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H-Bonding of Complex Indium Thiocyanates with Crown Ether Molecules

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Abstract—Supramolecular ensembles $[In(H_2O)_4(NCS)_2][In(H_2O)_2(NCS)_4] \cdot 2(18C6)$ (**I**) and $[In(H_2O)_3(NCS)_3] \cdot 18C6$ (**II**) are synthesized and identified by the data of elemental analyses, IR spectra, and X-ray structure analysis for structure **I** and X-ray phase analysis for structure **II**. In spite of specific features of the H-bonding of the 18C6 molecules with the cationic, molecular, or anionic indium complexes, chain motives are observed in structures **I** and **II**.

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INTRODUCTION

A popular and efficient approach to the design of supramolecular compounds is the selection of mutually supplementing H-donors and acceptors to form H-bonded polymeric ensembles. This strategy turned out to be efficient in the synthesis of [*mer*-$In(H_2O)_3Cl_3$] · 18C6 and [gran-$In(H_2O)_3Cl_3$] · 18C6 · $2H_2O$ [1]. The indium thiocyanate complexes in supramolecular ensembles are characterized by the dependence of the stoichiometry (NCS : In molar ratio) on the synthesis conditions [2].

The purpose of the present work is to determine the influence of the synthesis conditions on the composition, structure, and specific features of the H-bonding of indium thiocyanates with the 18C6 macrocyclic molecules.

EXPERIMENTAL

The following commercial substances were used without additional drying or purification: $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$, $Ba(NCS)_2 \cdot 3H_2O$, and KNCS (high-purity grade), a solution of $InCl_3$ (synthesized from indium oxide and CCl_4), crown ether (18C6) 1,4,7,10,13,16-hexaoxocyclooctadecane (Aldrich), MeOH, *iso*-PrOH, and diethyl ether.

Indium was determined trilonometrically in an acidic medium with Xylenol Orange is the indicator. The content of the thiocyanate ion was determined by thiocyanometric titration.

IR spectra were recorded on a Specord IR75 spectrometer in the 400–4000 cm^{-1} region as suspensions in Nujol. The X-ray phasa analysis was carried out on a STOE STADI P diffractometer ($CuK_{\alpha 1}$ radiation, Ge monochromator).

Preparation of thiocyanate solutions of indium. *Solution A.* A solution of $Ba(NCS)_2 \cdot 3H_2O$ (6.4738 g, 21.0 mmoles of Ba) in H_2O (15 ml) was added to a solution of $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ (5.1939 g, 13.89 mmoles of In) in H_2O (15 ml). The resulting heterogeneous mixture was stored for a day, and a precipitate of $BaSO_4$ was separated on a glass filter. The In content in the obtained filtrate was 0.308 mmol/ml, and the NCS^- : In ratio was 3.

Solution B. A solution of $Ba(NCS)_2 \cdot 3H_2O$ (4.0825 g, 13.2 mmoles of Ba) in H_2O (10 ml) was added to a solution of $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ (2.4624 g, 6.58 mmoles of In) in H_2O (15 ml). The resulting heterogeneous mixture was stored for a day, and a precipitate of $BaSO_4$ was separated on a glass filter. The In content in the obtained filtrate was 0.2139 mmol/ml, and the NCS^- : In ratio was 4.

Synthesis of $[In(H_2O)_4(NCS)_2][In(H_2O)_2(NCS)_4] \cdot 2(18C6)$ (I). (1) A weighed sample of 18C6 (0.2401 g, 0.91 mmol) was dissolved in MeOH (10 ml), and solution *A* (0.3 ml, 0.924 mmoles of In) was added. After

10 days of isothermal evaporation, lilac crystals were obtained, separated on a glass filter, and dried in a vacuum desiccator over silica gel. The yield was 0.5 g.

For $C_{30}H_{60}N_6O_{18}S_6In_2$ (*M* 1214.77)

anal. calcd, %:	In, 18.90;	NCS, 28.68.
Found, %:	In, 18.76;	NCS, 28.15.

IR (cm^{-1}): 3250–3600 ν(H_2O), 2040 ν(CN), 1610 δ(H_2O), 1090 ν_{as}(COC), 940 ν(COC), 830 ν(CO)$^+$, 720 ν(CS), 470 δ(NCS).

(2) A weighed sample of 18C6 (0.2551 g, 0.97 mmol) was dissolved in MeOH (10 ml), and solution *B* (5 ml, 1.0695 mmoles of In) was added. After 7 days of isothermal evaporation, lilac crystals were obtained, separated on a glass filter, and dried in a vacuum desiccator over silica gel. The yield was 0.5 g.

For $C_{30}H_{60}N_6O_{18}S_6In_2$

anal. calcd, %:	In, 18.90;	NCS, 28.68.
Found, %:	In, 20.29;	NCS, 29.43.

IR (cm^{-1}): 3100–3500 ν(H_2O), 2050 ν(CN), 1600 δ(H_2O), 1080 ν_{as}(COC), 940 ν(COC), 830 ν(CO)$^+$, 730 ν(CS), 470 δ(NCS).

(3) Solution *B* (5 ml, 1.0695 mmoles of In) was introduced in 10 ml of diethyl ether. The ethereal extract was mixed with a solution of 18C6 (0.2528 g, 0.9562 mmol) in MeOH (5 ml). Violet-red crystals precipitated from a pink solution and were treated similarly to synthesis (2).

For $C_{30}H_{60}N_6O_{18}S_6In_2$

anal. calcd, %:	In, 18.90;	NCS, 28.68.
Found, %:	In, 18.63;	NCS, 25.79.

IR (cm^{-1}): 3100–3500 ν(H_2O), 2050 ν(CN), 1610 δ(H_2O), 1090 ν_{as}(COC), 920 ν(COC), 830 ν(CO)$^+$, 720 ν(CS), 480 δ(NCS).

Synthesis of $[In(H_2O)_3(NCS)_3] \cdot$ 18C6 (II). A weighed sample of KNCS (0.3303 g, 3.4 mmol) was dissolved in *iso*-PrOH (10 ml), and an aqueous solution of indium (0.3 ml, 1.0 mmol) was added. Potassium chloride that formed was filtered on a glass filter, and the resulting solution was mixed with a solution of 18C6 (0.2615 g, 1.0 mmol) in *iso*-PrOH (2 ml). After isothermal evaporation, a finely dispersed lilac solid phase was formed in the mother liquor and treated similarly to synthesis (2) washing with the mother liquor. The yield was 0.5 g.

For $C_{15}H_{30}N_3O_9S_3In$ (*M* 607.4)

anal. calcd, %:	In, 18.90;	NCS, 28.69.
Found, %:	In, 20.75;	NCS, 29.4.

IR ($^{-1}$): 3050–3500 ν(H_2O), 2050 ν(CN), 1600 δ(H_2O), 1070 ν_{as}(COC), 930 ν(COC), 820 ν(CO)$^+$, 720 ν(CS), 550 δ(NCS).

X-ray structure analysis of compound **I** prepared by synthesis (1) (according to the X-ray phase analysis, the products of syntheses (1)–(3) are the same) was carried out on a Siemens P4 diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The positions of non-hydrogen atoms in structure **I** were taken from the isostructural scandium compound [3]. The hydrogen atoms of the water molecules were determined from the difference Fourier syntheses, and the hydrogen atoms of the crown ether were calculated from geometric concepts. Structure **I** was refined by the full-matrix least-squares method in the anisotropic approximation taking into account the held stationary hydrogen atoms of the water molecules, and the hydrogen atoms of 18C6 were taken into account in the riding model. All calculations were performed using the SHELXS-97 [4] and SHELXL-97 [5] program packages.

Compound **II** was identified by the X-ray phase data. The X-ray pattern of complex **II** was indexed by the Ito method and refined (table) using the WinXpow program [6]. Unfortunately, the presence of an unidentified admixture (~3%) in the sample did not allow us to refine structure **II**.

Selected crystallographic data and the refinement results for structures **I** and **II** are given in the table.

The structural data for compound **I** were deposited with the Cambridge Structural Data Base (no. 692 506).

RESULTS AND DISCUSSION

According to the data of elemental analysis, IR spectra, and X-ray structure and phase analyses, the products prepared in syntheses (1)–(3) are independent of the synthesis conditions. When using an aqueous solution of indium thiocyanate *A* (synthesis (1)) or solution *B* (synthesis (2)) with the molar ratio NCS$^-$: In = 3 or 4, respectively, or an ethereal extract from an aqueous solution of indium thiocyanate (synthesis (3)), the compound with the ratios NCS$^-$: In = 3 and 18C6 : In = 2 was obtained. Compound **I** contains the cationic and anionic complexes $[In(H_2O)_4(NCS)_2]^+$ and $[In(H_2O)_2(NCS)_4]^-$ in a ratio of 1 : 1, which are formed due to the disproportionation of the molecular complex $In(H_2O)_3(NCS)_3$.

Selected crystallographic characteristics and refinement details for structures **I** and **II**

Parameter	Value	
	I	**II**
Temperature, K	295	295
Radiation	MoK_{α}	Cu$K_{\alpha1}$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbcn*
a, Å	15.8067(18)	10.819(3)
b, Å	27.164(3)	15.245(5)
c, Å	11.9225(12)	13.473(3)
V, Å^3	5119.2(10)	2222.2(8)
Z	4	4
ρ_{calcd}, g/cm^3	1.576	1.653
μ, mm^{-1}	1.214	1.415
Crystal sizes, mm	0.25 × 0.20 × 0.10	
θ, deg	2.14–25.00	5.00–2.00
Collected reflections	7214	
Independent reflections	4604	
R_{int}	0.0359	
Reflections with $I > 2\sigma(I)$	1510	
Number of refined parameters	295	
Goodness-of-fit (F^2)	1.096	
R_1, wR_2 ($I > 2\sigma(I)$)	0.0590, 0.1037	
R_1, wR_2 (all reflections)	0.1505, 0.1508	
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	1.692, –0.676	
Number of peaks		37
F(30)		24.5 (0.013, 98)
Volume per one non-hydrogen atom, Å^3	20.6	17.9

In structure **I**, the cationic and anionic complexes together with the 18C6 molecules form chains due to hydrogen bonds (Fig. 1). The structure the scandium analog of complex **I** was considered in detail [3].

A different ensemble of indium thiocyanate with 18C6 is formed in the synthesis of complex **II**. The substitution of MeOH for *iso*-PrOH and the replacement of indium thiocyanate solutions by the system In-Cl-KNCS for the precipitation of chloride result in the isolation of an ensemble with the molecular complex $[In(H_2O)_3(NCS)_3] \cdot 18C6$ (**II**).

Compound **II** is isostructural to [*mer*-$In(H_2O)_3Cl_3$] · 18C6 (**III**) [1] ($a = 10.7903(11)$ Å, $b = 14.7633(12)$ Å, $c = 13.6751(12)$ Å, $V = 2178.4(3)$ Å^3, $Z = 4$, space group *Pbcn*). A comparison of the unit cell parameters for compounds **II** and **III** shows that the replacement of the chloride ion by the thiocyanate ion mostly changes the *b* parameter (increases by 0.6 Å), which agrees with crystal structure **III**. In the latter, the complexes and crown ether molecules form piles directed along the *z* axis. The Cl(1), In(1), and O(2) atoms are localized in axis 2 (parallel to the *y* axis), and the Cl(2) atom occupies the general position (Fig. 2). Naturally, the thiocyanate ion replacing Cl(1) also lies in axis 2, and the linear size of the complex along axis 2 increases by ~2.4 Å. The piles in structure **II** are arranged in a chess order, and an increase in the *b* parameter only by 0.6 Å can compensate this change.

The *a* parameter remains almost unchanged (increases only by 0.02 Å), because the Cl(2*B*) and Cl(2*D*) atoms are related to axis 2 and short contacts that are formed upon the replacement of the chloride ion by the thiocyanate ion disappear, when the complex slightly turns about axis 2 and the InNC bond angle decreases. The increase in the *c* parameter by ~0.1 Å is explained by the turn of the complex about axis 2, resulting in some motions in the piles.

Thus, under the synthesis conditions, when the crown ether enters the crystal structure as free molecules (hydrogen atom acceptors), the donors of H-bonds become complementary to these molecules: cationic aqua complexes with the formation of sandwiches with the macrocycle molecules, molecular forms $M(H_2O)_3X_3$ (X = Cl, NCS, M = Ga, In), and anionic aqua complexes $[M(H_2O)_2(NCS)_4]^-$ (M = Sc, In). Regardless of the composition and charge of the metal complex, the system of hydrogen bonds with 18C6 leads to the formation of polymeric chains.

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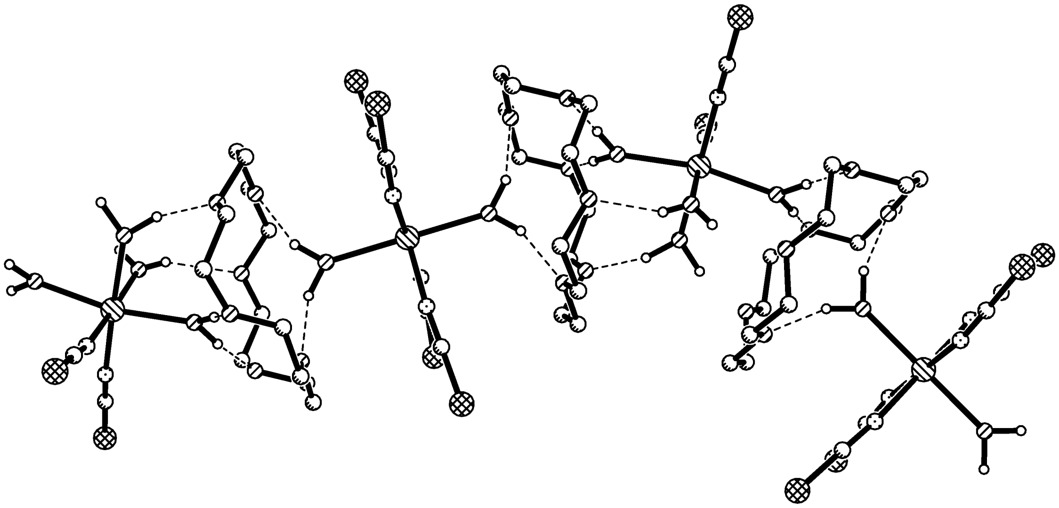

Fig. 1. Structure of piles in structure **I**.

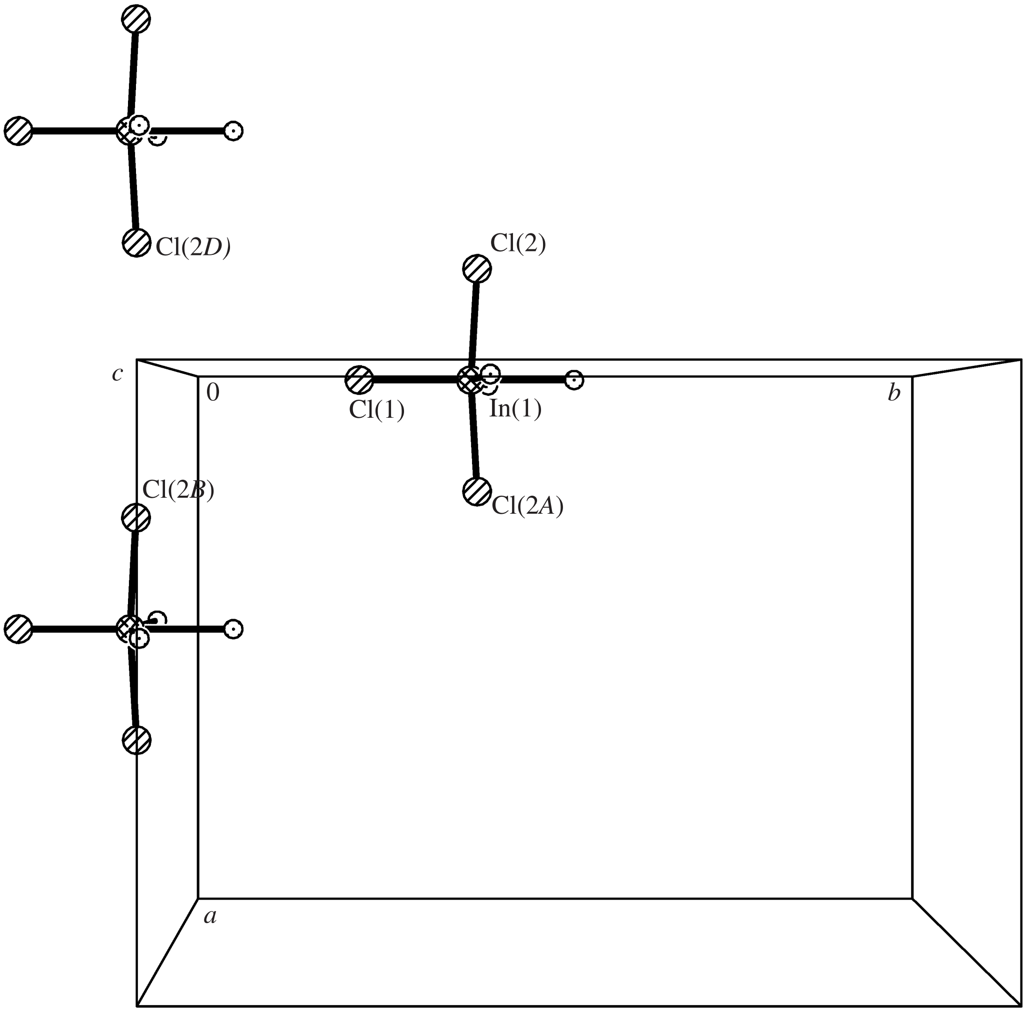

Fig. 2. Fragment of structure **III** (spacings Cl(1)···Cl(2*B*,*D*) 5.68, Cl(2*B*)···Cl(2*D*) 5.97 Å).

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