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Di-aqua-di-isothiocyanato-tin(II)-bis(18-crown-6), $Sn(NCS)_2 \cdot 2(18\text{-crown-}6) \cdot 2H_2O$ – A supramolecular compound of a low-valent main group element with bent sandwich architecture

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RESEARCH ARTICLE

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ABSTRACT

The crystal structure of the title compound, di-aqua-di-isothiocyanato-tin(II)-bis(18-crown-6), was determined by single crystal X-ray structure analysis. The compound crystallizes in the monoclinic space group $C2/c$ with half a molecule of the point group C_2 in the asymmetric unit. The supramolecular arrangement of the three different building blocks, a bent $Sn(NCS)_2$ one, a water molecule, and an 18-crown-6 molecule exhibits a bent sandwich-like structure with an opening angle of 48.1(1)° referring to the least-squares planes through the oxygen atoms of the crown ether molecules. Bond lengths and angles within this aggregate indicate that the isothiocyanate groups bond to the central, bivalent tin atom via covalent 2e-2c-bonds based on two orthogonal *p* orbitals of the metal atom, and the oxygen atoms of the water molecules via a symmetrical 3c-4e bond by use of the third metal *p* orbital. The crown ether molecules do not have oxygen-tin contacts but are hydrogen-bonded to the water molecules. Their conformation has similarities with that of an ideal D_{3d} conformation.

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1. Introduction

As formally electron-deficient compounds, inorganic tin(II) halides and pseudohalides, $SnHal_2$ with X = F, Cl, Br, and I, are excellent Lewis acids which are reflected in a large number of coordination compounds, $SnHal_2 \cdot n$LB, with n = 1 or 2 and unidentate Lewis bases, LB. Typical neutral Lewis bases which are used in this context for crystal structure determinations are oxygen-containing donor molecules such as sulfoxides (LB = DMSO, n = 1, Hal = F [1, 2]; n = 2, Hal = Cl [3], Hal = Br, I [1]) and carbonyl (LB = DMF, n = 1, Hal = Cl, Br, I [1]; LB = acetone, n = 2, Hal = Br [4]), ether (LB = THF, n = 2, Hal = Br [4], Hal = I [5]), pyridine-*N*-oxide (LB = ^{4}MePyNO, n = 1,2 [6]) or phosphine oxide (LB = Me_3PO/Ph_3PO, n = 2, Hal = Cl [2,7]) derivatives. Some of these complexes have been discussed as potential precursors for the preparation of tin-based perovskites for solar cell applications [1]. In contrast, little information is available on comparable compounds with the much more important solvent and Lewis base water, H_2O, although dihalides are water soluble or are prepared in a water solution [8].

The reason for this behavior is that the corresponding complexes undergo hydrolysis after their initial formation, resulting in mononuclear and polynuclear, anionic, cationic or neutral secondary products depending on the concentration, temperature, and pH value. Species crystallographically described are: $[Sn(H_2O_3)]^{2+}$ [9], $[Sn_3(OH)_4]^{2+}$ [10], $[Sn_3O(OH)_2]^{2+}$ [11], $Sn_6O_4(OH)_4$ [12,13], $[Sn(OH)_3]^-$ [14] and $[Sn_2O(OH)_4]^{2-}$ [14,15] as well as the so-called basic tin(II) halides $Sn_{21}Cl_{16}(OH)_{14}O_6$ [16] and $Sn_9F_{13}O(OH)_3 \cdot 2H_2O$ [17]. An exception is found in the case of the so-called dihydrate of tin dichloride, $SnCl_2 \cdot 2H_2O$, the formula of which corresponds to a tin dichloride coordination compound with n = 2 but was found to exist in solid as a trigonal-pyramidal $SnCl_2(H_2O)$ complex with one additional hydrogen bonded water molecule [18]. Although there are references in the literature to hydrates of tin dibromide like $2SnBr_2 \cdot H_2O$ [19], $3SnBr_2 \cdot H_2O$ [20], and $6SnBr_2 \cdot 5H_2O$ [21] in which individual water molecules are said to be bound to tin atoms, too, the crystal structures, however, cannot be verified due to the lack of transmitted atomic coordinates.

In terms of Lewis acidity and the associated tendency to form complexes, tin(II) thiocyanate, $Sn(NCS)_2$, a wide bandgap semiconductor [22,23] with almost linear pseudohalide ions $(NCS)^-$ instead of spherical halide ions, Hal^-, behaves [24] like dihalides but complexes with H_2O are also unknown.

Table 1. Crystal data and details of the structure refinement for compound **1**.

Parameters	**Compound 1**
Empirical formula	$C_{26}H_{52}N_2O_{14}S_2Sn$
Formula weight (g/mol)	799.50
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	*C*2/*c*
a, (Å)	22.2129(8)
b, (Å)	8.3990(4)
c, (Å)	21.0467(8)
α (°)	90
β (°)	112.743(2)
γ (°)	90
Volume (Å^3)	3621.3(3)
Z	4
ρ_{calc} (g/cm^3)	1.466
μ (mm^{-1})	0.884
F(000)	1664.0
Crystal size (mm^3)	0.367 × 0.23 × 0.106
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	4.196 to 55.998
Index ranges	$-29 \le h \le 29, -11 \le k \le 11, -27 \le l \le 27$
Reflections collected	184691
Independent reflections	4371 [R_{int} = 0.0538, R_{sigma} = 0.0125]
Data/restraints/parameters	4371/0/211
Goodness-of-fit on F^2	1.084
Final R indexes [I≥2σ (I)]	R_1 = 0.0221, wR_2 = 0.0628
Final R indexes [all data]	R_1 = 0.0247, wR_2 = 0.0646
Largest diff. peak/hole (e.Å^{-3})	0.68/-0.43

In this study, we report on the crystal growth and determination of the single crystal structure of the first coordination compound with two water molecules bonded directly to a unhydrolyzed tin(II) compound obtained by the reaction of the tin(II) thiocyanate, $Sn(NCS)_2$, in the presence of water and 18-crown-6 during an experiment in which the inclusion of the divalent tin ion in the cavity of the crown ether was intended.

2. Experimental

2.1. Sample preparation

The title compound was prepared in a microscale experiment according to a procedure the setup, advantages and disadvantages of which have previously been described [25]. On a Petri dish, approximately 235 mg (1 mmol) of tin(II) thiocyanate, $Sn(NCS)_2$, [26] and 264 mg (1 mmol) of 18-crown-6, $C_{12}H_{24}O_6$, (264.32 g/mol Sigma-Aldrich) were placed side by side. After addition of 2-3 drops of water, the solids partially dissolved before, after some hours, the crystal growth of colorless, plate-like single crystals could be observed in the microscope. Crystals were stable in air for some days as long as they were wet, but became opaque and decomposed quickly when dried.

2.2. Single crystal structure determination

A suitable single crystal was selected from the reaction mixture and carefully freed from contamination by impurities from other crystals. The crystal was mounted on a 50 µm MicroMesh MiTeGen MicromountTM using FROMBLIN Y perfluoropolyether (LVAC 16/6, Aldrich) before it was centered on a standard Bruker Kappa APEX II CCD-based 4-circle X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) of a fine focus molybdenum-targeted X-ray tube operating at 50 kV and 30 mA. Cooling to 100(2) K was achieved with a Kryoflex low-temperature device.

Integrated intensities were obtained with the Bruker SAINT software package [27] using a narrow-frame algorithm performing spatial corrections of frames, background subtractions, Lorenz and polarization corrections, profile fittings and error analyses. Semi-empirical absorption corrections based on equivalent reflections were made by use of the program SADABS [27]. Structures were solved by Direct methods and subsequent difference Fourier syntheses of the program SHELXS [28] and refined by full-matrix least-squares techniques on F^2 with SHELXL [28] applying anisotropic displacement factors for all non-hydrogen atoms. All hydrogen atoms could be localized in a difference Fourier analysis. Their positions have been refined in stereochemical idealized positions with d(C-H) = 0.95 Å. The positions of the hydrogen atoms of the water molecules have been refined with d(O-H) = 0.96 Å and a bond angle of 104.9° before they were allowed to ride (AFIX 3) on the corresponding oxygen atom with a common isotopic displacement factor.

Figures were drawn using DIAMOND [29], POVRAY [30] and Mercury [31]. In the ball-and-stick models all atoms are drawn as thermal displacement ellipsoids of the 50% level with the exception of the hydrogen atoms which are shown as spheres of arbitrary radii. In the space-filling models, atoms are visualized as single-colored or truncated, two-colored spheres according to their van der Waals radii and cut-offs based on the intersection of the two spheres with cut-off faces showing the color of the interpenetrating atom. Atom colors and van der Waals radii [32] (Å) are as follows: O = red/1.47, H = white/1.10, C = grey/1.70, N = blue/1.55, S = yellow/1.86 and Sn = brass/2.17. Crystal data, data collection, and structure refinement details for the compound are summarized in Table 1.

3. Results and discussion

Crystal structure analysis reveals that the tin complex crystallizes in the centrosymmetric monoclinic space group *C*2/*c*. The asymmetric unit consists of one molecule of 18-crown-6, one water molecule, and half a $Sn(NCS)_2$-unit with a twofold rotation axis between both thiocyanate ligands. The supramolecular arrangement of these building units corresponds to that of metallocene with a bent sandwich structure best known from bis(π-cyclopentadienyl) titanium(IV) dichloride, most often referred to titanocene dichloride [33], η_5-Cp_2TiCl_2, with an opening angle defined by the least squares plane through the oxygen atoms of the crown ether molecules of 48.1° (Figure 1).

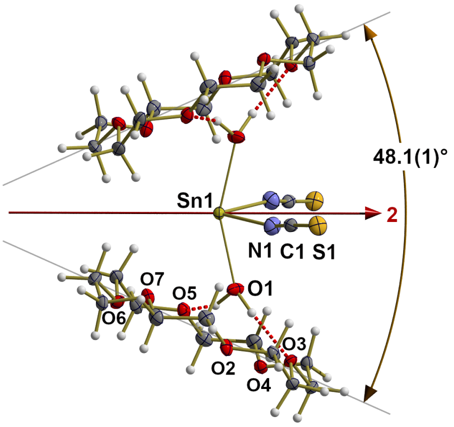


Figure 1. Ball-and-stick model of the bent sandwich molecular structure of compound **1** with local point group symmetry C2, showing the atom numbering of the asymmetric unit, the orientation of the two-fold rotation axis (red 2, arrow) and the opening angle defined by the least squares planes through the oxygen atoms of the 18-crown-6 molecules. For clarity, numbering of the carbon atoms within the 18-crown-6 molecule has been omitted.

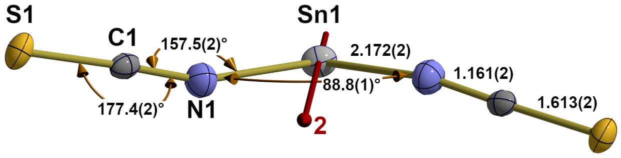


Figure 2. Ball-and-stick model of the $Sn(NCS)_2$ building unit with bond lengths [Å], angles [°]. and orientation of the crystallographic, two-fold rotation axis (red arrow, labelled 2).

The starting material, $Sn(NCS)_2$ represents in solid a one-dimensional coordination polymer neglecting weak interchain Sn···S interactions with one terminal κ^1-*N* [d(Sn-N) = 2.198(2) Å] and one bridging κ^2-*NS* [d(Sn-N = 2.284(2) Å, d(Sn-S) = 2.8209(5) Å] thiocyanate group resulting in a trigonal-pyramid coordination geometry with the tin atom at the apex and the nitrogen and sulfur atoms in the basal plane [22]. In comparison with this compound, the Sn-N distances in the title compound are significantly shorter (Figure 2) and there are no additional Sn···S contacts below 4.8 Å. The isothiocyanate ion is usually almost linear with a N-C bond length of 1.161(2) Å that corresponds to a triple bond and a C-S bond length of 1.613(2) Å that corresponds to a single bond in accordance with the assumption of *sp*-hybridized carbon and nitrogen atoms.

The direct neighbourhood of the electron-deficient tin atom of the $Sn(NCS)_2$ building unit consists of two equidistant oxygen atoms of two water molecules related to each other via the two-fold rotation axis passing through the tin atom. Since the tin atom with the two electrons of the donor oxygen atoms exceeds the electron octet in the case of covalent, dative 2c-2e bonds, the oxygen atoms can only be bonded to the tin atom via a 3c-4e bond, as originally formulated for the triiodide ion [34]. In accordance with this idea, the corresponding tin-oxygen distances of 2.349(1) Å are longer in comparison to similar distances in, for example, the trigonal-pyramidal $[Sn(H_2O)_3]^{2+}$ ion with an electron octet at tin based on three covalent, dative 2c-2e-bonds: there Sn-O bond lengths of 2.207(2) - 2.254(2 Å), 2.222(2) - 2.237(2) [35] Å, and 3 × 2.201(7) Å [9] are observed. With the finding that two Lewis base molecules are axially bound to the tin atom at the same distance, the coordination mode of the tin atom can be described as 3_1-s, applying the nomenclature that easily assigns the observed stereochemistry to a potential binding scheme [25].

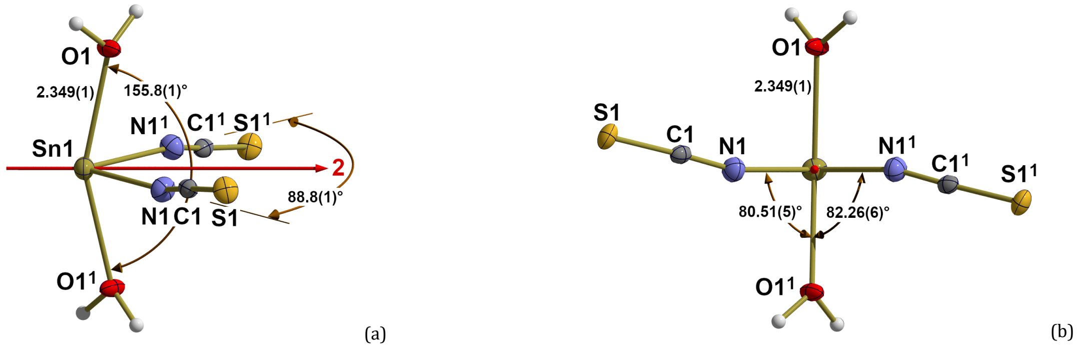
Therefore, incorporating the two water molecules into the first coordination sphere of the tin atom, a seesaw coordination results with the two isothiocyanate ions in equatorial and the two water molecules in axial positions (Figure 3). As usually for this kind of tin(II) coordination, the axis is not linear (as in the triiodide anion) but bent with an bond angle of 155.8(1)° and the bond angles between the equatorial and axial ligand atoms strongly [80.51(5)°/82.26(6)°] deviate from orthogonality. The deviations from the ideal values probably result from the double occupied 5*s* orbital of the divalent tin atom, whose actually spherical electron density is deformed in the opposite direction to the one-sided bonds.

Both hydrogen atoms of the water molecules are involved into hydrogen bonds to the oxygen atoms O(3) and O(5) of the 18-crown-6 molecules (Figure 4a). The corresponding donor acceptor distances are 2.825(2) Å [(O1···O3] and 2.860(2) Å [O(1)···O(5)] with bridging angles at hydrogen atoms of 165.7° [H(1)] and 151.0° [H(2)]. The two-hydrogen bonded 18-crown-6 molecules are in a mutual relationship via the twofold rotation axis like the two water molecules and isothiocyanate ligands. The individual bond lengths and angles in the asymmetric 18-crown-6 molecules are listed in Table 2. The carbon-carbon bond lengths range from 1.981(2) to 1.500(2) Å with a mean value of 1.498(6) Å, that corresponds to a single bond, as do the carbon-oxygen bond lengths that range from 1.4100(2) to 1.423(2) Å, mean value 1.418(6) Å. Both are somewhat shorter than the corresponding values [1.423(4)/ 1.510(3)] in the solid state of pure crown ether [36]. Regarding the bond angles, those at the carbon atoms [mean value: 109.1(5)°, range: 108.4(1)° - 110.0(1)°] are somewhat smaller than the bond angles at the oxygen atoms [mean value = 111.5(6)°, range: 110.7(1)° - 112.2(1)°]. In the pure 18-crown-6 molecule, the bond angles at the carbon atoms are insignificantly longer109.3(28)° but have a significantly greater variance, as the standard deviation shows, whereas the bond angles at the oxygen atoms are considerably larger 112.8(2)° than in the title compound.

The conformation analysis of the 8-crown-16 molecule based on the torsion angles (Table 2) has been performed using a polar coordinate map introduced by Fyles & Gandour [37]. In this kind of diagram, the 18 bonds of the crown ether molecule are numbered cyclically, whereby the starting point and direction are freely selectable.

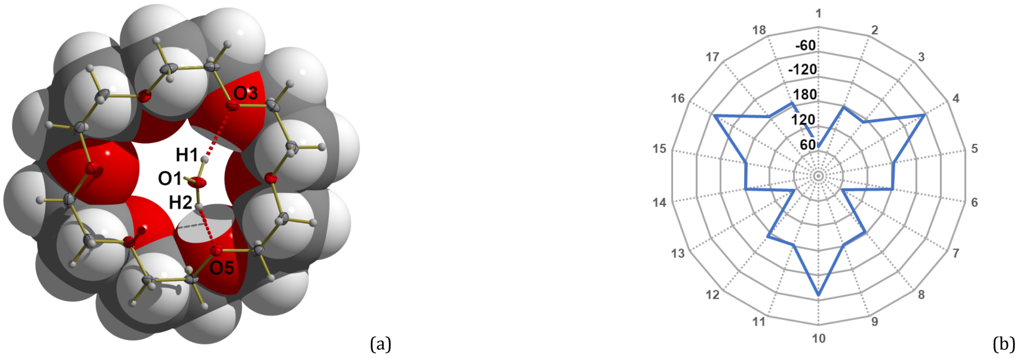
Table 2. Bond lengths [Å], bond angles [°] and torsion angles [°] of the 18-crown-6 molecule in compound **1**.

Bond length		**Bond angles**		**Torsion angles**	
O(2)-C(2)	1.414(2)	O(2)-C(2)-C(3)	108.9(1)	O(2)-C(2)_C(3)-O(3)	67.2(2)
C(2)-C(3)	1.503(2)	O(3)-C(3)-C(2)	109.1(1)	C(2)-C(3)-O(3)-C(4)	175.3(1)
C(3)-O(3)	1.423(2)	C(3)-O(3)-C(4)	110.7(1)	C(3)-O(3)-C(4)-C(5)	176.3(1)
O(3)-C(4)	1.433(2)	O(3)-C(4)-C(5)	109.2(1)	O(3)-C(4)-C(5)-O(4)	-72.6(2)
C(4)-C(5)	1.499(2)	O(4)-C(5)-C(4)	109.5(1)	C(4)-C(5)-O(4)-C(6)	176.4(1)
C(5)-O(4)	1.423(2)	C(6)-O(4)-C(5)	111.0(1)	C(5)-O(4)-C(6)-C(7)	-169.6(1)
O(4)-C(6)	1.420(2)	O(4)-C(6)-C(7)	109.1(1)	O(4)-C(6)-C(7)-O(5)	68.7(2)
C(6)-C(7)	1.502(2)	O(5)-C(7)-C(6)	108.4(1)	C(6)-C(7)-O(5)-C(8)	179.3(1)
C(7)-O(5)	1.419(2)	C(7)-O(5)-C(8)	112.2(1)	C(7)-O(5)-C(8)-C(9)	177.3(1)
O(5)-C(8)	1.429(2)	O(5)-C(8)-C(9)	109.7(1)	O(5)-C(8)-C(9)-O(6)	-69.3(2)
C(8)-C(9)	1.493(3)	O(6)-C89)-C(8)	109.1(1)	C(8)-C(9)-O(6)-C(10)	-173.7(1)
C(9)-O(6)	1.415(2)	C(9)-O(6)-C(10)	111.6(1)	C(9)-O(6)-C(10)-C(11)	-172.4(1)
O(6)-C(10)	1.420(2)	O(6)-C(10)-C(11)	110.0(1)	O(6)-C(10)-C(11)-O(7)	70.7(2)
C(10)-C(11)	1.491(2)	O(7)-C(11)-C(10)	108.9(1)	C(10)-C(11)-O(7)-C(12)	177.4(1)
C(11)-O(7)	1.419(2)	C(12)-O(7)-C(11)	111.3(1)	C(11)-O(7)-C(12)-C(13)	168.8(1)
O(7)-C(12)	1.412(2)	O(7)-C(12)-C(13)	109.1(1)	O(7)-C(12)-C(13)-O(2)	-65.7(2)
C(12)-C(13)	1.500(3)	O(2)-C(13)-C(12)	108.4(1)	C(12)-C(13)-O(2)-C(2)	-175.3(1)
C(13)-O(2)	1.415(2)	C(2)-O(2)_C(13)	112.2(1)	C(13)-O(2)-C(2)-C(3)	-178.7(1)



(a) (b)

Figure 3. (a) Side and (b) front view of the seesaw coordinated tin atom in the $Sn(NCS)_2(H_2O)_2$ complex as ball-and-stick models with bond lengths [Å], angles, and orientation of the two-fold rotation axis (red arrow, labeled 2), symmetry operations used to generate equivalent atoms: ^{1} -*x*+1, *y*, -*z*+1/2.



(a) (b)

Figure 4. (a) Ball-and-stick model of the 18-crown-6 molecule with the position of the hydrogen-bonded water molecule underlaid with its space-filling model in which the oxygen atoms of the hydrogen bonds are drawn by capped spheres resulting from the overlap with the hydrogen atoms of the water molecule. (b) Polar coordinate map of torsion angles according to the conventions of Fyles & Gandour [37].

The torsion angle of each bond is then plotted by the bond number on a polar coordinate system from the center at 0 ° to the outer edge at 360° and the negative torsion angles are plotted as 360° plus the negative torsion angles. The resulting graph (Figure 4b) shows a high degree of agreement with that of an 18-crown-6 molecule in an ideal *D*3d conformation (Figure 1) [37].

Although the arrangement of the building blocks looks very compacted (Figure 5), there are no direct contacts between the central tin atom and the peripheral 18-crown-6 molecules. The corresponding tin-oxygen distances are all longer than 4.8 Å which is larger than the sum of the covalent radii of tin and oxygen. The cohesion of the different building blocks in this supramolecular arrangement therefore only results from the covalent shared 2c-2e bonds between the tin atom and the nitrogen atoms of the thiocyanate ligands, the symmetrical 3c-4e-bond between the tin atom and the water molecules, and the hydrogen bonds between the water molecules and the 18-crown-6 molecules.

4. Conclusion

The isolation and crystallographic characterization of the title compound provides impressive new insights into the processes involved in the dissolution of tin(II) compounds in water and shows that before the onset of hydrolysis, not only species are formed in which one donor water molecule is bound to the divalent tin atom but also two. In the resulting 1:2-aqua complex the tin atom is then fourfold, seesaw coordinated with the inorganic anions in equatorial bound via covalent 2c-2e bonds and the two water molecules in axial positions bound via a 3c-4e bond.

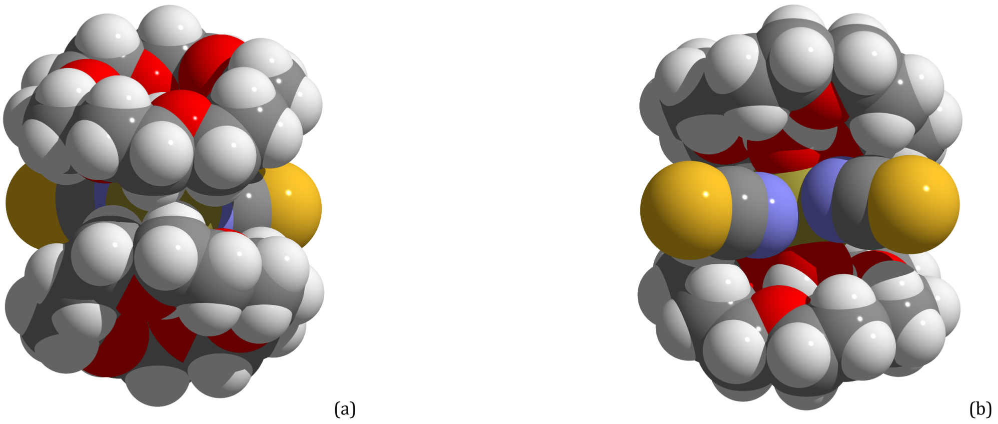

(a) (b)

Figure 5. Space-filling models of the supramolecular assemblance from the back (a) and front (b) side showing the cover of the central two-valent tin atom by the 18-crown-6 molecules and thiocyanate ligands, respectively.

The results also show the importance of the crown ether molecules for the trapping and crystallization of such species, as they shield the divalent tin atom on the back of the bonds and thus prevent hydrolysis.

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Supporting information

CCDC-2419940 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.

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