrone's states that "*Every compound has different polymorphic forms, and that, in general, the number of forms known for a given compound is proportional to the time and money spent in research on that compound.*"[9]

However, quite often, polymorphism appears by surprise during investigation in different subjects. Some of our recent research deals also with the use of crown ethers as scaffolds for channel systems.[14–19] The dibenzo-crown ethers seem to be stiffer than the simple crown ethers and show fewer conformations. The larger these dibenzo-crowns, the more flexible they become. Herein, we present a new polymorph of dibenzo-24-crown-8 and its complexation behavior towards mercury iodide.

Results and Discussion

The first synthesis of dibenzo-24-crown-8 (DB24C8) (**1**) was published by *Pedersen* in 1967[20] and the first crystal structure of uncoordinated **1** (Figure 1) was reported by *Truter*[21] in 1976. In this publication, **1**, which will be called α-**1** from now on, crystallizes by slow evaporation from a mixture of dichloromethane and ethanol in the monoclinic space group $P2_1/c$.

During our investigations with this ligand, a polymorph of DB24C8 (β-**1**) (Figure 2) crystallized from a solution of THF by slow evaporation in air and also by crystallization from a mixture of THF and heptane at 4 °C. A series of measurements of the unit cell at different temperatures confirmed that α-**1** and β-**1** are true polymorphs. β-**1** crystallizes also in the monoclinic space group $P2_1/c$, but with a Z of 4, in contrast to α-**1**, which has a Z value of 2. In both forms, compound **1** adopts a chair conformation, whereas the main difference between the

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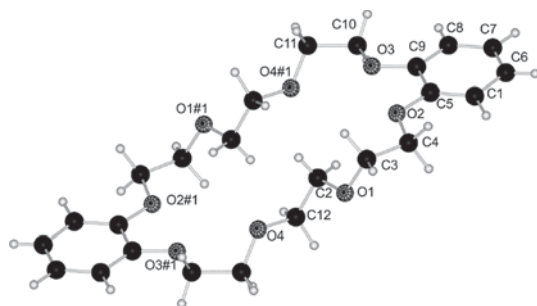
Figure 1. Molecular structure of the polymorph of dibenzo-24-crown-8 (1967) (α-**1**).

two structures resides in the distance between the two planes, which contain the phenyl-groups, and in the torsion angles of the O–CH₂–CH₂–O moieties. For α-**1** the distance between the mean planes formed by the phenyl moieties is around 3.57 Å, whereas for β-**1** it is with 4.78 Å by more than 1 Å larger. The distances between the centroids of the phenyl-rings and the geometrical middle of the crown ether part are around 6.32 Å for α-**1** and 5.86 Å for β-**1**, indicating the flatter and more stretched out conformation of the first form. The torsion angles O2–O1–O4–O3#1 and O1#1–O2–O3–O4 are +/– 18° in α-**1** and +/– 67° in β-**1**. In the central cavity the two nearest atoms are C2 and C12#1 in α-**1** for a distance of 4.05 Å and this two closest atoms are O4 and C9#1 with a distance of 5.48 Å. Figure 3 compares the profile of the two polymorphs.
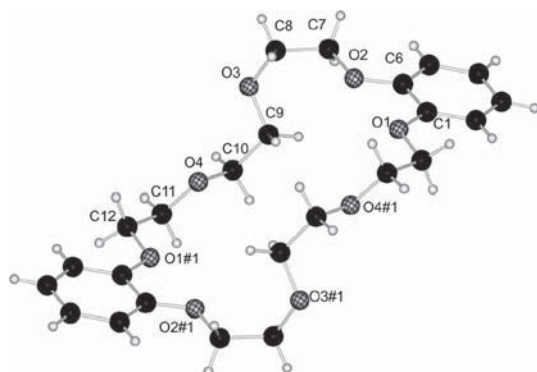

Figure 2. Molecular structure of the polymorph of dibenzo-24-crown-8 (2011) (β-**1**).
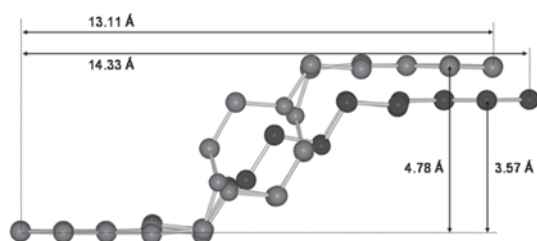

Figure 3. Superposition of the two molecular structures of dibenzo-24-crown-8 (α-**1** in dark grey β-**1** in clear grey), hydrogen atoms are omitted for clarity.
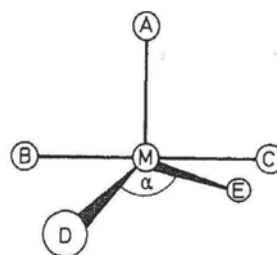
In order to better compare the two polymorphs, their energy was calculated in the gas phase by DFT in B3LYP mode and 6-311gd as basis set. This calculation shows that the more stable polymorph in terms of conformation seems to be α-**1** (–1535.42905745 a.u. versus –1535.42406677 for β-**1**). Additionally, the TG measurement indicates a phase transition at 83 °C when heating the α-form to yield the β-phase. All these observations let us conclude that we are in presence of a conformational polymorphism (Table 1).

In 1999, *Luis*[22] used the ligand **1** for the complexation of (DB24C8)-dicyano-mercury(II) monohydrate, and in 2000, *Willey*[23] published the structure of (μ₂-DB24C8)-bis(dichloro)-mercury(II). We use non-cyclic and cyclic polyethereal ligands in order to synthesize and characterize new metal halide compounds, which can be used as precursors for oxide materials.[24–27] In this context, as well as for comparison with the literature mercury compounds mentioned above, and also comparing the conformation of the ligand upon coordination with its free form, we tested **1** as ligand for HgI₂. Indeed, the ligand **1** as well as the starting compound HgI₂ has two polymorphic forms, the red and the yellow HgI₂ in the latter case.[28,29] We wondered which of the metal halides was stabilized by which conformation of **1**.

The coordination reaction of **1** with HgI₂ in solution yields the complex [(DB24C8)HgI₂] (**2**) (Figure 4). Compound **2** crystallizes in the orthorhombic space group *Pbca*. The coordination arrangement around the metal ion can be described as an extremely distorted trigonal bipyramid with two iodide anions and one oxygen atom O2 in equatorial positions, and O1 and O3 in the axial positions (Figure 4). The Hg1–I distances are 2.6019(9) Å and 2.596(1) Å for I1 and I2, respectively, and the Hg–O bonds are 2.935(7) Å for O1, 2.707(1) Å for O2, and 2.902(7) Å for O3. The angle between the two iodide anions is 167.71(3)°, and between the neighboring oxygen atoms 58.7(2)° (O1–Hg1–O2) and 63.2(2)° (O2–Hg1–O3). The angles between the iodide anions and the oxygen atoms are 87.8(1)° (I1–Hg1–O1), 96.0(2)° (I1–Hg1–O2) and 89.9(1)° (I1–Hg1–O3), 101.7(1)° (I2–Hg1–O1), 95.6(2)° (I2–Hg1–O2) and 91.8(1)° (I2–Hg1–O3).
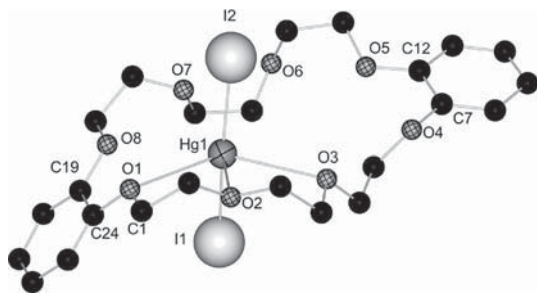
In order to verify the polyhedral arrangement of Hg1, an evaluation of a structural index parameter can be made. This parameter was introduced in 1984 by *Addison* et al.,[30] they used this parameter to determine if the arrangement is more trigonal bipyramidal or rather close to square pyramidal. In the five coordinated model, the metal atom *M* is coordinated by the five atoms A, B, C, D, and E, like below, in a square-pyramidal arrangement, with α = β = 180°, for A as the axial ligand (β is the greater of the basal angles, BMC).

They finally defined the geometric parameter τ = (β–α)/60, "*which is applicable to five coordinated structures as an index*

Table 1. Unit cells of **1** as a function of temperature. α-**1** Data comes from.[21]

	T /K	a /Å	b /Å	c /Å	β /°
α-**1**	283–303	9.187(2)	4.913(2)	26.462(5)	104.93(1)
β-**1**	123	4.593(6)	13.243(17)	17.51(2)	90.276(14)
	173	4.610(8)	13.30(2)	17.61(3)	90.071(16)
	233	4.630(7)	13.34(2)	17.70(3)	90.171(15)
	273	4.627(12)	13.30(3)	17.69(4)	90.31(2)

Figure 4. Molecular structure of **2**, hydrogen atoms are omitted for clarity.

of the degree of the trigonality, within the structural continuum between trigonal bipyramidal and rectangular pyramidal. For a perfectly tetragonal geometry τ is equal to zero, while it becomes unity for perfectly trigonal bipyramidal geometry". Application of this parameter to our compound **2**, gives a value of 0.78, which indicates that the arrangement of polyhedron is clearly nearest form trigonal bipyramidal than tetragonal.

If we compare the angles I–Hg–I of red (103°, 107°, and 112°) and yellow HgI$_2$ (173° and 174°) with the angle in **2** [167.71(3)°] we can argue that in this case the complex is closest of the β-HgI$_2$ than the α-form. This argumentation can be reinforced by the comparison of the distance of these two iodides in the complex and the two iodides forming the angle of 174.43° are distant of the mercury by 2.4 Å and 2.7 Å. Moreover, if we look the β-form, the mercury is hexacoordinate but the four other bonds are 3.1 Å and 3.2 Å. All these clues point in the same direction, in this complex, HgI$_2$ is more yellow-HgI$_2$ than red-HgI$_2$.

In the literature, we can find examples of other mercury(II) halides coordinated with polyethers, particularly with crown ether ligands, such as [HgI$_2$C$_{12}$H$_{24}$O$_6$],[31] and [(HgCl$_2$)$_2$(C$_{24}$H$_{32}$O$_8$)].[23] In the latter crown ether compound, two mercury atoms are pentacoordinate, and two oxygen atoms of the crown ether ligand are not used for the coordination. In 1993, *Rogers* published the structure of diiodo-tetraethylene-glycol-mercury(II)[32] and in this compound the mercury is also pentacoordinate, with two iodide and three oxygen atoms. In a previous paper on "polyether adducts of *d*-block metal compounds as starting materials for new cluster compounds",[26] we have already observed this extremely distorted trigonal bipyramidal conformation of mercury(II) iodide upon coordination of an open polyether to HgI$_2$, namely in the structure of diiodo-(diethylene glycol dimethyl ether)-mercury(II) (= [HgI$_2$(diglyme)]). The distances Hg–I are identical in the two

structures, around 2.6 Å, and the distances Hg–O2 are very similar as well (2.707(6) Å in **2** and 2.73(1) Å in [HgI$_2$(diglyme)]). For Hg–O1 and Hg–O3 the distances are different with 2.935(7) Å and 2.902(7) Å for O1 and O3 in **2** and much shorter with 2.69(2) Å and 2.73(1) Å in [HgI$_2$(diglyme)]. This difference is due to the limitation of freedom, the strain, associated to the crown ether molecule. This difference in the number of degrees of freedom on the ligand has an impact on the angles, I1–Hg1–I2 is 167.71(3)° for **2** and 160.95(5)° for [HgI$_2$(diglyme)] and O1–Hg1–O2 and O2–Hg1–O3 are 58.7(2)° and 63.2(2)° for **2** and 62.0(4)° and 61.9(4)° in [HgI$_2$(diglyme)]. Concerning the torsion angles in the ligand, the conformation of the ligand in **2** does not correspond at all to α-**1**, but they are close to β-**1** with 70° for O1–O2–O3–O4 and 76° for O5–O6–O7–O8. Contrary to compound **2**, complex [(HgCl$_2$)$_2$(DB24C8)] are closest to α-**1** with a torsion angle of 10°. For these two complexes the mercury was tricoordinate by oxygen atoms of the crown but with mercury cyanide, the metal ion is hexacoordinate by oxygen atoms of the crown. In this case with torsion angles of 116° and 139°, the ligand does not correspond at all to α-**1** or to β-**1**.

In conclusion, we have crystallized a polymorph of dibenzo-24-crown-8 and we have identified, which type of polymorphism is involved in this case. We have also highlighted a new complex of mercury halides with dibenzo-24-crown-8. This new complex is the third example of mercury complex with dibenzo-24crown-8 and has a similar arrangement than complex obtained with diglyme.[26]

Experimental Section

Crystallization of β-1: Compound **1** (0.7 g, 1.56 mmol) was dried for 3 h under vacuum at 100 °C and dissolved in dried THF (30 mL). The solution was heated to reflux under magnetic stirring during 20 min. Afterwards, dried heptane (15 mL) was added and the solution was left at 4 °C. Colorless needles of β-**1** suitable for X-ray analysis grow within one week. DSC: m.p.: 104 °C, phase transition: 83 °C (α to β), f.p.: 73 °C.

Synthesis of 2: Compound **1** (0.7 g, 1.56 mmol) was dried for 3 h under vacuum at 100 °C and dissolved in dried THF (30 mL), the solution was heated to reflux under magnetic stirring during 20 min. This solution was added to HgI$_2$ (1.36 g, 3 mmol), which was previously dried under vacuum at 300 °C. Afterwards, dried heptane (15 mL) was added and the solution was left at 4 °C. Colorless needles of **2** suitable for X-ray analysis grow within one week. **¹H NMR** ([D$_8$]THF, 360 MHz): δ = 3.72 (s, 8H), 3.81 (t, 8H, 4 Hz, 5 Hz), 4.08 (t, 8H, 5 Hz, 4 Hz), 6.82–6.87 (m, 8H). **MS** (THF/MeOH): found 777.08588 m/z, calculated ([M – I]$^+$ 777.08468 m/z.

Single Crystal X-ray Structure Determination: Crystals were mounted on loops and all geometric and intensity data were taken from this crystal. Data collection took place using Mo-K_α radiation (λ = 0.71073 Å). The measurement of β-**1** was performed at 150 K with a Bruker AXS Apex2 diffractometer, while **2** was measured at 150 K with a STOE IPDS-II diffractometer. Both diffractometers are equipped with an Oxford Cryosystem open flow cryostat.[33] Absorption correction was partially integrated in the data reduction procedure.[34] The structures were solved by SIR2004 and refined using full-matrix least-squares on F^2 with the SHELX-97 package.[35,36] All heavy atoms could be refined anisotropically. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions.

Crystal Data for β-1: $C_{24}H_{32}O_8$, M = 224.25 g·mol^{-1}, monoclinic, $P2_1/c$ (Nr. 14), a = 4.5946(2); b = 13.2530(5); c = 17.5017(7) Å, V = 1065.71(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.398 g·cm^{-3}, $F(000)$ = 480, T = 150 K, λ = 0.71073 Å, μ(Mo-K_α) = 0.120 mm^{-1}, 1° < θ < 25°, 8063 reflections of which 905 unique and 743 observed, 145 parameters refined, GOOF (on F^2) = 1.043, $R_1 = \Sigma|F_o–F_c|/\Sigma F_o$ = 0.0370, wR_2 = 0.1075 for I > 2$\sigma(I)$ and R_1 = 0.0706, wR_2 = 0.1586 for all data.

Crystal Data for 2: $C_{24}H_{32}HgI_4O_8$, M = 902.89 g·mol^{-1}, orthorhombic, $Pbca$ (Nr. 61), a = 8.6542(3); b = 23.2287(12); c = 28.1070(12) Å, V = 5650.2(4) Å^3, Z = 8, $\rho_{calcd.}$ = 2.123 g·cm^{-3}, $F(000)$ = 3408, T = 150 K, λ = 0.71073 Å, μ(Mo-K_α) = 0.120 mm^{-1}, 1.8° < θ < 29.2°, 7630 reflections of which 7630 unique and 2578 observed, 317 parameters refined, GOOF (on F^2) = 0.531, $R_1 = \Sigma|F_o–F_c|/\Sigma F_o$ = 0.038, wR_2 = 0.162 for I > 2$\sigma(I)$ and R_1 = 0.060, wR_2 = 0.086 for all data.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depository numbers CCDC-795955 (β-**1**) and CCDC-795956 (**2**). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Supporting Information (see footnote on the first page of this article): Pictures of compounds described in the communication and comparative table.

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