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**[Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] and CdI<sub>2</sub>(18-crown-6) 2I<sub>2</sub>:  
Two Layered Iodine Networks with Crown-ether  
Coordinated Pb<sup>2+</sup> and Cd<sup>2+</sup>**

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**[Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] and CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub>:  
Two Layered Iodine Networks with Crown-ether  
Coordinated Pb<sup>2+</sup> and Cd<sup>2+</sup>**

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Keywords:	metal iodide, crystal structure, ionic liquid, iodine, synthesis



1 **[Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] and CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub>: Two Layered Iodine**  
2 **Networks with Crown-ether Coordinated Pb<sup>2+</sup> and Cd<sup>2+</sup>**  
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6 *Dedicated to Professor Bernd Harbrecht on the occasion of his 60<sup>th</sup> birthday*  
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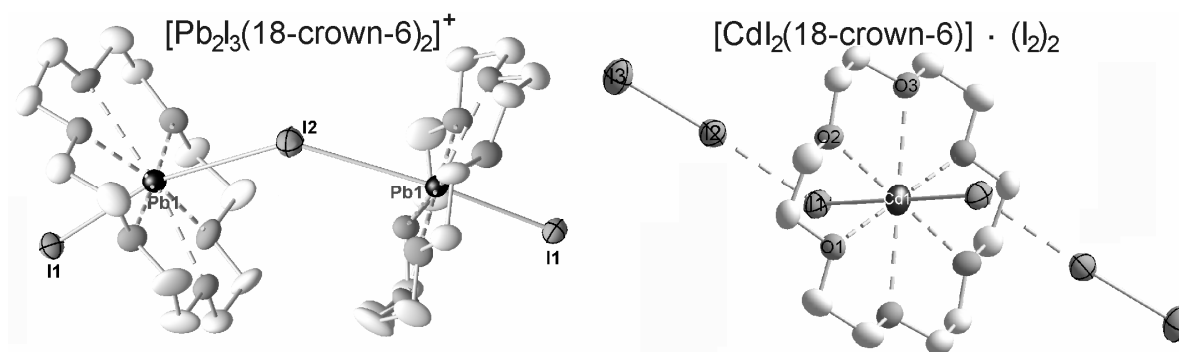
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27 **Abstract.** [Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] (**1**) and CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> (**2**) were prepared by reaction of  
28 PbI<sub>2</sub>, SnI<sub>4</sub> and 18-crown-6 as well as CdI<sub>2</sub>, I<sub>2</sub> and 18-crown-6. All reactions were performed in the ionic  
29 liquid [NMe(*n*-Bu)<sub>3</sub>][N(Tf)<sub>2</sub>], which serves as polar but aprotic liquid-phase providing a fast diffusion  
30 of the reactants at moderate temperatures (≤100 °C). **1** exhibits V-shaped [Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>]<sup>+</sup> cations  
31 and trigonal-bipyramidal [SnI<sub>5</sub>]<sup>-</sup> anions. In CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> (**2**), the building unit CdI<sub>2</sub>(18-crown-  
32 6) formally contains linear CdI<sub>2</sub> molecules that are interlinked by molecular iodine via long-ranging I-I  
33 contacts.  
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41 **Keywords:** Iodometallate; Crown-ether complex; ionic liquid; lead iodide; cadmium iodide.  
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2 **Table of content text:**  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  with a V-shaped  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$  cation and  
3  
4  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$ , formally containing a linear  $\text{CdI}_2$  molecule.  
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## Introduction

In comparison to standard solvents used in inorganic synthesis – ranging from liquid ammonia, water, alcohols to molten alkali metal halogenides – up-coming ionic liquids (IL's) exhibit a very unusual portfolio of properties [1]. Namely, this is a wide liquid range (–50 to +400 °C), an excellent thermal stability (up to 400 °C), a wide electrochemical window (–4 eV to +4 eV) and a low vapor pressure. Since the composition nowadays can be selected from more than 100 different cations and anions, the physical and chemical properties of IL's (e.g. polarity, miscibility with other solvents, solubility of salts) can be adjusted and fine-tuned to an extent, which can be hardly realized based on standard solvents [2,3]. Comparably high costs and a dramatical drop in quality and properties when impurified with even low traces of water or impurities – e.g. stemming from the synthesis or thermal decomposition of the IL – can be regarded as major current drawbacks.

Due to there exceptional features, IL's have attracted considerable interest in recent years and especially have gained significant impact on organic synthesis [4] as well as on the synthesis of functional nanomaterials [5,6]. On the contrary, exploration towards a beneficial use of IL's in inorganic synthesis has just begun and already lead to promising results, for instance, fascinating germanium clathrates [7] or the chemistry of non-coordinating anions [8]. As part of our studies, IL's are used as polar, but aprotic liquids that guarantee a sufficient diffusion at comparably low temperatures (<100 °C) [9]. In the following we aim at the synthesis of novel iodometallates in ionic liquids. Our focus is especially on halogen-rich compounds and novel structural building units [10,11]. In general, iodometallates have already gained interest due to complex supramolecular networks and unexpected semiconductor-type properties [12–15]. With  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  and  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  in the following a first compound in the system Pb(II)–Sn(IV)–I as well as a compound that formally contains  $\text{I}_2$ -interlinked  $\text{CdI}_2$  molecules are presented.

## Experimental Section

All experimental and analytical studies were performed under argon or vacuum (i.e. glove-boxes or Schlenk techniques). The commercially available starting materials ( $\text{SnI}_4$ :  $\geq 99.999\%$ , Sigma-Aldrich;  $\text{PbI}_2$ :  $\geq 99.999\%$ , Sigma-Aldrich;  $\text{CdI}_2$ :  $\geq 99.999\%$ , Sigma-Aldrich; 18-crown-6:  $\geq 99\%$ , Acros) were used subsequent to overnight drying in vacuum. Iodine ( $\geq 99.5\%$ , Sigma-Aldrich) was purified by double sublimation. The ionic liquid (IL),  $[\text{NMe}(n\text{-Bu})_3][\text{N}(\text{Tf})_2]$  ( $\text{Tf} = \text{SO}_2\text{CF}_3$ ), was synthesized as described elsewhere [16].

*Synthesis of  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  (I):* 135.9 mg ( $2.17 \cdot 10^{-4}$  mol) of  $\text{SnI}_4$ , 200 mg ( $4.34 \cdot 10^{-4}$  mol) of  $\text{PbI}_2$  and 104.8 mg ( $4.34 \cdot 10^{-4}$  mol) of 18-crown-6 were added to 1 mL of  $[\text{NMe}(n\text{-Bu})_3][\text{N}(\text{Tf})_2]$  at 100 °C. Dark-red, plate-shaped, moisture-sensitive crystals were obtained after cooling

1 to room temperature with at 5 °C/h. These crystals were separated from the IL by filtration through a  
2 glass filter and by washing three times with 4 mL of dried tetrahydrofuran. Finally, the crystals were  
3 dried in vacuum and obtained with a yield of about 90 %.

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5 *Synthesis of  $CdI_2(18\text{-crown-6}) \cdot 2I_2$  (2):* 100 mg ( $2.73 \cdot 10^{-4}$  mol) of  $CdI_2$ , 72.2 mg ( $2.73 \cdot 10^{-4}$  mol) of  
6 18-crown-6 and 69.3 mg ( $2.73 \cdot 10^{-4}$  mol) of  $I_2$  were added to 1 mL of  $[NMe(n\text{-Bu})_3][N(Tf)_2]$  at 80 °C. **2**  
7 crystallized as dark-red cubes within 14 days. The crystals were separated from the IL by filtration  
8 through a glass filter and by washing several times with 5 mL of dried diethyl ether. Finally,  $CdI_2(I_2)_2 \cdot$   
9 (18-crown-6) was dried in vacuum and obtained with a yield of about 50 %. Surprisingly, the crystals  
10 turned out to be stable in air.

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12 *Data collection and refinement:* Single crystal X-ray diffraction analysis was carried out with an IPDS II  
13 diffractometer (STOE, Darmstadt) using Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ , graphite monochromator). A  
14 suited crystal was selected for both title compounds directly from the mother liquor and fixed onto a  
15 glass filament begird in perfluorated oil (Kel-F). Data collection was performed at 200 K. Subsequent to  
16 data reduction via X-RED [17], space group determination was carried out on the basis of the reflection  
17 conditions via XPREP. Structure solution and refinement were performed with SHELXTL [18]. The  
18 results are listed in Table 1. All non-hydrogen atoms were refined with anisotropic parameters of  
19 displacement. The position of hydrogen could not be fixed via Fourier refinement and was therefore  
20 modeled based on idealized C–H bonds. X-SHAPE was used to apply a numerical absorption correction  
21 based on crystal-shape optimization for the data of compound (1) [19]. Illustrations of the crystal  
22 structures were prepared via DIAMOND [20]. More details concerning the crystallographic data can be  
23 requested from the Cambridge Crystallographic Data Center [deposit@ccdc.cam.ac.uk] with the  
24 deposition numbers CCDC ?????? and ??????.

25  
26 *Powder diffraction pattern* were obtained with a STADI-P diffractometer (Stoe, Darmstadt) using  
27 germanium monochromatized Cu- $K_{\alpha 1}$  radiation. The samples were filled in a glass capillary and  
28 measured at ambient temperature. Powder diffraction pattern (not pictured) were used to confirm the  
29 setting of the unit cells as well as the purity of the title compounds.

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31 *Energy-dispersive X-ray analysis (EDX):* EDX was carried out using an AMETEC EDAX mounted on a  
32 Zeiss SEM Supra 35 VP scanning electron microscope. Crystals of  $[Pb_2I_3(18\text{-crown-6})_2][SnI_5]$  were  
33 fixed on conductive carbon pads on aluminum sample holders. In contrast  $[Sn_2I_3(18\text{-crown-6})_2][SnI_5]$   
34 [11] the presence of lead was clearly visible in the title compound **1**.

## Results and Discussion

### $[Pb_2I_3(18\text{-crown-}6)_2][SnI_5]$ (**1**)

By reaction of  $PbI_2$ ,  $SnI_4$  and 18-crown-6 in the ionic liquid  $[NMe(n\text{-}Bu)_3][N(Tf)_2]$ , moisture-sensitive dark-red crystals with the composition  $[Pb_2I_3(18\text{-crown-}6)_2][SnI_5]$  were obtained. According to X-ray structure analysis based on single crystals, the title compound crystallizes monoclinically with space group  $P2/n$  (Table 1). The unit cell displays  $[SnI_5]^-$  anions and  $[Pb_2I_3(18\text{-crown-}6)_2]^+$ -cations as the constituents of **1** (Figure 1).

The  $[SnI_5]^-$  anion exhibits only a slight deviation from a trigonal-bipyramidal symmetry (Figure 1). This view is confirmed by angles  $I_{eq}\text{-Sn-}I_{eq}$  of  $120\pm 2^\circ$ , and  $I_{ax}\text{-Sn-}I_{eq}$  of  $90\pm 1^\circ$ . The Sn–I bond lengths with 271.7 to 285.4 pm are close to those of  $SnI_4$  (263 pm), but differ significantly from  $SnI_2$  (300–325 pm) [21,22]. Taking the widened coordination from 4 ( $SnI_4$ ) to 5 ( $SnI_5^-$ ) into account, the bond lengths clearly point to the presence of  $Sn^{4+}$ . Such a trigonal-bipyramidal coordination, in general, is much less common for iodostannates(IV) than the well-known octahedral coordination, most often leading to merged building units [23]. Beside  $[SnI_5]^-$ , which has been first observed in the mixed-valent iodostannate  $[Sn(II)I_3(18\text{-crown-}6)_2][Sn(IV)I_5]$  [11], only  $[SnI_6]^{2-}$  has been described as an isolated building unit so far [24].

The novel **dinuclear** cation  $[Pb_2I_3(18\text{-crown-}6)_2]^+$  consists of two symmetry equivalent crown-ether molecules, each of them entrapping  $Pb^{2+}$ . Similar to  $[Sn_2I_3(18\text{-crown-}6)]^+$  [11], each lead cation is coordinated not only by 18-crown-6, but also to a terminal iodine atom as well as to a joint bridging iodide (Figure 2). This connectivity results in a V-shaped  $[Pb_2I_3(18\text{-crown-}6)]^+$  building unit that exhibits angles of  $164.2^\circ$  (I–Pb–I) and  $142.8^\circ$  (Pb–I–Pb). Noteworthy, the terminal iodide with 292.7 pm shows a significantly shorter Pb–I distance than the bridging I<sup>−</sup> (350.4 pm) (Table 2). Consequently, the bonding situation can be also described as two  $[PbI(18\text{-crown-}6)]^+$  units linked by a single iodide anion. A cation  $[PbI(18\text{-crown-}6)]^+$  is known from  $Pb(18\text{-crown-}6)I_2$  **I**<sub>2</sub> [36] and exhibits a similar Pb<sup>2+</sup>–I distance (290 pm) as observed here (293 pm).  $Pb^{2+}$  is positioned exactly inside the plane of the crown ether molecule, but slightly deflected from its center (Figure 3). This finding results in a shortened (266.8(1) pm), a lengthened (285.1(1) pm) and four largely equivalent (270.9(1)–274.5(1) pm) Pb–O distances. All relevant Pb–O and Pb–I distances are summarized and compared to literature data in Table 2. In comparison to  $[Sn_2I_3(18\text{-crown-}6)]^+$ ,  $Pb^{2+}$  is less deflected from the center of the crown ether than  $Sn^{2+}$ . This finding is in accordance with the increased radius as well as with a less pronounced lone-pair effect [25,26]. All C–O and C–C bond lengths of 18-crown-6 match with literature data [27]. Although a description of **1** based on ionic constituents  $[Pb_2I_3(18\text{-crown-}6)_2]^+$  and  $[SnI_5]^-$  is reasonable, long-ranging I–I interactions can not be disregarded (Figure 4). Attractive bonding with distances below the doubled van-der-Waals radius of iodine (i.e. 420 pm, [28]) are observed between I1 and I3 (402.1

pm) as well as between I2 and I4 (406.4 pm). Only I5 remains without any significant I–I contact. In sum, long-ranging I–I contacts interconnect  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$  and  $[\text{SnI}_5]^-$  to infinite helices along [001] and [100] to form a two-dimensional iodometallate network. Finally it should be mentioned that  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  first contains  $\text{Pb}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\Gamma^-$  in combination. In general, the system Pb–Sn–I is with limited examples namely  $[(\text{NH}_3\text{CH}_3)\text{Pb}(\text{II})_{0.17}\text{Sn}(\text{II})_{0.83}]_3\text{I}_3$  and  $\text{PbSnI}_4$  [29,30].

### *CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> (2)*

$\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  was prepared by reaction of one equivalent of  $\text{CdI}_2$  and 18-crown-6 with two equivalents of  $\text{I}_2$  in the ionic liquid  $[\text{NMe}(n\text{-Bu})_3][\text{N}(\text{Tf})_2]$ . Dark reddish, cube-shaped and air-stable single crystals were crystallized within two weeks. According to X-ray structure analysis based on single crystals, **2** crystallizes monoclinically with space group *C2/c* (Table 1). The unit cell displays  $\text{CdI}_2(18\text{-crown-6})$  units as well as molecular iodine (Figure 5).

$\text{Cd}^{2+}$  is positioned almost centrally inside the crown ether with Cd–O distances ranging from 265.7(1) to 280.8(1) pm. All C–O and C–C distances match with the expectation [27]. In addition to 18-crown-6, cadmium is further coordinated by two iodine atoms, which are themselves in contact to two  $\text{I}_2$  molecules (Figure 6). Here, the question arises whether the observed structural building unit is indeed related to a molecular situation such as  $[\text{Cd}(18\text{-crown-6})\text{I}_2] \cdot 2\text{I}_2$  or whether a description  $[\text{Cd}(18\text{-crown-6})]^{2+}[\text{I}_3^-]_2$  with the well-known triiodide  $\text{I}_3^-$  is more appropriate. According to the bond lengths (Figure 6), I2–I3 (273.3(1) pm) corresponds very well to solid  $\text{I}_2$  (I–I: 272 pm, [31]), whereas I1–I2 (321.9(1) pm) is considerably elongated. With regard to the angles, I1–Cd–I1 (180 °) turned out to be exactly linear, whereas I1–I2–I3 (172.9(1) °) clearly deviates from linearity. Altogether, these findings are in contrast to what was reported for various crystal structures addressing  $\text{I}_3^-$  as a polyiodide anion. The latter in fact possesses an almost linear geometry and I–I bond lengths ranging from 285 to 295 pm [28]. The above argumentation is also consistent with the related compound  $\text{CdI}_2(\text{benzo-18-crown-6}) \cdot \text{I}_2$  [32]. Herein, the  $\text{CdI}_2(\text{benzo-18-crown-6})$  building unit is in contact to  $\text{I}_2$ , too. Bond lengths (I1–I2: 314.8 pm, I2–I3: 275.3 pm) and angles (I1–I2–I3: 170.9 °) are very similar to the title compound **2**. Compared to  $\text{CdI}_2(\text{benzo-18-crown-6}) \cdot \text{I}_2$ , however, two significant differences are evident for  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  (**2**): First, the I–Cd–I angle in **2** matches exactly 180 ° due to inversion symmetry at the  $\text{Cd}^{2+}$  site whereas  $\text{CdI}_2(\text{benzo-18-crown-6}) \cdot \text{I}_2$  shows an angulated conformation (I1–Cd–I1: 167.0 °). Second, the  $\text{CdI}_2$  molecule in **2** is connected to two  $\text{I}_2$  molecules, in contrast to only a single  $\text{I}_2$  molecule in  $\text{CdI}_2(\text{benzo-18-crown-6}) \cdot \text{I}_2$ . The latter can be most probably ascribed to the volume and steric demand of benzo-18-crown-6, which obviously prevents addition of a second iodine molecule.

Surprisingly, the Cd–I1 distance in  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  with 269.3(1) pm is significantly shorter as compared to bulk- $\text{CdI}_2$  (Cd–I: 299 pm, [33]). In contrast, the observed value matches very well with



1 what is discussed for CdI<sub>2</sub> molecules in the gas phase (260 pm, [34,35]). Taking both aspects – the I–I  
2 as well as the Cd–I distances – into account, the structural building unit CdI<sub>2</sub>(18-crown-6) in sum can be  
3 described as a linear CdI<sub>2</sub> molecule with Cd<sup>2+</sup> additionally coordinated by the crown ether and each  
4 iodide atom weakly bound to I<sub>2</sub> molecules. CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> altogether exhibits the highest iodine  
5 content of all cadmium compounds known by now.  
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8  
9 Taking all long-ranging I–I contacts with distances below the doubled van-der-Waals radius (420 pm,  
10 [28]) into account, additional attractive interactions (I<sub>2</sub>–I<sub>3</sub> with 399.5(1) pm) become obvious (Figure  
11 6). Accordingly, CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> forms an infinite two-dimensional network via I<sub>2</sub> molecules.  
12 Formally, this network is constituted of distorted Cd<sub>2</sub>I<sub>14</sub>-rings that form zigzagged layers along [110]  
13 (Figure 7). Even though no hexagonal close-packing of iodide is observed here, the structure is  
14 **nevertheless related** to the CdI<sub>2</sub>-type of structure. Based on a 2x2 super cell, CdI<sub>2</sub> as well as **2** show  
15 stacked “I–Cd–I–I–Cd–I” layers, in general. However, the stacking sequence  
16 I(A)–Cd(1)–I(B)–I(A)–Cd(2)–I(B) in CdI<sub>2</sub> is different from I(A)–Cd(1)–I(A)–I(B)–Cd(2)–I(B) in **2**.  
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19 In summary, two novel layered iodide networks have been gained with [Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] and  
20 CdI<sub>2</sub>(18-crown-6) · 2I<sub>2</sub> via ionic liquid based reaction. Although we can naturally not exclude other  
21 preparative methods as access to the title compounds, a sufficient diffusion and reactivity of the starting  
22 materials in the IL at moderate temperature (<100 °C) is obvious. Concretely, thermal decomposition of  
23 metal iodides, temperature-driven loss of iodine as well as undesired redox processes due to elemental  
24 iodine and metal iodides can be avoided.  
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### 34 Acknowledgments

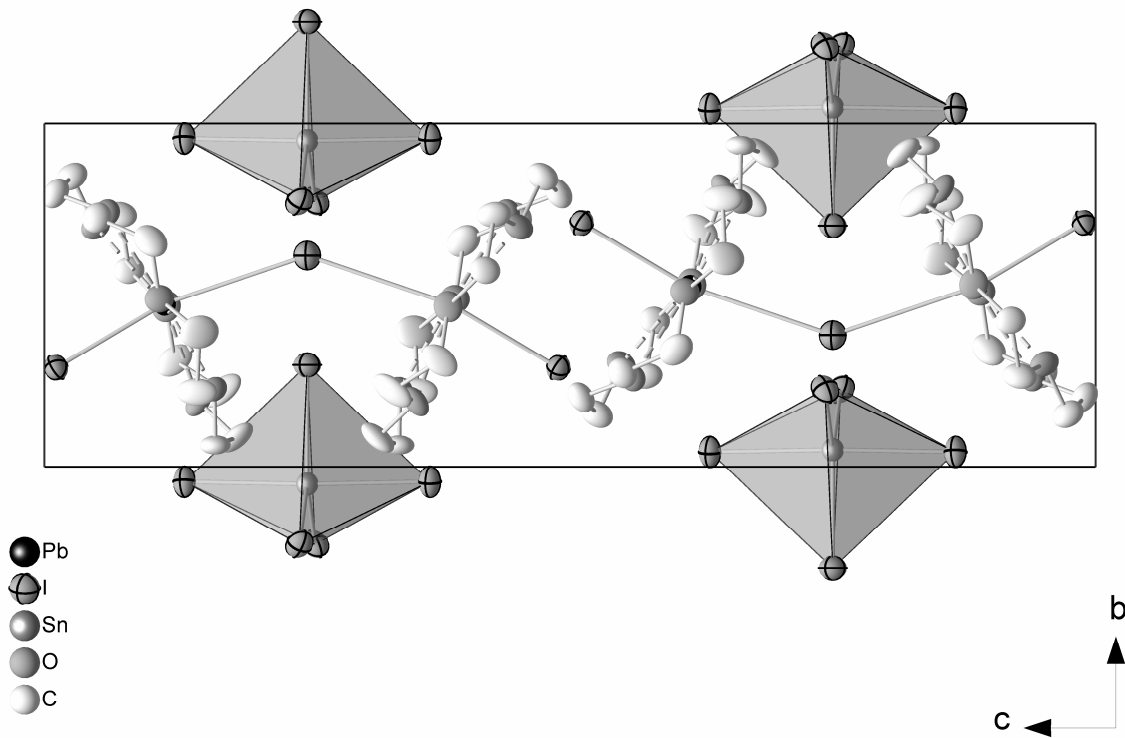
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**Table 1.** Crystallographic data of the title compounds.

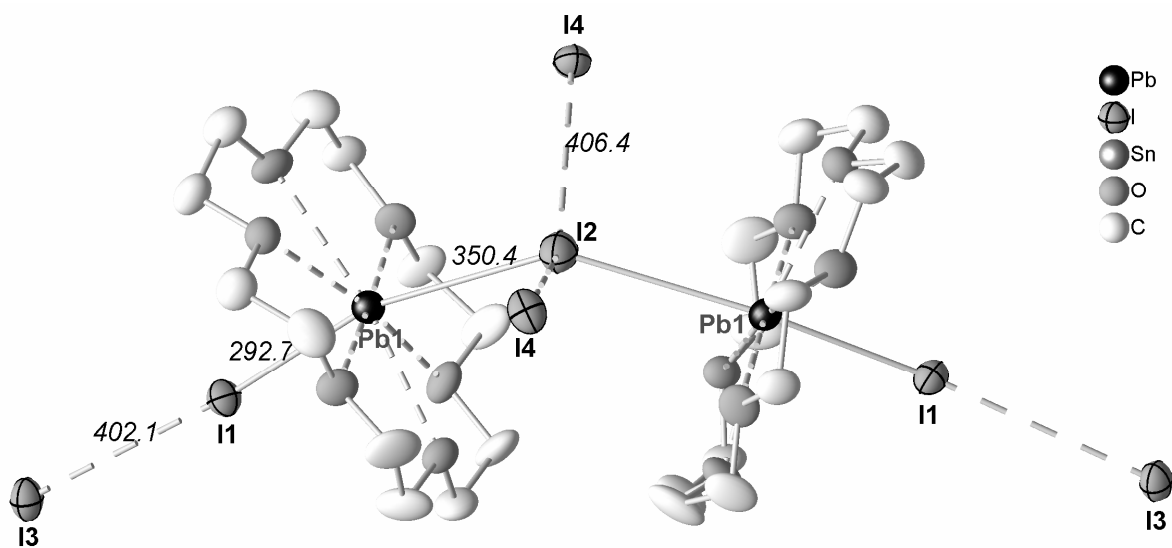
	[Pb <sub>2</sub> I <sub>3</sub> (18-crown-6) <sub>2</sub> ][SnI <sub>5</sub> ] (1)	CdI <sub>2</sub> (18-crown-6) · 2I <sub>2</sub> (2)
Formula	C <sub>24</sub> H <sub>48</sub> O <sub>12</sub> Pb <sub>2</sub> SnI <sub>8</sub>	C <sub>12</sub> H <sub>24</sub> O <sub>6</sub> CdI <sub>6</sub>
crystal system / space group	monoclinic / P2/n (no. 13)	monoclinic / C2/c (no. 15)
cell parameters	$a = 12.375(3) \text{ \AA}$ $b = 7.866(2) \text{ \AA}$ $c = 24.395(5) \text{ \AA}$ $\beta = 91.99(3)^\circ$ $V = 2373.2(9) \text{ \AA}^3$	$a = 12.591(3) \text{ \AA}$ $b = 10.137(2) \text{ \AA}$ $c = 20.637(4) \text{ \AA}$ $\beta = 95.47(3)^\circ$ $V = 2621.9(9) \text{ \AA}^3$
formula units per cell	$Z = 2$	$Z = 4$
calculated density	$\rho_{calc} = 2.91 \text{ g cm}^{-3}$	$\rho_{calc} = 2.88 \text{ g cm}^{-3}$
temperature	$T = 200 \text{ K}$	$T = 200 \text{ K}$
measurement device	imaging plate diffraction system (IPDS II, STOE)	imaging plate diffraction system (IPDS II, STOE)
radiation	graphite-monochromated Mo K $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )	graphite-monochromated Mo-K $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
measurement limits	$3.3^\circ \leq 2\theta \leq 58.6^\circ$ $-16 \leq h \leq 16, -10 \leq k \leq 10, -31 \leq l \leq 33$	$4.0^\circ \leq 2\theta \leq 58.4^\circ$ $-17 \leq h \leq 17, -13 \leq k \leq 13, -28 \leq l \leq 26$
absorption correction	numerical	numerical
absorption coefficient	$T_{min} = 0.165; T_{max} = 0.223$ $\mu = 12.81$	$T_{min} = 0.032; T_{max} = 0.085$ $\mu = 7.94$
no. of reflections	23184 (6351 unique) measured	11619 (3536 unique)
data averaging	$R_{int} = 0.037$	$R_{int} = 0.044$
structure refinement	full matrix least-squares on $F_o^2$ anisotropic displacement parameters for all non-hydrogen atoms	full-matrix least-squares on $F_o^2$ anisotropic displacement parameters for all non-hydrogen atoms
no. of parameters	216	117
residual electron density	$-3.45 \text{ to } 2.35 \text{ e \AA}^{-3}$	$-1.54 \text{ to } 2.03 \text{ e \AA}^{-3}$
figures of merit	$R1 = 0.049$ (all data) $R1 (3834 F_o^2 > 4\sigma(F_o^2)) = 0.045$ $wR2 = 0.131$ $Goof = 1.091$	$R1 = 0.060$ (all data) $R1 (2893 F_o^2 > 4\sigma(F_o^2)) = 0.047$ $wR2 = 0.137$ $Goof = 1.086$

**Table 2.** Selected bond lengths (pm) in  $[M_nI_m(18\text{-crown-6})]^+$  complexes (M = Pb, Sn).

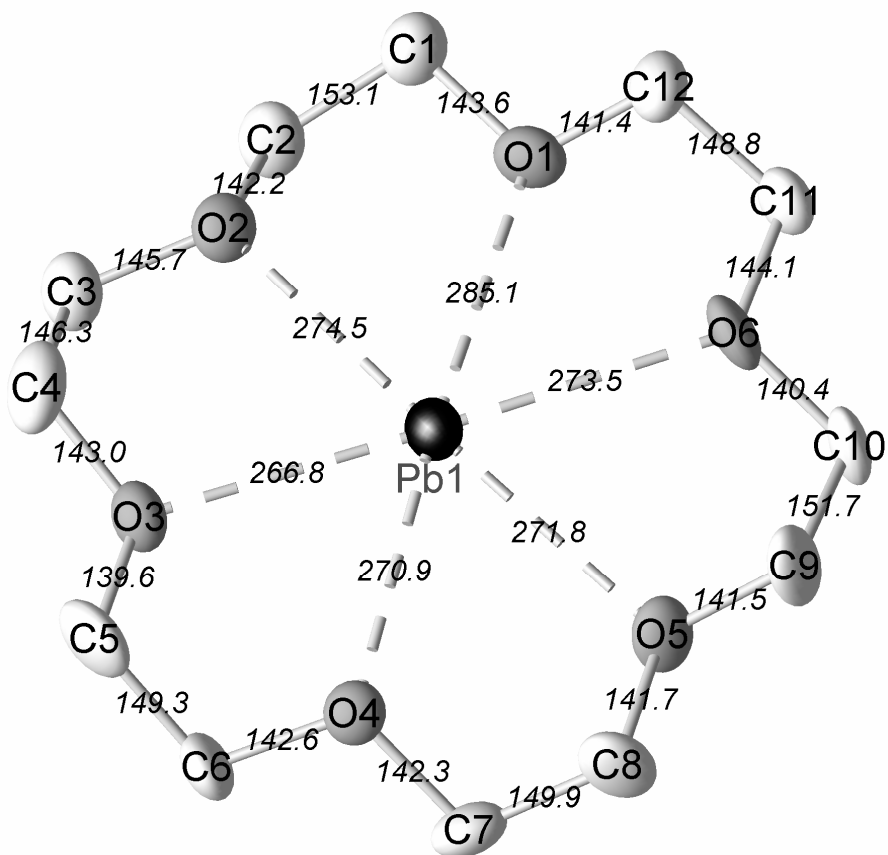
	$[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$	$[\text{PbI}(18\text{-crown-6})]^+$ [36]	$[\text{Sn}_2\text{I}_3(18\text{-crown-6})]^+$ [11]
M–O	266.8 – 285.1	271.5 – 278.5	261.2 – 293.7
M–I1	292.7	290.1	287.2
M–I2	350.4	–	355.0



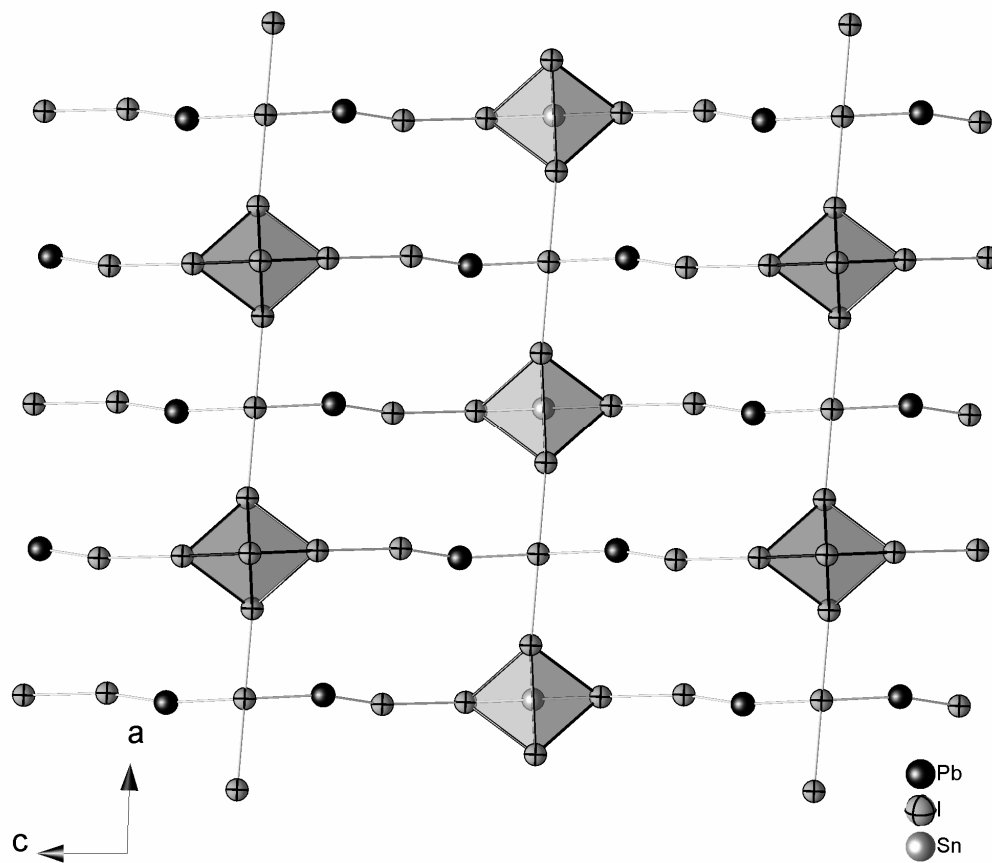
31 **Figure 1.** Unit cell of  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  (**1**) (thermal ellipsoids with 50 % probability of  
32 finding).  
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34  
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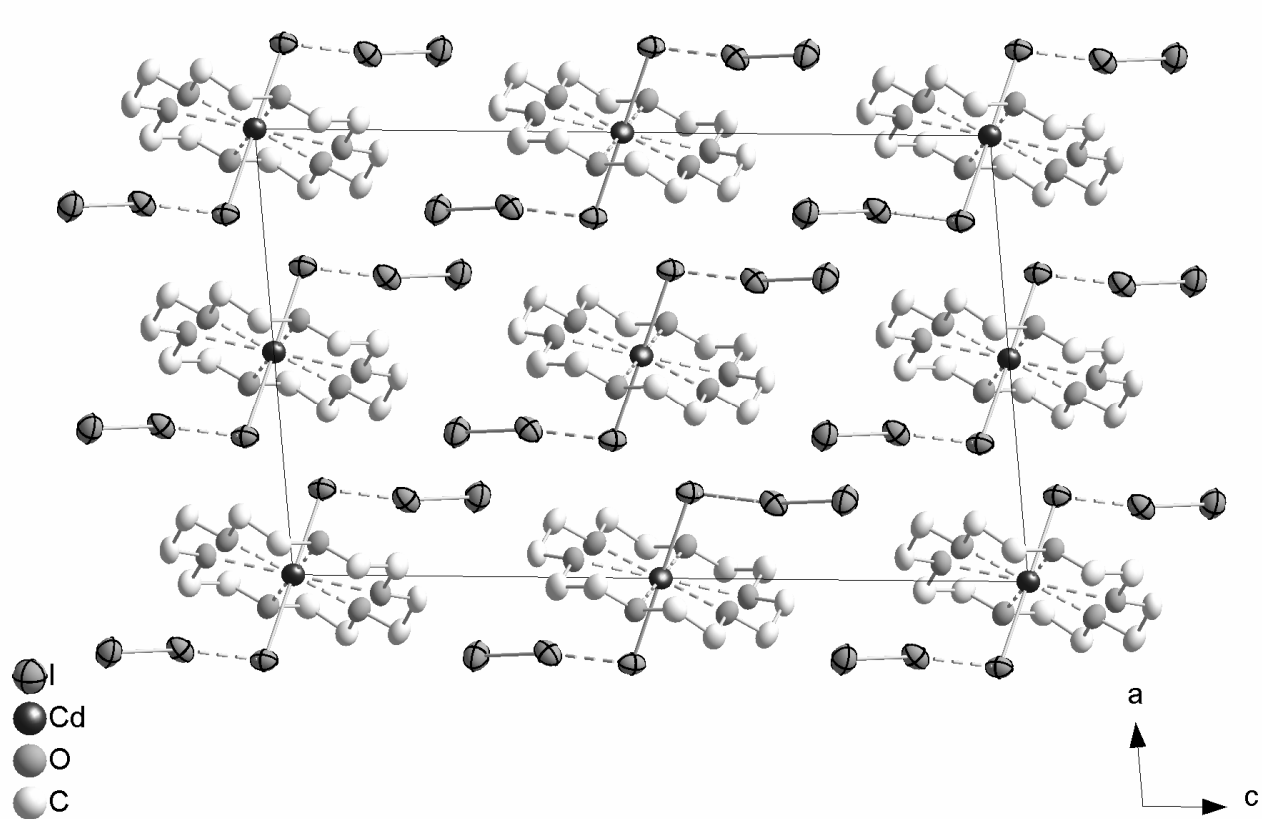
57 **Figure 2.**  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$ -cation in  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  (**1**) (thermal ellipsoids with 50 %  
58 probability of finding).  
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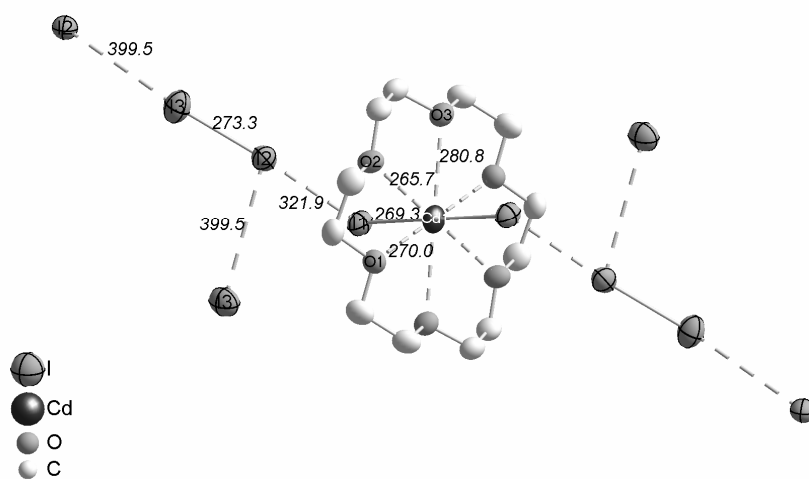
**Figure 3.** Coordination of Pb<sup>2+</sup> by 18-crown-6 in **1** (bond lengths in pm; thermal ellipsoids with 50 % probability of finding).



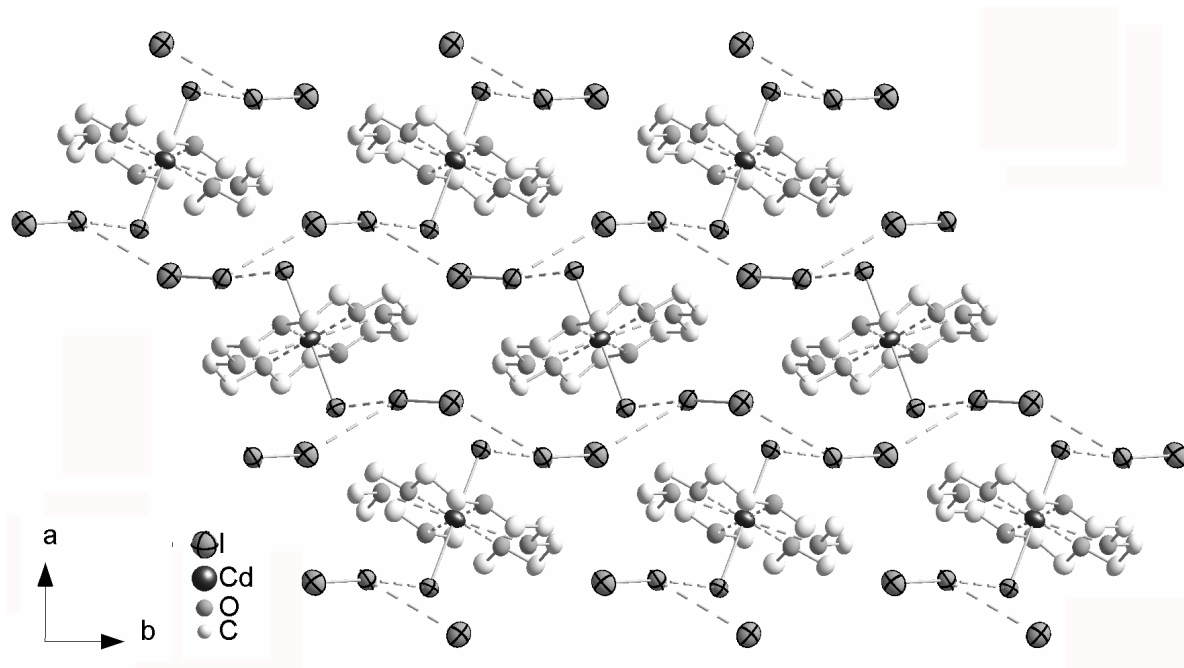
**Figure 4.** The two-dimensional iodometalate network in **1** interlinking the cation  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$  as well as the anion  $[\text{SnI}_5]^-$  via long-ranging I–I contacts, (18-crown-6 not shown for clarity).



29 **Figure 5.** Unit cell of  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  (**2**) (thermal ellipsoids with 50 % probability of finding).



55 **Figure 6.** Connectivity and selected bond length in  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$  (**2**) (in pm; thermal ellipsoids  
56 with 50 % probability of finding).



**Figure 7.** The two-dimensional network of  $[\text{CdI}_2(18\text{-crown-6})]^{2+}$  and molecular  $\text{I}_2$  in **2** along  $[110]$  (thermal ellipsoids with 50 % probability of finding).



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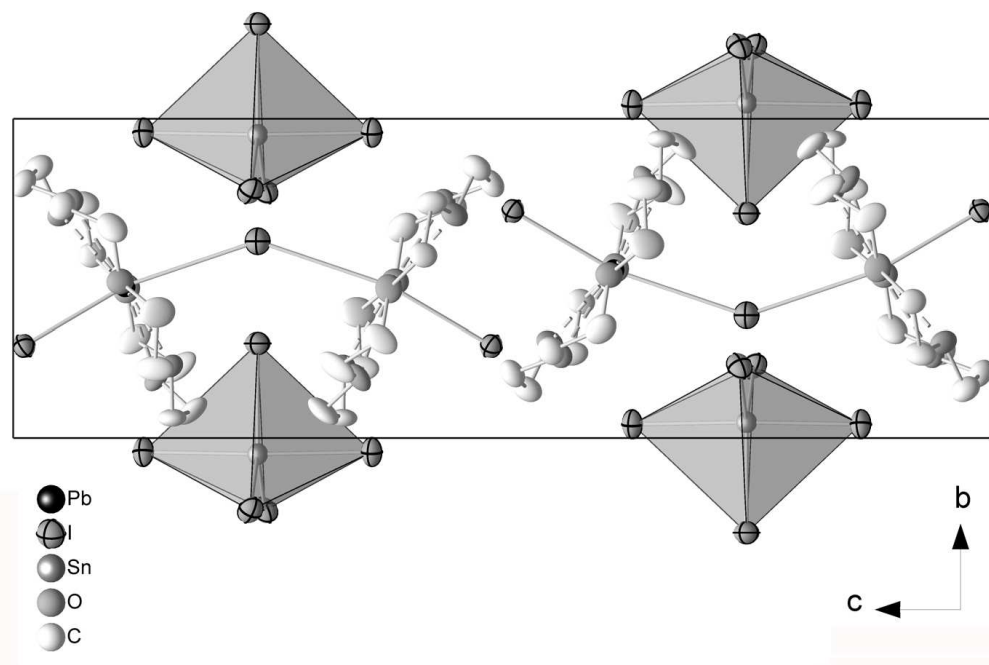


Figure 1. Unit cell of  $[\text{Pb}_2\text{I}_3(18\text{-crown-}6)_2][\text{SnI}_5]$  (1) (thermal ellipsoids with 50 % probability of finding).

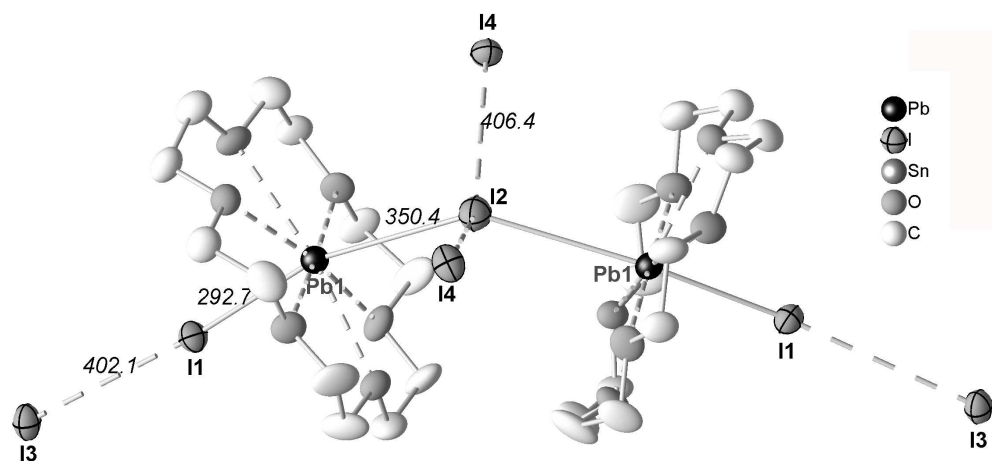


Figure 2. [Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>]<sup>+</sup>-cation in [Pb<sub>2</sub>I<sub>3</sub>(18-crown-6)<sub>2</sub>][SnI<sub>5</sub>] (1) (thermal ellipsoids with 50 % probability of finding).

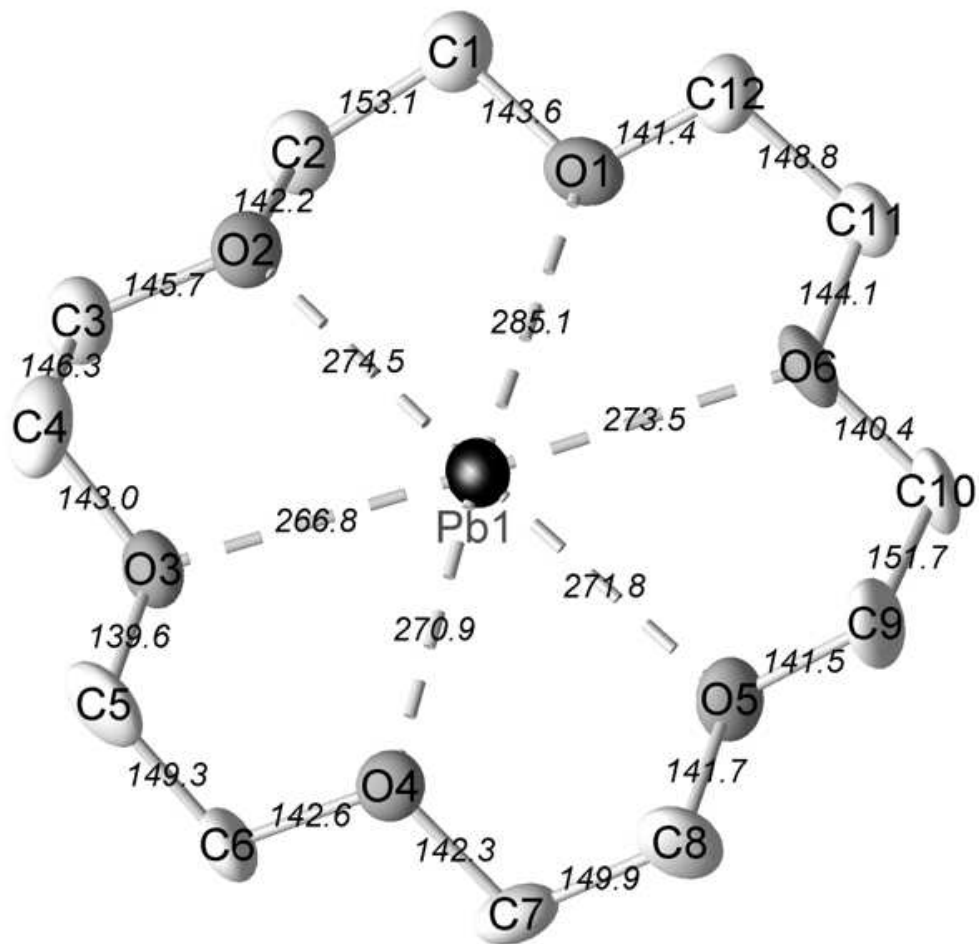


Figure 3. Coordination of Pb<sup>2+</sup> by 18-crown-6 in 1 (bond lengths in pm; thermal ellipsoids with 50 % probability of finding).

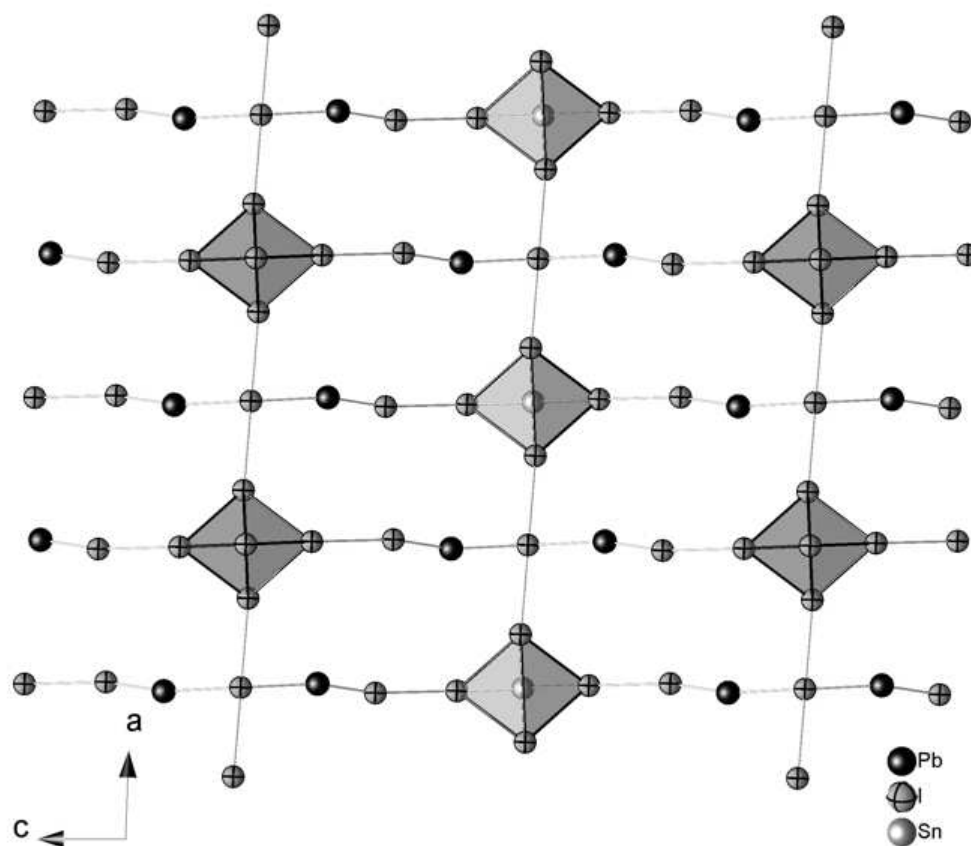


Figure 4. The two-dimensional iodometalate network in **1** interlinking the cation  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$  as well as the anion  $[\text{SnI}_5]^-$  via long-ranging I–I contacts, (18-crown-6 not shown for clarity).

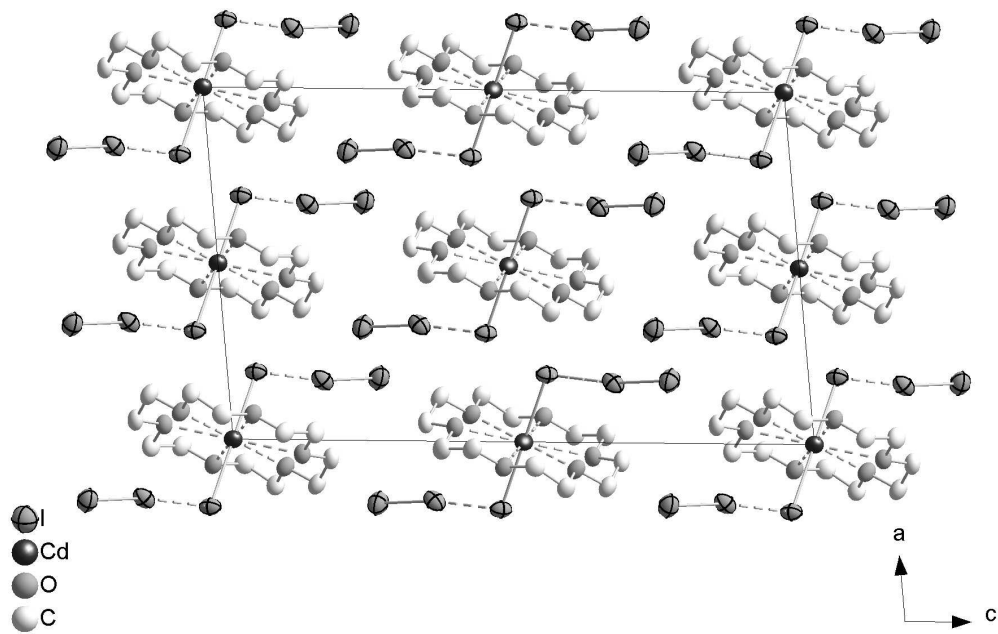


Figure 5. Unit cell of  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2 (2)$  (thermal ellipsoids with 50 % probability of finding).

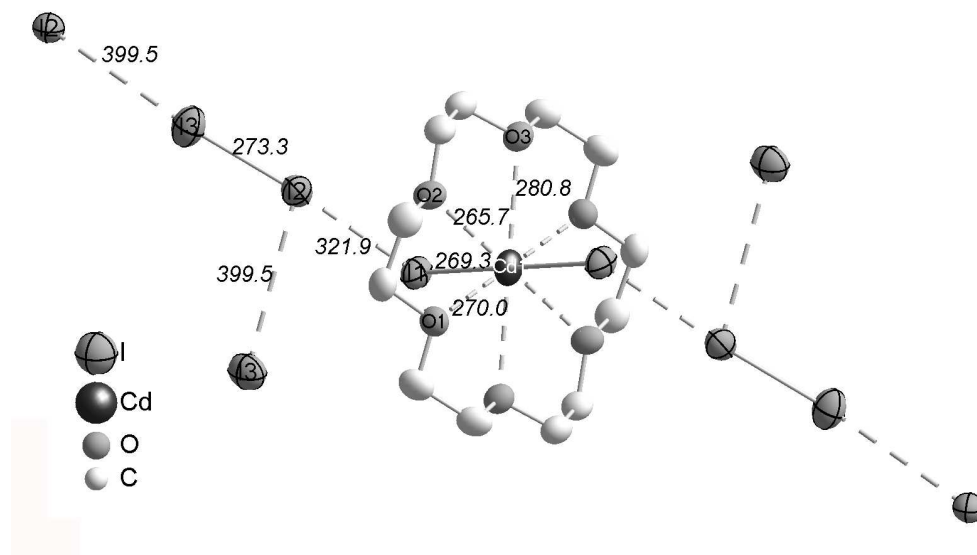


Figure 6. Connectivity and selected bond length in CdI<sub>2</sub>(18-crown-6) · 2H<sub>2</sub>O (in pm; thermal ellipsoids with 50 % probability of finding).



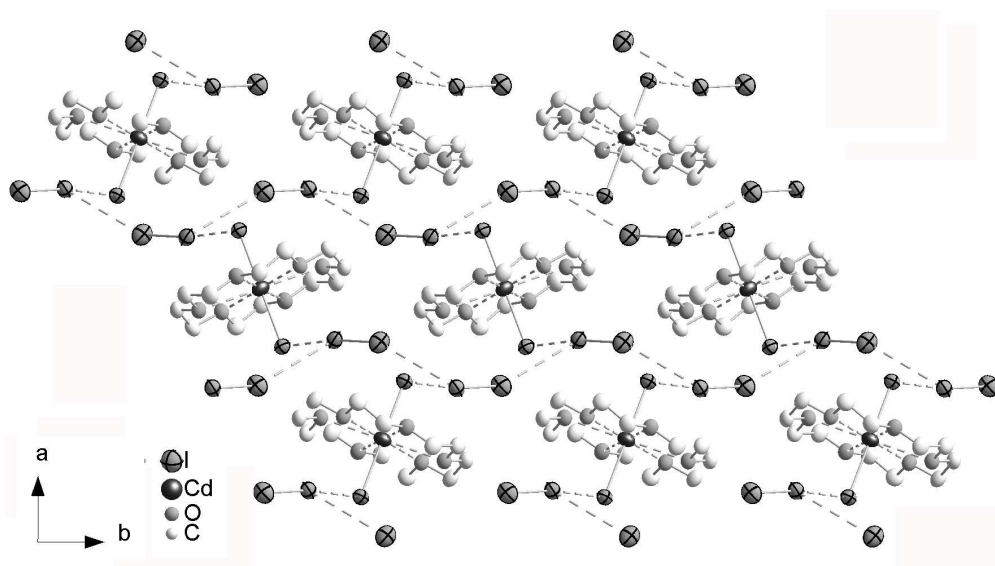


Figure 7. The two-dimensional network of [CdI<sub>2</sub>(18-crown-6)]<sup>2+</sup> and molecular I<sub>2</sub> in 2 along [110] (thermal ellipsoids with 50 % probability of finding).

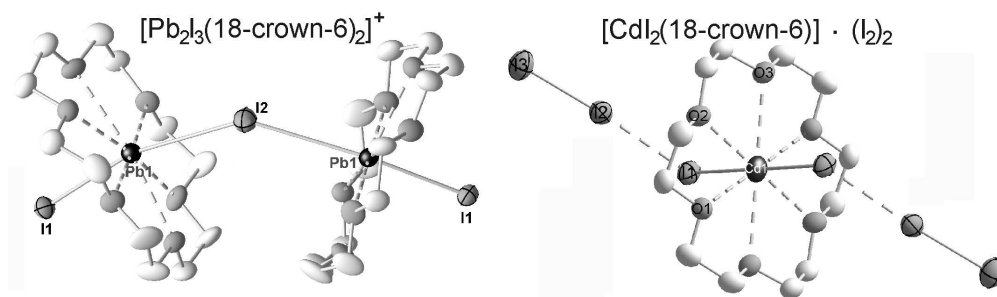


Table of contents text:  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2][\text{SnI}_5]$  with a V-shaped  $[\text{Pb}_2\text{I}_3(18\text{-crown-6})_2]^+$  cation and  $\text{CdI}_2(18\text{-crown-6}) \cdot 2\text{I}_2$ , formally containing a linear  $\text{CdI}_2$  molecule.