

Cobaltocene intercalate of the layered compounds $\text{SnS}_x\text{Se}_{2-x}$

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Received 15 December 1986

The layered $\text{SnS}_x\text{Se}_{2-x}$ ($0 \leq x \leq 2$) compounds react with cobaltocene vapour forming polycrystalline layer-type complexes with the composition of $\text{SnS}_x\text{Se}_{2-x} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$. Intercalates have been studied by X-ray diffraction analysis and infrared absorption spectroscopy. Cobaltocene forms molecular monolayers between adjacent slabs of the host crystal structure, the fivefold symmetry axes of cobaltocene molecules lying parallel to the layers. The intercalation process involves an electron donation to the host, the cobaltocene being present as cobalticenium cation.

Слоистые соединения со строением, отвечающим формуле $\text{SnS}_x\text{Se}_{2-x}$ ($0 \leq x \leq 2$), реагируют с газообразным кобальтоценом, образуя поликристаллические слоистые комплексы типа $\text{SnS}_x\text{Se}_{2-x} \cdot 0,33\text{Co}(\text{C}_5\text{H}_5)_2$. Эти комплексы, возникающие в результате интеркаляции, были исследованы рентгенографическим методом и были изучены их инфракрасные спектры. Кобальтоцен образует в слоистой структуре решетки-хозяина мономолекулярные слои, и его молекулы ориентированы так, что их главная ось симметрии направлена параллельно пластам. Металлоцен существует в решетке в виде катиона $[\text{Co}(\text{C}_5\text{H}_5)]^+$. Перенос электрона из молекул-гостей на решетку является неотделимой частью процесса интеркаляции.

A number of layer metal dichalcogenides have been shown recently to react with metallocene to form intercalation compounds. Only metallocenes with a low first ionization potential were found to react although that condition is not a sufficient one.

The present work was undertaken to investigate intercalations of cobaltocene in the layered structures of SnS_2 , SnSe_2 , and $\text{SnS}_x\text{Se}_{2-x}$ ($0 \leq x \leq 2$) and to obtain some information about the unit-cell parameters of intercalates, about the orientation of the guest species with respect to the layers, and about the charge transfer from the guest molecules to the structure of the host.

All the host structures — SnS_2 , SnSe_2 , and $\text{SnS}_x\text{Se}_{2-x}$ [1, 2] — are isomorphous members of a group of compounds which crystallize in the characteristic CdI_2 layer structure. The atomic stacking sequence is — XSnX—XSnX— (X is S or Se). Since primary valency is satisfied within the sandwich — XSnX— only weak van der Waals forces hold adjacent layers together. A schematic representation of this structure is shown in Fig. 1 (A).

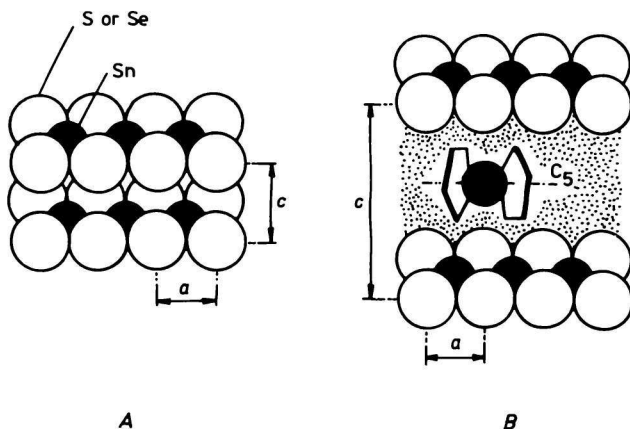


Fig. 1. Schematic representation of the layered structure of $\text{SnS}_x\text{Se}_{2-x}$ ($0 \leq x \leq 2$) (A) and $\text{SnS}_x\text{Se}_{2-x} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$ (B).

Experimental

The polycrystalline $\text{SnS}_x\text{Se}_{2-x}$ ($x = 2, 1.5, 1, 0.5,$ and 0) compounds were prepared (at 850°C , for 48 h) in evacuated silica ampoules from the stoichiometric amounts of elements (5 N purity) [1]. Powdered host phases were obtained by the pulverization in a vibration mill. The powder fraction with particle size from 0.01 mm to 0.02 mm was used.

Cobaltocene was prepared in a standard way [3] and purified by vacuum sublimation.

The intercalates were synthesized in evacuated glass ampoules (50 cm^3), containing *ca.* 1.5 g $\text{SnS}_x\text{Se}_{2-x}$ and 0.5 g $\text{Co}(\text{C}_5\text{H}_5)_2$. The mixture was kept at 130°C for 14 days. After this treatment unintercalated cobaltocene was sublimated into the other end of the ampoule.

The powder data were obtained with a HZG-4 X-ray diffractometer (VEB Freiburger Präzisionsmechanik, GDR) using $\text{CuK}\alpha$ (for angles $2\theta < 35^\circ$, $\lambda = 0.15418\text{ nm}$) and $\text{CuK}\alpha_1$ (for $2\theta > 35^\circ$, $\lambda = 0.15405\text{ nm}$) radiation with discrimination of the $\text{CuK}\beta$ radiation by Ni-filter. The obtained data of the lattice parameters were refined by the least-squares program minimizing $\Sigma(2\theta_{\text{exp}} - 2\theta_{\text{calc}})^2$.

IR spectra were recorded on a Perkin—Elmer 684 spectrometer in the $\tilde{\nu} = 200\text{—}4000\text{ cm}^{-1}$ range at room temperature. The samples were dispersed in nujol or fluorolube and in KBr pressed pellets.

Results and discussion

Intercalation occurs when $\text{SnS}_x\text{Se}_{2-x}$ ($0 \leq x \leq 2$) samples are treated with vapours of cobaltocene in vacuum. The X-ray patterns of $\text{SnS}_x\text{Se}_{2-x}$ disappear

completely if intercalation reaction proceeds at temperatures of 130 °C for 5 to 14 days.

The intercalates are black powders relatively stable in air at room temperature liberating cobaltocene when heated in vacuum.

The composition of all the obtained intercalates $\text{SnS}_x\text{Se}_{2-x} \cdot n\text{Co}(\text{C}_5\text{H}_5)_2$, where $n = 0.33 \pm 0.02$, was determined from the results of atomic absorption analysis (Sn and Co determination) and checked using X-ray phase analysis.

Table 1

Variation of the unit-cell dimensions a , c and volumes V of $\text{SnS}_x\text{Se}_{2-x}$ crystal structures during their cobaltocene intercalation

Compounds	Unit-cell parameters		Unit-cell volumes
	a/nm	c/nm	V/nm^3
SnS_2	0.3646*	0.5896*	0.06788
$\text{SnS}_2 \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$	0.3850**	1.1216**	0.14398
$\text{SnS}_{1.5}\text{Se}_{0.5}$	0.3697	0.5981	0.07079
$\text{SnS}_{1.5}\text{Se}_{0.5} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$	0.3886	1.1289	0.14764
SnSSe	0.3742*	0.6053*	0.07339
$\text{SnSSe} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$	0.3906	1.1363	0.15011
$\text{SnS}_{0.5}\text{Se}_{1.5}$	0.3775	0.6103	0.07532
$\text{SnS}_{0.5}\text{Se}_{1.5} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$	0.3929	1.1442	0.15294
SnSe_2	0.3811*	0.6132*	0.07714
$\text{SnSe}_2 \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$	0.3933	1.1511	0.15418

* Ref. [1] gives the following values for the unit-cell parameters of the host structures:

SnS_2 : $a = 0.3646 \text{ nm}$; $c = 0.5891 \text{ nm}$

SnSSe : $a = 0.3723 \text{ nm}$; $c = 0.6047 \text{ nm}$

SnSe_2 : $a = 0.3799 \text{ nm}$; $c = 0.6131 \text{ nm}$

** Ref. [4, 9] give parameters $a = 0.3850 \text{ nm}$ and $c = 1.122 \text{ nm}$ for the intercalated SnS_2 structure.

The crystal data of all the starting compounds and their intercalates are presented in Table 1. Intercalation leads to the increase of the dilation between the adjacent —XSnX— layers. The average value of the dilation ($\Delta c = 0.533 \text{ nm}$) indicates that the cobaltocene forms molecular monolayers between the slabs of the host crystal structure. Sterical arguments based on the size of the cobaltocene molecule [4] and the magnitude of the dilation suggest that this guest lies, with its fivefold symmetry axis, parallel to the host layers. It

Table 2

Observed infrared frequencies of η^5 -bonded cyclopentadienyl rings in cobaltocene, cobalticenium salt, and in the prepared intercalates

Compound	Medium	$\nu(\text{C—H})$ $\tilde{\nu}/\text{cm}^{-1}$	$\nu(\text{C—C})$ $\tilde{\nu}/\text{cm}^{-1}$	$\delta(\text{C—H})$ $\tilde{\nu}/\text{cm}^{-1}$	$\pi(\text{C—H})$ $\tilde{\nu}/\text{cm}^{-1}$	Ring tilt.	$\nu(\text{Co—Ring})$ $\tilde{\nu}/\text{cm}^{-1}$	Ref.	
Cobaltocene	KBr	3041 m	1412 m	1101 m	995 s	778 s	464 m	355 m	[11, 12]
Cobalticenium salt	nujol	3088 m	1413 s	1113 w	1007 s	864 s	500 m	461 m	[13]
	CHCl_3	3094 m	1419 s	1113 w	1010 s	856 s	495 m	455 m	[13]
$\text{SnS}_x\text{Se}_{2-x} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$ ($0 \leq x \leq 2$)	nujol	3091 m	1414 s	—	1006 m	858 s	497 w	458 s	—
	KBr	3093 m	1413 s	1111 w	1005 m	856 s	500 w	460 s	—

means that identically to the other systems $\text{MX}_2\text{—Co}(\text{C}_5\text{H}_5)_2$ [5—10] the cobaltocene molecules penetrate into van der Waals gaps of the host crystal structures giving the structure shown schematically in Fig. 1 (B).

The parameter a of the host crystal structure changes only a little during the intercalation, on the average $\Delta a = 0.0167$ nm. The highest change $\Delta a = 0.0204$ nm was found for the SnS_2 , the smallest $\Delta a = 0.0122$ nm for the SnSe_2 intercalated crystal structure.

The increase of $\text{SnS}_x\text{Se}_{2-x}$ unit-cell volume during the penetration of cobaltocene molecules is remarkably constant for all the samples ($x = 2, 1.5, 1, 0.5$, and 0), and is about $\Delta V = 0.077$ nm³. It means that cobaltocene molecule occupies in the intercalate structure an effective volume 0.231 nm³ which is by 12 % greater than the one in the structure of the cobaltocene crystal ($V_m = 0.206$ nm³).

All the polycrystalline samples of intercalates $\text{SnS}_x\text{Se}_{2-x} \cdot 0.33\text{Co}(\text{C}_5\text{H}_5)_2$ ($x = 2, 1.5, 1, 0.5, 0$), measured as nujol mulls and as KBr pressed pellets, yield the same infrared spectrum. The observed absorption bands of intercalated samples corresponding with vibration modes of metallocene skeleton are presented in Table 2. The bands of cobaltocene and cobalticenium salt given in the literature are presented in the same place for comparison. It is evident that the IR spectra of intercalates correspond with those of cobalticenium ion. Transfer of charge from the guest molecules to the host crystal structure seems to be the driving force for intercalate origination in this case, too.

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Translated by J. Kalousová