Wrap-around Encapsulated Cs(dibenzo-24-crown-8)+ Cations form Linear Coordination Polymers with Dicyanoargentate Anions Ag(CN)₂⁻

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Dibenzo-24-crown-8, Caesium Macrocyclic Complexes, Dicyanoargentate, X-Ray Data, One-dimensional Polymer

The new macrocyclic dicyanoargentate complex Cs(dibenzo-24-crown-8)[Ag(CN)₂] has been prepared and studied by means of X-ray diffraction (monoclinic, space group P2₁/a, with a = 12.730(3), b = 15.443(3), c = 15.323(3) Å, V = 3005(1) Å³, Z = 4, R₁ = 0.041; wR2 = 0.048 for 5488 unique reflections with I > 3σ(I)). The lattice consists of complex Cs(db-24-crown-8)+ cations (as an example of the “wrap-around” structure) and [Ag(CN)₂]- anions forming a one-dimensional polymeric structure. The caesium atoms are coordinated with 8 oxygen atoms of the macrocycle and two nitrogen atoms of the dicyanoargentate groups, bonding to the cation on both sides of the crown-ether. It is the first structure of a dibenzo-24-crown-8 complex with a large metal cation such as Cs⁺.

Introduction

The important biological role of the alkali and alkaline earth cations attracts considerable attention aiming at an understanding of the factors influencing their behavior towards neutral molecules [1-5] such as macrocyclic polyethers (crown ethers) [6]. X-ray investigations of the crown ether complexes demonstrate a remarkable variety of structures: half-sandwiches M(L)⁺⁺, sandwiches M(L)₂⁺⁺ [2, 4], multidecker sandwiches M₂(L)₂⁺⁺ [7], and “wrap-around” encapsulates M(L)⁺⁺ [2].

The relation between the metal cations and the crown ligands may be controlled through a variation of the counter anion.

Molecular recognition and supramolecular chemistry in the solid state (“crystal engineering”) are useful concepts for the design of crown ether coordination compounds [2, 8, 9]. We have shown that singly charged centrosymmetric anion (X⁻) in the compound of composition M(18-crown-6)X (X⁻ = AuCl₄⁻, HL⁻, where L⁻ = benzoylcyanoximate, benzothiazolylcyanoximate anion) may constrain the macrocyclic M(18-crown-6)⁺⁺ moiety to be centrosymmetric in the crystal even in complexes with large Rb⁺ [10, 11], TI⁺ [8] and non-centrosymmetric NH₃⁺ [12] cations (Type I). However, in the crystal structure of Cs(18-crown-6)Ag(CN)₂ (with singly charged and potentially centrosymmetric dicyanoargentate anion) a zig-zag polymeric chain (Type II) was found [13]. Evidently, the Cs(18-crown-6)⁺⁺ moieties have an usual half-sandwich structure because the radius of Cs⁺ (1.67 Å [5]) is larger than that of Rb⁺ (1.52 Å [5]). It may be predicted that in a caesium complex with a crown ligand possessing a larger cavity size than 18-crown-6, the spatial arrangement may be a linear coordination polymer (Type I) in which the metal atom is situated in the center of the crown ether cavity.
Herein, we report the synthesis and X-ray structure analysis of a caesium dicyanoargentate(I) complex with dibenzo-24-crown-8 (db-24-crown-8).

**Experimental**

**Preparation of the compound**

All chemicals were commercial products of reagent grade, used without further purification. All experiments were carried out in air. The caesium complex with dibenzo-24-crown-8 was synthesized in the same fashion as the 18-crown-6 analog [13] according to the scheme:

\[
\text{MI} + 2 \text{AgCN} \rightarrow \text{MAg(CN)_2} + \text{AgI} \quad (1)
\]
\[
\text{MAg(CN)_2} + \text{db24-crown-8} \rightarrow \text{M(db24-crown-8)Ag(CN)_2} \quad (2)
\]

Single crystals of the final product were obtained from a DMF solution.

To a hot (50 - 60 °C) solution of 0.7 g (2.38 mmol) of CsAg(CN)\(_2\) in 10 ml of DMF 1.07 g (2.38 mmol) of db-24-crown-8 was added. The mixture was stirred for 3 h. Colorless prismatic crystals of Cs(db-24-crown-8)-{Ag(CN)\(_2\)} were obtained at room temperature. Yield 1.2 g (68%).

Analysis for Cs(db-24-crown-8){Ag(CN)\(_2\)}:

\[
\text{CsAgC}_{26n}n_2n_2n_8 (741.32)
\]

Calcd C 42.75 H 4.48 N 4.47 Ag 15.20%,

Found C 42.12 H 4.35 N 3.87 Ag 14.55%.

**Crystal structure determination**

All X-ray diffraction measurements were performed at 296 K on a Rigaku AFC6S four-circle diffractometer using graphite monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). A colorless prismatic crystal of the dimensions 0.3 x 0.06 x 0.25 mm\(^3\) was used. Unit cell parameters were obtained from least-squares analysis of the setting angles of 23 high angle reflections (15 < \(2\theta\) < 18°) in which the appropriate monoclinic cell angles were constrained to 90°. A total of 5748 reflections were collected within the range 1.8 < \(2\theta\) < 25°, of which 5488 were unique (\(\text{R_{int}} = 0.040\)).

The structure was solved by direct methods and using MITHIRL and DIRDIF [14, 15] and refined by full-matrix least squares techniques with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed using the TEXAN crystallographic software package of Molecular Structure Corporation [16].

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**Table I. Crystallographic data for Cs(db-24-crown-8)-{Ag(CN)\(_2\)}**

<table>
<thead>
<tr>
<th>Formula</th>
<th>C(<em>2)nH(</em>{3n})nAgCsN(_n)O(_n)X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>741.32</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/n)</td>
</tr>
<tr>
<td>(a) [Å]</td>
<td>12.730(3)</td>
</tr>
<tr>
<td>(b) [Å]</td>
<td>15.443(3)</td>
</tr>
<tr>
<td>(c) [Å]</td>
<td>15.324(3)</td>
</tr>
<tr>
<td>(\beta) [°]</td>
<td>93.93(2)</td>
</tr>
<tr>
<td>(U) [Å(^3)]</td>
<td>3005(1)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(D_{calc}) [g cm(^{-3})]</td>
<td>1.638</td>
</tr>
<tr>
<td>(\mu) (Mo-K(_\alpha)) [cm(^{-1})]</td>
<td>18.93</td>
</tr>
<tr>
<td>F(000)</td>
<td>1472</td>
</tr>
</tbody>
</table>

**Data collection:**

\(2\theta_{max}\) [°] | 49.9 |

Index ranges | 0 < \(h\) < 15, 0 < \(k\) < 18, -18 < \(l\) < 18 |

Reflections collected | 5748 |

Unique data | 5488 |

\(R_{int}\) | 0.040 |

**Structure refinement:**

Data used \([I > 3\sigma(I)]\) | 2786 |

Parameters refined | 343 |

Data to parameters ratio | 8.12 |

\(R1\) | 0.041 |

\(R_w\) | 0.048 |

GOF on \(F^2\) | 2.56 |

Largest peak and hole in final difference map \([e \text{ Å}^{-3}]\) | 0.39 and -1.02 |

\(\text{Ag(CN)}_2\) complexes were obtained at room temperature. Yield 1.2 g (68%).

Analysis for Cs(db-24-crown-8){Ag(CN)\(_2\)}:

CsAgC\(_{26n}n_2n_8\) (741.32)

Calcd C 42.75 H 4.48 N 4.47 Ag 15.20%

Found C 42.12 H 4.35 N 3.87 Ag 14.55%

| Cs-O(1) | 3.376(6) O(1)-C(9) | 1.41(1) |
| Cs-O(2) | 3.239(6) C(1)-N(1) | 1.06(1) |
| Cs-O(3) | 3.347(7) C(2)-N(2) | 1.10(1) |
| Cs-O(4) | 3.275(7) C(3)-C(4) | 1.37(2) |
| Cs-N(1) | 3.437(9) C(9)-C(10) | 1.48(1) |
| Cs-N(2a) | 3.24(1) C(9)-C(10) | 1.49(2) |
| Ag-C(1) | 2.05(1) C(21)-C(22) | 1.49(1) |
| Ag-C(2) | 1.97(1) C(23)-C(24) | 1.49(1) |
| O(1)-Cs-O(2) | 51.5(2) O(1)-C(3)-C(4)-O(8) | -2(1) |
| O(1)-Cs-O(5) | 159.4(2) O(4)-C(15)-C(16)-O(5) | 2(1) |
| N(1)-Cs-O(1) | 118.4(2) C(3)-C(4)-O(8)-C(6) | 177.2(9) |
| N(1)-Cs-O(5) | 82.0(2) C(12)-O(3)-C(13)-C(14) | 179.6(9) |
| N(1)-Cs-N(2) | 160.7(3) O(1)-C(9)-C(10)-O(2) | -64(1) |
| C(1)-Ag-C(2) | 179.2(6) O(6)-C(23)-C(24)-O(7) | 58(1) |
| N(1)-C(1)-Ag | 178(1) O(7)-C(25)-C(26)-O(8) | 59(1) |
| Ag-C(2)-N(2) | 175(1) |
| Cs-N(1)-C(1) | 164(1) |
| C(2)-N(2)-Cs(a) | 176(1) |

\(a\) Symmetry transformations used to generate equivalent atoms: \(x + 1, y, z\).

Full crystallographic data have been deposited at the Cambridge Crystallographic Data Center and may be obtained by quoting the number CCDC 116707.
Results and Discussion

The structure of an isolated unit Cs(db-24-crown-8)Ag(CN)2 is shown in Fig. 1, while an extended view of the packing is provided in Fig. 2. The lattice consists of complex Cs(db-24-crown-8)+ cations bridged by AgCN2− anions between neighboring cations [(x, y, z) and x + 1, y, z] to produce a one-dimensional coordination polymer along the x direction (Fig. 2). There are no short intermolecular contacts between the neighboring chains in the crystal [17]. The closest distance between those is C(6)-C(6) (−x, −y, −z) - 3.517 Å.

The frame of the fragment Cs(db-24-crown-8)+ is an example of the “wrap-around” structure and is similar to the structure of the potassium complex with db-30-crown-10 [18].

Dicyanoargentate groups are bound to the metal center on both sides of the crown-ether to form infinite chains (Fig. 1). The caesium atom is coordinated to two nitrogen atoms of the Ag(CN)2− groups N1 and N2a (x + 1, y, z) (Cs-N 3.437(9), 3.24(1) Å, Table II), (Fig. 1). Besides those N atoms, the Cs atom coordinates with 7 oxygen atoms of the macrrocyclic ligand with Cs-O distances in the range 3.223(8) - 3.376(6) Å (Table II), which is typical for related macrocyclic compounds [2]. The Cs-N1 (3.437(9) Å) and Cs-O8 (3.503(7) Å, Table II) distances are longer than the sum of the ionic radii and may be characterized as weak ion-dipole interactions [3, 6]. The structure is a relatively compact arrangement for a high (10) coordination number of a caesium atom.

The Ag(CN)2− group forms effectively colinear bonds with the caesium atoms (angle Cs-N1-C1 (165(1)°) and Cs-N2a-C2a (x + 1, y, z) (176(2)°, Table II) similar to the arrangement in Cs(18-crown-6)Ag(CN)2 [13]. Geometric parameters of the dicyanoargentate ion are typical for such complexes [19]. In the crown ligand the average mean aliphatic C-C distance is 1.47 Å, in the benzene ring 1.38 Å, and the average C-O distance is 1.42 Å (Table II). These values are the same as those found in other polyether complexes of this type [20 - 23].

The torsional angles about the aliphatic C-C bonds are ca. 60° corresponding to the gauche conformation. The torsional angles C-C-O-C in most cases are close to 180° (Table II) and corre-
spond to those in other cyclic polyethers [20 - 23]. The benzene rings are both on the same side of the crown (cis-conformation), thus enhancing the bowl-shaped (“wrap-around”) nature of the ligand.

Previous crystallographic studies of the complexes of db-24-crown-8 have shown it to be an ideal molecule for complexing alkaline metals [23]. The structure of the title compound presents a one-dimensional polymer, in which fragments Cs(db-24-crown-8)+ are bound by the nearly linear singly-charged anions Ag(CN)2−. However, a coplanar arrangement of the oxygen atoms around the caesium ion is not attained because the cavity size of the db24-crown-6 is too large in comparison with the size of the caesium cation. It is the first structure of a dibenzo-24-crown-8 complex with a large metal cation such as Cs+.