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Supramolecular Ensembles of Indium Thiocyanates with the $[K(18C6)]^+$ Complexes

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Abstract—Supramolecular ensembles containing cations $[K(18C6)]^+$ and anions $[In(NCS)_6]^{3-}$ were isolated from the $InCl_3$–KNCS–18C6–CH_3OH system. The associates were identified by the data of elemental analysis, IR spectra, and X-ray phase analysis. The X-ray diffraction analyses for $[K(18C6)]_2[In(MeOH)(NCS)_5]$ and $K[K(18C6)]_2[In(NCS)_6]$ showed the formation of heterometallic polymer fragments due to the bridging coordination of the NCS groups In–NCS–K.

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INTRODUCTION

We earlier [1–3] considered the regularities of the self-organization of the halide aqua complexes and thiocyanates of the tricharge Ga, In, and Sc cations with the 18C6 macrocycle into supramolecular ensembles. During the synthesis, when crown ether incorporates into the crystal structure as free molecules (acceptors of hydrogen atoms in hydrogen bonds), the macrocycles are associated with donors of hydrogen atoms, namely, molecular, cationic, or anionic gallium, indium, and scandium aqua complexes.

However, a different situation is observed in solutions, where the cationic complexes $[M(18C6)]^+$ can be formed. These complexes recognize anionic forms of metal complexes even in an acido ligand deficient [2, 4].

In the present work, we studied the formation of supramolecular ensembles of the $K[(18C6)]^+$ cationic complexes with the indium thiocyanate complexes.

EXPERIMENTAL

A solution of $InCl_3$ synthesized from indium oxide and CCl_4 was used. The commercial reagents KNCS, crown ether 18C6 (1,4,7,10,13,16-hexaoxocyclooctadecane (Aldrich)), MeOH, and diethyl ether were used as received.

Indium was determined trilonometrically in an acetate buffer with Xylene Orange as the indicator. The content of the thiocyanate ion was determined by thiocyanometric titration.

IR spectra were recorded on a Specord IR-75 spectrometer in the region from 400 to 4000 cm^{-1} (suspensions in Nujol, KBr glasses).

The X-ray phase analysis was carried out on a STOE STADI P diffractometer (Cu$K_{\alpha 1}$ radiation, Ge monochromator).

Synthesis 1. A weighed sample of KNCS (0.5874 g, 6.04 mmol) was dissolved in MeOH (10 ml). An aqueous solution of $InCl_3$ (1.0 mmol, 0.3 ml) was added. Potassium chloride that formed was filtered off on a glass filter, and the resulting solution was mixed with a solution of 18C6 (0.5240 g, 2.0 mmol) in MeOH (2 ml). Weakly colored crystals were obtained after isothermal evaporation. They were separated on a glass filter washing with MeOH and dried in a vacuum desiccator above silica gel (first crystallization). The yield was 0.57 g.

The solid pink phase was formed in the mother liquor (second crystallization). The phase was transferred onto the glass filter and washed with diethyl ether. Next day the solid phase gained a saturated yellow color. The yield was 0.28 g.

First crystallization:

For $C_{42}H_{76}InK_3N_6O_{20}S_6$ (FW = 1406.8)		
anal. calcd. (%:	In, 8.16;	NCS, 24.73.
Found (%):	In, 8.35;	NCS, 24.54.

IR, cm^{-1}): 3250–3520 $\nu(H_2O)$, 2070 ν(CN), 1610 $\delta(H_2O)$, 1090 ν_{as}(COC), 940 ν(COC), 830 $\nu(CO)^+$, 720 ν(CS), 480 δ(NCS).

Second crystallization:

For $C_{42}H_{72}InK_3N_6O_{18}S_6$ (FW = 1372.8)

anal. calcd. (%):	In, 8.36;	NCS, 25.35.
Found (%):	In, 8.76;	NCS, 25.57.

IR, cm^{-1}): 2070 ν(CN), 1090 ν_{as}(COC), 950 ν(COC), 830 $\nu(CO)^+$, 710 ν(CS.

A single crystal of $[K(18C6)]_2[In(MeOH)(NCS)_5]$ (**I**) suitable for X-ray diffraction analysis was selected from the product of the second crystallization.

Synthesis 2. A weighed sample of KNCS (0.5728 g, 5.9 mmol) was dissolved in MeOH (10 ml). An aqueous solution of $InCl_3$ (1.0 mmol, 0.3 ml) was added, and KCl that formed was filtered off on a glass filter. The resulting solution was mixed with a solution of 18C6 (0.2646 g, 2.0 mmol) in MeOH (2 ml). A pinkish solid phase was formed after isothermal evaporation and treated similarly to synthesis 1, washing with MeOH. The yield was 0.45 g.

For $C_{30}H_{48}InK_3N_6O_{12}S_6$ (FW = 1108.72)

anal. calcd. (%):	In, 10.35;	NCS, 31.44.
Found (%):	In, 11.20;	NCS, 34.8.

IR, cm^{-1}): 2050 ν(CN), 1090 ν_{as}(COC), 940 ν(COC), 830 $\nu(CO)^+$, 700 ν(CS).

Single crystals, whose X-ray diffraction analysis showed that these were the $K[K(18C6)]_2[In(NCS)_6]$ (**II**) polymer (**II**), were obtained from the mother liquor of synthesis 2.

The X-ray diffraction analyses were carried out for compounds **I** and **II** (Bruker AXS SMART 100 diffractometer, MoK_α radiation, graphite monochromator, ω scan mode) [5]. A semiempirical absorption correction was applied (SADABS) [6]. Structures **I** and **II** were solved by a direct method. Aliphatic hydrogen atoms were calculated geometrically, and the hydrogen atom of the alcohol group in compound **I** was not located. The structure was refined by the full-matrix least-squares method in the anisotropic approximation, and hydrogen atoms were taken into account by the riding model. All calculations were performed using the SHELXS-97 [7] and SHELXL-97 [8] program packages. The absence of the inversion center in structure **I** was checked by the PLATON program [9].

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

The coordinates of atoms and other parameters of structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (nos. 705832 and 705833 for compounds **I** and **II**, respectively; deposit@ccdc.cam.ak.uk).

Selected crystallographic data and results of refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Formula	$C_{30}H_{52}InK_2N_5O_{13}S_5$	$C_{30}H_{48}InK_3N_6O_{12}S_6$
Temperature, K	296	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/m$
a, Å	8.6645(4)	10.8889(9)
b, Å	21.6115(10)	14.9077(13)
c, Å	13.4479(6)	15.8645(13)
β, deg	104.9940(10)	101.6463(13)
V, Å^3	2432.42(19)	2522.2(4)
Z	2	2
ρ(calcd), g/cm^3	1.426	1.461
μ, m^{-1}	0.928	1.019
Crystal sizes, mm	0.40 × 0.30 × 0.25	0.18 × 0.15 × 0.11
θ, deg	1.57–30.00	1.89–30.00
Collected reflections	16580	29677
Independent reflections	9889	7602
R_{int}	0.027	0.0234
Reflections with $I > 2\sigma(I)$	7064	5939
Number of refined parameters	504	283
Goodness-of-fit (F^2)	1.020	1.047
R_1, wR_2 ($I > 2\sigma(I)$)	0.0441, 0.0934	0.0403, 0.1028
R_1, wR_2 (all reflections)	0.0711, 0.1074	0.0544, 0.1173
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.54, –0.39	0.67, –0.71

RESULTS AND DISCUSSION

The compounds in which the NCS^- to In ratio is 6, according to the elemental analysis data, were obtained in synthesis 1 by the first and second crystallizations. The intense absorption band at 2070 cm^{-1} in the IR spectrum indicates the N-coordination of the thiocyanate ion by indium. The absorption band at 1090 cm^{-1} agrees with the presence of 18C6. It is interesting that the absorption bands for the water molecules (3250–3520 and 1610 cm^{-1}) appear only in the spectrum of the first crystallization product, and these bands are absent from the second crystallization product.

Since the obtained ratio NCS^- : In is 6, it can be assumed that the internal sphere of indium is saturated and the water molecules do not enter into the coordina-

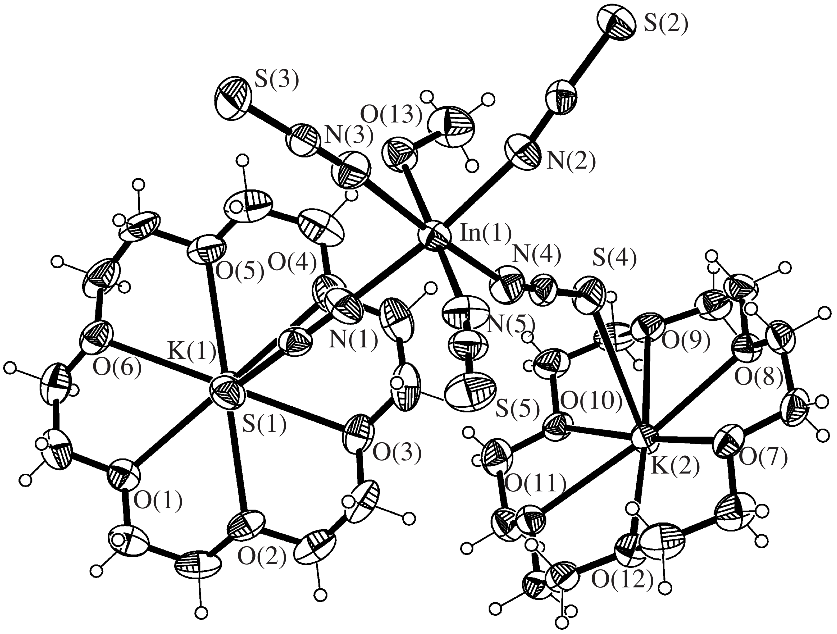

Fig. 1. Fragment of the structure $K(18C6)]_2[In(MeOH)(NCS)_5$ (**I**).

tion sphere but form a crystalline hydrate of the supramolecular ensemble $[K(18C6)]_3[In(NCS)_6] \cdot 2H_2O$, which is isolated in the first crystallization (anhydrous analog $[K(18C6)]_3$ $[In(NCS)_6]$ is formed in the second crystallization). Correctness of this assumption is confirmed by the X-ray diffraction analysis of impurity single crystals of compound $K(18C6)]_2[In(MeOH)(NCS)_5$, which was isolated from the second crystallization product.

Structure **I** is formed by the complex cations $[K(18C6)]^+$ and anions $[InMeOH(NCS)_5]^{2-}$ (Fig. 1). All the five In–N bond lengths of the pseudooctahedral environment of the indium atom coincide with an accuracy of 3σ (2.155(5)–2.170(5) Å).

The coordination polyhedron of each of the two potassium atoms is a hexagonal bipyramid formed by six oxygen atoms of the crown ether in the base and two sulfur atoms of the thiocyanate ions in the apical positions (Fig. 2). The potassium atoms shift from the root-mean-square planes of the coordinated oxygen atoms of the crown ethers by 0.10 and 0.17 Å for K(1) and K(2), respectively.

Each anion in structure **I** is bonded with four cations, and each cation is bound to two anions. This interaction, along with the ratio of cations and anions 2 : 1 in structure **I**, determines the layered structure (Fig. 2). The S(5) atom that remained “free” is involved in the formation of the O(13)–H···S(5) hydrogen bond ((O···S 3.193 Å, angle In–O···S 116.9°) joining the layers into the framework.

Compound **I** is an impurity in synthesis 1. The comparison of the X-ray pattern of the second crystallization product in synthesis 1 and the theoretical X-ray pattern calculated from the data for single crystal **I** (Fig. 3) showed that the surface area of the strongest peak in the X-ray pattern of compound **I** is less than 3% of the surface area of the peak from the synthesis product. It can be asserted that the resulting mixture contains more than two compounds, because the attempts to index the X-ray pattern were unsuccessful. Note that crystals **I** decompose in air with time.

Unlike synthesis 1, synthesis 2 was carried out at the ratio 18C6 : In = 1 (NCS^- : In = 6). According to the elemental analysis data, the NCS^- : In ratio in the product obtained is 6. The intense absorption band at 2050 cm^{-1} in the IR spectrum indicates the N-coordination of the thiocyanate ion by indium. The absorption band at 1090 cm^{-1} is consistent with the presence of 18C6. The IR spectrum contains no absorption bands $\nu(H_2O)$.

Structure **II** is formed by the complexes cations $[K(18C6)]^+$, anions $[In(NCS)_6]^{3-}$, and potassium cations. All the three crystallographically independent potassium atoms, as well as the indium atom, lie on the plane *m*. Two of the three potassium atoms coordinate the crown ether molecules, and the third atom (K(3)) has a pseudooctahedral environment formed by the sulfur atoms of the thiocyanate ions (Fig. 4). The K(3) atom and the complex anion form infinite chains along the *x* axis. The K(1) and K(2) potassium atoms complete the coordination by one and two sulfur atoms, respectively. The $[K(1)(18C6)]^+$ fragment approaches to the chain from the side of one S(4) sulfur atom, whereas the $[K(2)(18C6)]^+$ fragment is equally remote from two atoms S(3,3*A*). Naturally, in the latter case, the carbon atoms of the crown ether approach to the sulfur atom. To minimize the repulsion, the K(2) atom shifts from

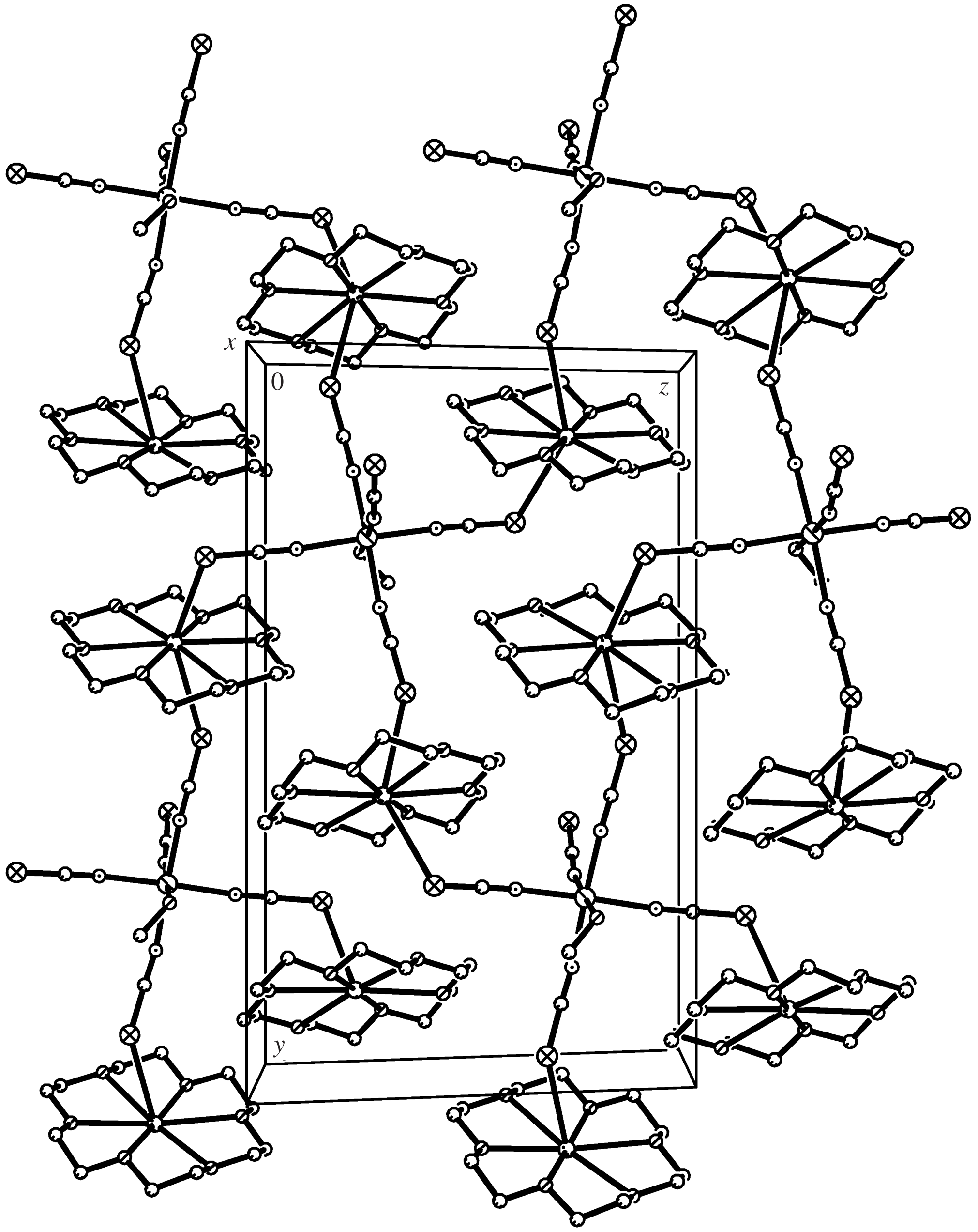

Fig. 2. Projection of structure **I** along the *x* axis.

the root-mean-square plane formed by the oxygen atoms of “its” crown ether by 0.82 Å (the K(1) atom shifts only by 0.02 Å). Nevertheless, the shortest S···C(18C6) contacts are 3.91 and 4.09 Å for S(3) and S(4), respectively. The K(1)–S(4) bond length is of the same order as K(3)–S (3.24 and 3.27–3.32 Å, respectively). The K(2)–S(3) distance (3.82 Å) can reasonably be explained as the secondary interaction. The differences in the K–S interactions of two cations are observed for the geometric parameters of the crown ethers. The OCCO torsion angles of 18C6 coordinated by the K(1) atom range from 67.5° to 67.7°, whereas in the second fragment the values of the two OCCO angles are 68.5°, while the other four angles are 61.2°.

The product of synthesis 2, as in the case of synthesis 1, is heterogeneous (Fig. 5). The content of crystals **II** in this product is about 40%. The peaks of the reaction products, which remained after the theoretical X-ray pattern of compound **II** was subtracted, are not indexed. Therefore, the reaction product contains at least three compounds.

It should be mentioned that with a decrease in the 18C6 to K ratio from 2 to 6 in synthesis 1 to 1 : 6 in syn-

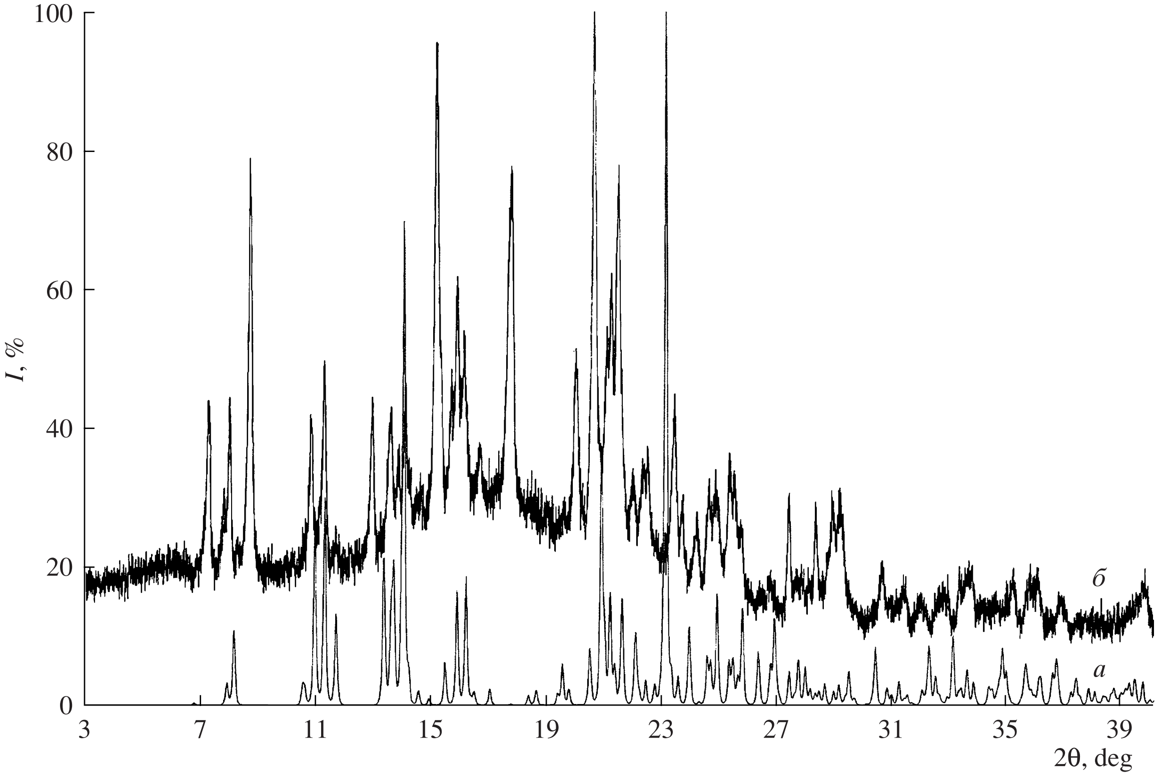

Fig. 3. X-Ray diffraction patterns of the (a) $[K(18C6)]_3[In(NCS)_6] \cdot 2H_2O$ powder and (b) $[K(18C6)]_2[In(MeOH)(NCS)_5]$ single crystal.

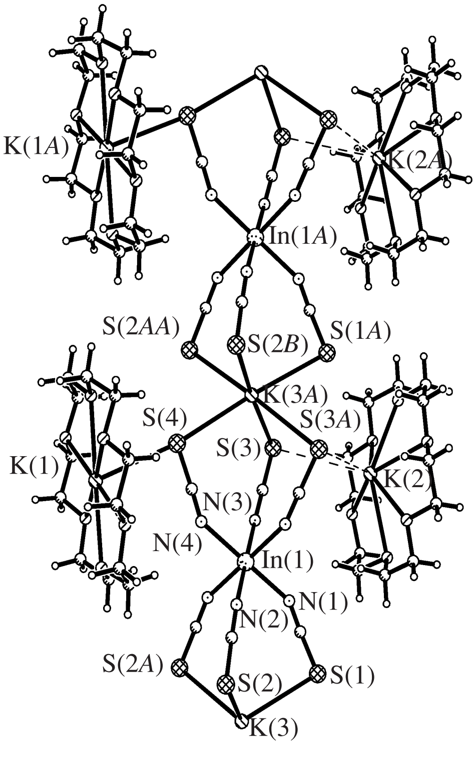

Fig. 4. Fragment of the structure $K[K(18C6)]_2[In(NCS)_6]$ (**II**).

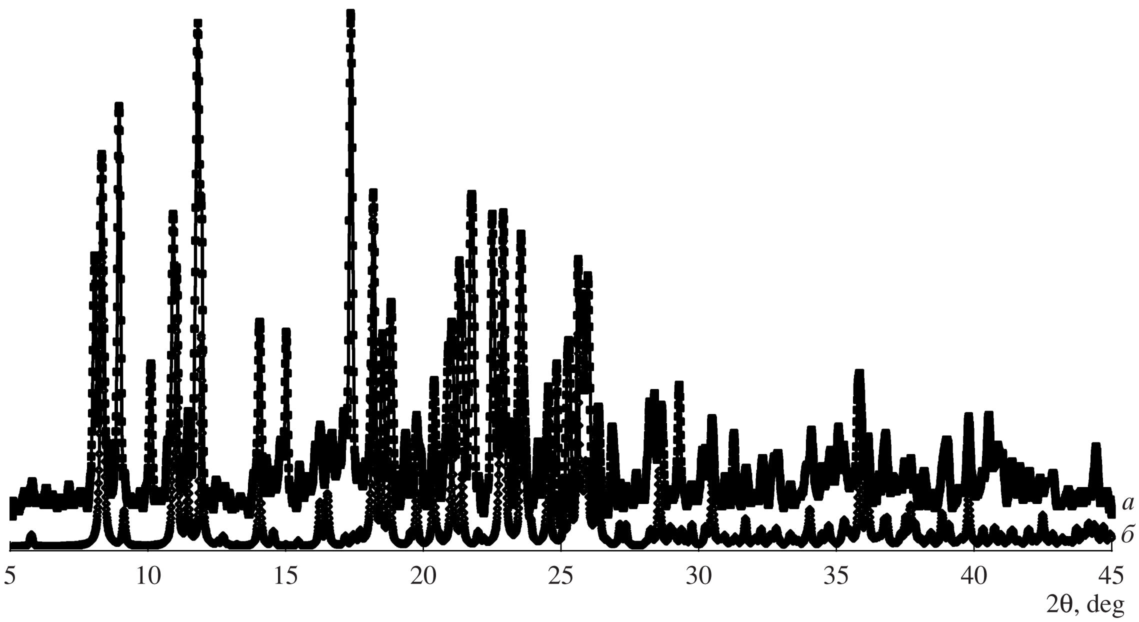

Fig. 5. X-Ray diffraction patterns of the (a) product of synthesis 2 and (b) isolated single crystals $K[K(18C6)]_2[In(NCS)_6]$.

thesis 2 a deficient of the macrocycle in the reaction medium results in the insertion of the free potassium cation into the heterometallic chain binding the indium and potassium cations by the NCS bridging group.

In spite of the seeming structural rigidity, the thiocyanate pseudooctahedral complexes are rather labile: the InNC bond angles vary in two considered structures from 147.4° to –175.6°. The structural diversity of the $[K(18C6)]^+$ cationic complex is described by one parameter: the deviation of the potassium atom from the root-mean-square plane of the oxygen atoms of the crown ether. The combination of two structurally labile fragments in the solution is a reason for the heterogeneity of the crystalline reaction products. The difference in the solubility of the complexes can lead to the situation when the single crystal suitable for X-ray diffraction analysis gives an impurity product, and the heterogeneity of the finely crystalline phase does not allow one to identify all reaction products.

Thus, the heterogeneous products are formed, as a rule, in syntheses 1 and 2, when the $[K(18C6)]^+$ cations are present in the reaction solutions. The primary crystallization of the hydrate $[K(18C6)]_3[In(NCS)_6] \cdot 2H_2O$ is due, most likely, to a lower solubility compared to that of the $[K(18C6)]_3[In(NCS)_6]$ complex, which is the major component of the second crystallization. The heterometallic polymeric fragments In–NCS–K are formed in the impurity structures $[K(18C6)]_2[In(MeOH)(NCS)_5]$, and $K[K(18C6)]_2[In(NCS)_6]$ due to the bridging function of the NCS groups. It cannot be excluded that similar polymer motifs are also observed in the structures $[K(18C6)]_3[In(NCS)_6] \cdot 2H_2O$ and $[K(18C6)]_3[In(NCS)_6]$.

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REFERENCES

1. Ilyukhin, A.B. and Petrosyants, S.P., *Koord. Khim.*, 2007, vol. 33, no. 4, p. 275 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 33, no. 4, p. 265].
2. Petrosyants, S.P. and Ilyukhin, A.B., *Koord. Khim.*, 2007, vol. 33, no. 10, p. 747 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 33, no. 10, p. 734].
3. Ilyukhin, A.B., Dobrokhotova, Zh.V., and Petrosyants, S.P., *Koord. Khim.*, 2008, vol 34, no. 9, p. 651 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 34, no. 9, p. 641].
4. Petrosyants, S.P. and Ilyukhin, A.B., *Koord. Khim.*, 2007, vol. 33, no. 3, p. 163 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 33, no. 3, p. 155].
5. *SMART (control) and SAINT (integration) Software. Version 5.0*, Madison (WI, USA): Bruker AXS Inc., 1997.
6. Sheldrick, G.M., *SADABS. Program for Scaling and Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1997.
7. Sheldrick, G.M., *SHELXS-97. Program for the Solution of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
8. Sheldrick, G.M., *SHELXL-97. Program for the Refinement of Crystal Structures*,Göttingen (Germany): Univ. of Göttingen, 1997.
9. Spek, A.L., *J. Appl. Crystallogr.*, 2003, vol. 36, no. 1, p. 7.