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Intercalation of molybdenum disulfide with chlorobis(phenanthroline)copper(II)

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An intercalation compound of molybdenum disulfide with the copper complex $Cu^{II}(phen)_2Cl^+$ was found to form by the interaction of the MoS_2 single-layer dispersions with the complex and by the treatment of the phenanthroline intercalation compound with $CuCl_2$. The compositions and structures of the compounds formed were determined by powder diffractometry and electron microscopy.

Key words: molybdenum disulfide, single-layer dispersions, intercalation compounds, electron microscopy.

It has previously been shown[1,2] that intercalation compounds of molybdenum disulfide with metal complexes can be synthesized using single-layer dispersion of molybdenum disulfide, which are produced by hydration of crystalline $LiMoS_2$ (Eq. (1)). The formation of the MoS_2 compounds with metal complexes is based on exchange of lithium cations from the dispersion composition by complex cations and formation of solid-phase heterolayer compounds involving the MoS_2 single layers that exist in solutions.[3]

$$LiMoS_2 \xrightarrow{H_2O} [Li^+ + (MoS_2)^{x-} + (1-x)\,OH^-]_{aq} + (1-x)/2\,H_2 \quad (1)$$

$$[Li^+ + (MoS_2)^{x-} + (1-x)\,OH^-]_{aq} + ML_n{}^+ \longrightarrow (ML_n)^+{}_x(MoS_2)^{x-} \quad (2)$$

This method was used to synthesize layered compounds with the areneruthenium complexes,[3] cobalt chalcogenidephosphine clusters,[4] iron porphyrin complexes,[5] alkaline metal complexes with crown ethers,[6] and iron(II), cobalt(II), and nickel(II) trisphenanthroline and trisbipyridine complexes.[7,8]

This is not a versatile method, because sometimes the process is accompanied by complex transformations (*e.g.*, condensation to binuclear ruthenium complexes,[3] loss of some phosphine ligands by the cobalt clusters[4]) and intercalation of the transformation products. Therefore, it was of interest to examine another route for the synthesis of compounds of this class by assembling a complex in the interlayer space of solid-phase intercalation compounds of molybdenum disulfide containing organic ligands in the interlayer space.

$$[Li^+ + (MoS_2)^{x-} + (1-x)\,OH^-]_{aq} \xrightarrow{L/H^+} (HL)^+{}_xL_y(MoS_2)^{x-} \xrightarrow{M^+} (ML_n)^+{}_z(MoS_2)^{z-} \quad (3)$$

A few described reactions of single-layer dispersions with metal complexes use the complexes being reduced forms of the corresponding redox pairs (in particular, Fe^{II}/Fe^{III},[7] Ru^{II}/Ru^{III} (see Ref. 3). Taking into account the recent data[9] on the ability of the negatively charged MoS_2 layers to manifest reduction properties, we intended to study a possibility of reducing complex cations in single-layer dispersions of molybdenum disulfide and reveal specific features of intercalation of cations, which can be reduced in this system *via* reaction (2) or (3).

In the present work, we used the copper(II) complex $[Cu(phen)_2Cl]^+$ as an example to study the reduction effect of single-layer dispersions on this compound and both routes of formation of layered MoS_2 compounds involving this complex.

Experimental

The salt $LiMoS_2$ was prepared by the treatment of natural powdered MoS_2 (DM-1) with an excess of 1.6 *M* solution of *n*-butyllithium in hexane at 20 °C for 7 days followed by washing with hexane and drying *in vacuo*. The dispersion of $LiMoS_2$ (1 g L^{-1}) prepared by ultrasonication in water or an acetonitrile—water (70 : 30, vol/vol) mixture under argon.

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Intercalation compounds with 1,10-phenanthroline $(phen)_xMoS_2$ (x = 0.1, 0.3) were synthesized according to a described procedure[10] using an aqueous dispersion of MoS_2 and an aqueous solution of 1,10-phen • HCl (Aldrich). Compound with $x = 0.095$. Found (%): C, 7.63; H, 1.08; Mo, 53.36; N, 1.57. Calculated (%): C, 7.72; H, 0.45; Mo, 53.93; N, 1.01. Compound with $x = 0.295$. Found (%): C, 19.55; H, 1.22; Mo, 44.56; N, 3.47. Calculated (%): C, 19.93; H, 1.11; Mo, 45.04; N, 3.88.

The reaction of $(phen)_xMoS_2$ (x = 0.1, 0.3) with $CuCl_2$ (prepared by dehydration of $CuCl_2 \cdot 2H_2O$ under reflux in $SOCl_2$) was conducted with stirring of a suspension of $(phen)_xMoS_2$ (0.07 g) in 50 mL of a solution of $CuCl_2$ (3 moles per mole of MoS_2) in MeCN. The solid phase was filtered off, washed with MeCN, and dried *in vacuo*. Compound with x = 0.3. Found (%): C, 13.34; H, 0.77; Cl, 1.49; N, 2.25; Mo, 46.96. $Cu_{0.10}phen_{0.19}Cl_{0.09}MoS_2$.

Complex $[Cu(phen)_2Cl]BF_4 \cdot 0.5H_2O$ was synthesized according to a known procedure[11] by the addition of a solution of a mixture of $CuCl_2 \cdot 2H_2O$ (analytical grade, 0.9211 g, 5.4 mmol) and $NaBF_4$ (pure, 1.1867 g, 10.8 mmol) in water (20 mL) to a boiling solution of 1,10-phenanthroline (Aldrich, 2.1427 g, 10.8 mmol) in methanol (200 mL). The solution turned intensive green-blue. Crystals of the complex with the same color precipitated for one day were washed with water and dried *in vacuo*. Yield 2.81 g (93.7%). Found (%): C, 52.54; H, 2.75; Cl, 6.41; Cu, 12.77; N, 10.16. Calculated (%): C, 51.87; H, 3.06; Cl, 6.39; Cu, 11.44; N, 10.08. Absorption spectrum in MeCN, λ_{max}/nm: 732, 292, 269, 225, 213.

The interaction of a single-layer dispersion of MoS_2 with $[Cu(phen)_2Cl]BF_4$ was carried out by the addition with vigorous stirring of the complex as a 1% solution in MeCN in the ratio given in Table 1 to a dispersion of MoS_2 (100 mL) in a MeCN—H_2O mixture (acidified with HCl when the reaction is conducted in acidic media). After the dispersion coagulated, the precipitate was filtered off, washed with a MeCN—H_2O solution, and dried *in vacuo*. The pH value of the reaction medium was measured in the filtrate. The compositions of the compounds (see Table 1) were determined from elemental analysis data.

Table 1. Conditions of synthesis, interlayer distances (c), and composition of layered Cu—phen—MoS_2 compounds

Sample	MoS_2 : I (mole ratio)	pH	Time after synthesis /day	c/Å	Composition (mole (mole of MoS_2)$^{-1}$)
1	1 : 0.05	12.5	0	12.3	$Cu_{0.05}(phen)_{0.09}Cl_{0.01}$
			4	11.5	
			7*	9.8	
2	1 : 0.06	3	0	10.5	$Cu_{0.06}(phen)_{0.16}Cl_{0.02}$
			4*	9.8	
3	1 : 0.5	12.5	0*	13.1	$Cu_{0.25}(phen)_{0.25}Cl_{0.02}$
4	1 : 2	4.5	0	12.0	$Cu_{0.08}(phen)_{0.18}Cl_{0.03}$
			7*	11.5	
5	—**	—	5*	12.8	$Cu_{0.10}(phen)_{0.19}Cl_{0.09}$

* The diffraction pattern remains unchanged during further aging.

** The sample was prepared by the reaction of $(phen)_{0.3}MoS_2$ with $CuCl_2$.

Absorption spectra were recorded on a Uvikon 922 spectrophotometer (Kontron Instruments). Diffractometric studies were carried out on a DRON-3 diffractometer (Cu-Kα radiation, Ni filter).

High-resolution transmission electron microscopic images were obtained on a JEOL JEM-2010 instrument (resolution 0.14 nm, accelerating voltage 200 kV). Samples were deposited on perforated carbon supports mounted on standard copper grids and placed in a chamber of an electron microscope. The averaged interplanar distances were determined by Fourier analysis of the images of periodical structures. Fourier filtration was used to improve the quality of images.

Results and Discussion

The interaction of negatively charged molybdenum disulfide single layers in dispersions with the $[Cu(phen)_2Cl]^+$ complex cation (**I**) was expected to proceed *via* two routes. The first of them is the formation of layered compounds $[Cu(phen)_2Cl]^+_x(MoS_2)^{x-}$, which is not accompanied by the reduction of the complex cation.

Another reaction route can be the reduction of copper ions in the complex to Cu^I by the negatively charged layers $(MoS_2)^{x-}$ and the formation of the $[Cu(phen)_2]^+$ cation (**II**), which forms an intercalation compound $[Cu(phen)_2]^+_x(MoS_2)^{x-}$. This is based on the earlier[9] observation of the reduction of Cu^{2+} in aqueous solutions of the copper salts by the $(MoS_2)^{x-}$ layers and a comparison of the redox potentials for the copper ions ($E(Cu^{2+}/Cu^+)$ = +0.16 V) and for the complex under study ($E([Cu^{II}(phen)_2Cl]^+/[Cu^I(phen)_2]^+)$ = +0.30 V).[12]

In complex **I**, the coordination sphere of the Cu^{2+} ion contains four nitrogen atoms and one chlorine atom that form a distorted tetragonal pyramid (Fig. 1, *a*).[11] The reduction of this complex to compound **II** results in chlorine atom removal from the coordination sphere of copper, and the latter becomes tetrahedral (see Fig. 1, *b*).[13] The estimation of the minimum van der Waals thickness of a single layer of the complexes localized in the interlayer space of MoS_2 (layer thickness of intercalant Δc), which was performed using the structural data for these complexes,[11,13] gives Δc of ~6—7 and 5—5.5 Å for layered compounds with complexes **I** and **II**, respectively. The orientation of the C_2 axes of both complexes perpendicularly to the MoS_2 layers corresponds to these thickness values (see Fig. 1). Taking into account the thickness of the MoS_2 layer (6.15 Å), the periodicity in the direction perpendicular to its layers in the intercalation compounds (interlayer distance c) should be 12.2—13.2 and 11.2—11.7 Å for **I** and **II**, respectively. The maximum content of each complex in the interlayer space about 0.1 mole (mole of MoS_2)$^{-1}$ corresponds to these models.

Interaction of single-layer dispersions of molybdenum disulfide with the copper phenanthroline complexes. To

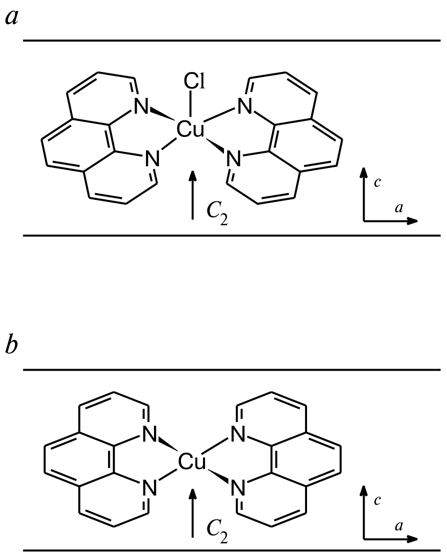

Fig. 1. Structures of the $[Cu(phen)_2Cl]^+$ (*a*) and $[Cu(phen)_2]^+$ (*b*) complexes and their assumed orientation relative to the MoS_2 layers.

confirm a possibility of the redox reaction between complex **I** and the $(MoS_2)^{x-}$ layers, a crystalline compound $Li^+(MoS_2)^-$ (4 mol mol^{-1}) was added to an acetonitrile solution of complex **I**. The color of the solution changed from blue to yellow, and the maximum in the absorption spectra shifted to 441 nm, *i.e.*, to the value characteristic of the copper(I) phenanthroline complexes.[14]

The interaction of the $(MoS_2)^{x-}$ single layers localized in single-layer dispersions (in an acetontrile—water medium) with complex **I** at different pH almost immediately produces solid black particles, which fact is typical of formation of layered molybdenum disulfide compounds from dispersions. In this case, the solution also changed its color to yellow, indicating the reduction of the complex. This phenomenon becomes especially pronounced at a low content of the complex in the reaction mixture ($\mathbf{I}/MoS_2 \approx 0.1$ mol mol^{-1}). Since the reduction ability of the $(MoS_2)^{x-}$ layers in dispersions depends on the value of their negative charge, we can conclude that dispersion (see Eq. (1)) decreases the charge of the layers compared to $LiMoS_2$ (1 e per Mo atom) but the charge, nevertheless, remains sufficient for the reduction of complex **I** in both alkaline and weakly acidic media. Noteworthy that the estimation of the charge state of the $(MoS_2)^{x-}$ ions from the composition of compounds containing Me_4N^+ and Cu^+ ions, which were obtained from single-layer dispersions, gives values of 0.3 [15] and ~0.7 e per Mo atom, respectively.[16]

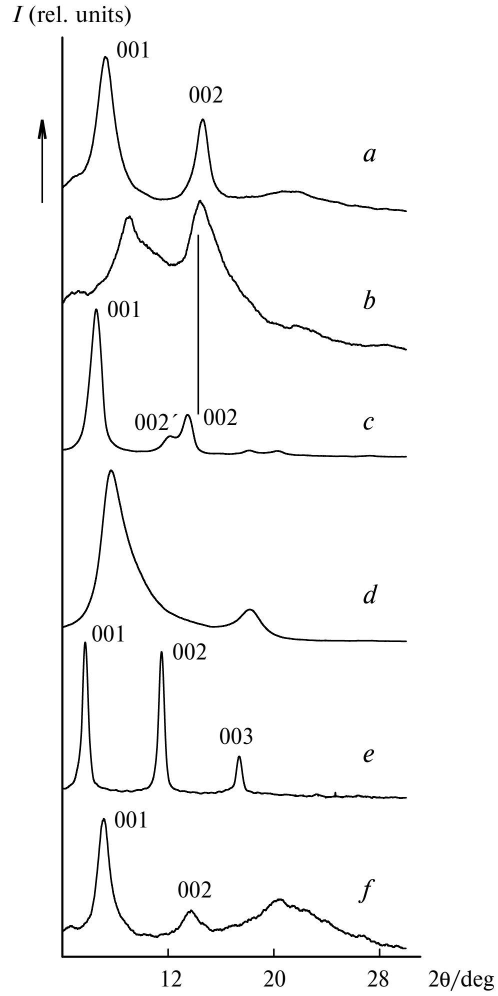

Fig. 2. Diffraction patterns of the intercalation compounds prepared at a low content of the complex in an alkaline medium (sample **1**) after isolation from the reaction mixture (*a*) and aged for 7 days (*b*) and prepared in an excess of the complex in alkaline (sample **3**, *c*) and acidic (sample **4**, *d*) media and the diffraction patterns of $(phen)_{0.3}MoS_2$ (*e*) and the product of its reaction with $CuCl_2$ (sample **5**, *f*). Vertical line shows the position of reflection 001 of Cu_xMoS_2.

According to the powder diffraction data, the precipitates isolated are poorly ordered substances with broadened diffraction lines, whose intensity decreases sharply with an increase in the reflection order (Fig. 2). For the compounds prepared in an alkaline medium at a low content of the complex in the reaction mixture (<0.1 mole (mole of $MoS_2)^{-1}$, see Table 1, sample **1**), the diffraction reflections immediately after isolation of the precipitate correspond to an interplanar distance of 12.5 Å, which is expected for a compound with complex **I** (see Fig. 2, *a*). However, after aging the compounds for several days, the reflections became asymmetric and reflection 001 shifts toward shorter distances, reaching 9.7—10 Å in 7 days (see Fig. 2, *b*). The latter value corresponds to the interlayer distance of the compound containing phenanthroline molecules oriented parallel to the MoS_2 layers.[10] The second reflection (see Fig. 2, *b*), most likely, is a superposition of reflections of the non-intercalated MoS_2 (6.2 Å) and Cu_xMoS_2 (6.3—6.4 Å). Heating of the compounds *in vacuo* results in the disappearance of the phase with c = 9.7—10 Å due to phenanthroline removal from the interlayer space, and only the reflection with c ~6.3 Å remains in the diffraction pattern. At a low content of the complex in a mixture (<0.1 mole (mole of MoS_2)$^{-1}$), the same regularities are observed for the compounds obtained in neutral and weakly acidic media. However, the main reflection shifts to c ~9.8 Å already upon washing and drying of the compounds (see Table 1, sample **2**).

With an increase in the amount of the complex in a mixture, the interlayer distance in the compounds prepared at different pH elongates and, according to the diffractometric data, their phase composition remains unchanged for a long time (see Table 1, samples **3** and **4**). Based on the reflection widths, in an excess of the complex, the more ordered compounds are formed in an alkaline medium (see Fig. 2, *c*). However, they are not single-phase. In addition to the main phase (c = 13.1 Å), line 002 (7.5 Å) referred to the phase with c ~15 Å also appears in the diffraction patterns. This c value is characteristic[10] of the intercalation compound with phenanthroline molecules inclined to the MoS_2 layers. The presence of the latter phase indicates that the complex dissociates under the experimental conditions, which can result in the intercalation of both liberated phenanthroline molecules and copper ions without ligand. Since the positions of reflection 002 of the main phase (6.55 Å) and reflection 001, which is expected from ternary sulfide Cu_xMoS_2 in this case (6.3—6.4 Å) are close, we cannot conclude unambiguously the presence of Cu_xMoS_2 by the diffraction data.

No reflections of Cu_xMoS_2 are observed in the diffraction patterns of the compounds prepared in a weakly acidic medium in an excess of the complex. However, the considerable broadening and asymmetry of the reflections can indicate that the intercalation compounds contain areas with different interlayer distances and small coherent regions (see Fig. 2, *d*).

The data on the composition of the obtained substances (see Table 1) show that the phen : Cu ratio in these compounds is close to two, except for sample **3** with a probability of formation of the Cu_xMoS_2 phase already in the reaction system. At the same time, the Cl : Cu ratio is much lower than unity, which indicates, most likely, the formation of a mixture of compounds $[Cu(phen)_2Cl]_xMoS_2$ and $[Cu(phen)_2]_xMoS_2$.

The observed facts can be interpreted as follows. Cationic complexes **I**, which were incorporated into the solvate shell of the $(MoS_2)^{x-}$ single layers in dispersions due to exchange of lithium cations present in these dispersions, are simultaneously involved in two processes: they are reduced by the $(MoS_2)^{x-}$ single layers to form complex cations **II** and participate together with the latter in the formation of a layered compound. The reduction process ceases, most likely, when the charge decreases to some critical value. Therefore, a mixture of complexes **I** and **II** gets into the interlayer space of the forming layered compounds, and the fraction of **I** increases with an increase in its content in the reaction mixture. In addition, an enhanced copper content in sample **3** indicates that in an alkaline medium these processes are accompanied by the dissociation of the complex favoring intercalation of copper ions without ligand.

The structural evolution of the compounds isolated from the reaction mixture shows that complex **II** is unstable in the interlayer space. The phenanthroline ligands are gradually replaced from the coordination sphere of the copper atoms by the sulfur atoms of molybdenum disulfide, resulting in the appearance and growth of areas containing phenanthroline molecules, which are oriented parallel to the layers (c = 9.8 Å), in particles of the compounds. This assumption agrees with the behavior of the reaction system in which a solution of complex **II** was added to the single-layer dispersion. In this case, particles of a layered compound are formed rapidly. However, the phase with c = 11.2 Å is detected only in the freshly isolated compounds and is completely transformed into the phase with c = 9.8 Å within several days.

Assembling of copper complexes in the interlayer space of intercalation compounds of molybdenum disulfide with phenanthroline. To study the formation of copper complexes in the interlayer space of ligand-containing molybdenum disulfide (see Eq. (3)), we prepared the intercalation compounds of MoS_2 with phenanthroline with different compositions and different packings of the "guest" molecules: $phen_{0.1}MoS_2$ (c = 9.7 Å, Δc = 3.5 Å) and $phen_{0.3}MoS_2$ (c = 15.4 Å, Δc = 9.2 Å). For this purpose, we used an earlier described method[10] based on the interaction of the salt phen • HCl with single-layer dispersions and resulting in simultaneous intercalation of the protonated and neutral phenanthroline molecules.

$$[Li^+ + (MoS_2)^{x-} + (1-x)\,OH^-]_{aq} \longrightarrow$$
$$\longrightarrow (phenH)_y(phen)_zMoS_2 \qquad (4)$$

It was found that stirring of the $phen_{0.3}MoS_2$ suspension in an acetonitrile solution of $CuCl_2$ for 5 days decreases the interlayer distance in the compound from 15.4 Å (see Fig. 2, *e*) to 12.8 Å (see Fig. 2, *f*), which agrees with the value expected for the intercalation compound with complex **I**. The fact that molecules of this complex are assembled in the interlayer space is indicated by the composition of the pretreated compound ($Cu_{0.1}(phen)_{0.19}Cl_{0.09}MoS_2$), which agrees with the presence of ~0.1 mole of the $Cu(phen)_2Cl^+$ complex per mole of MoS_2. Based on this composition, we can conclude that the content of the protonated phenanthroline molecules in the starting compound was also 0.1 mole (mole of MoS_2)$^{-1}$ (~1/3 of the total content of the "guest") and the formation of the complex in the layered compound can be described by the ion-exchange reaction

$$(\mathrm{phenH}^+)_{0.1}(\mathrm{phen})_{0.2}(\mathrm{MoS_2})^{0.1-} + 0.1\ \mathrm{Cu}^{2+} + 0.1\ \mathrm{Cl}^- \xrightarrow{\mathrm{phenH}^+}$$

$$\longrightarrow [\mathrm{Cu(phen)_2Cl}^+]_{0.1}(\mathrm{MoS_2})^{0.1-} + 0.1\ \mathrm{phenH}^+. \qquad (5)$$

It follows from the composition of the prepared compound that the $(\mathrm{MoS_2})^{x-}$ layers, whose vacant orbitals have only one excess electron per 10 Mo atoms ($x = 0.1$), do not reduce complex cation **I**, and its reduction in dispersions confirms that the layers bear a higher charge.

A similar treatment of $(\mathrm{phen})_{0.1}\mathrm{MoS_2}$ did not change the structural parameters of this compound during at least three weeks. This is related, most likely, to steric hindrance for complex assembling in a thin (Δc = 3.5 Å) intercalated layer or to an insufficient amount of the protonated phenH^+ molecules in this layer (and, correspondingly, to a too small negative charge of the matrix layers) for the ion-exchange reaction with the Cu^{2+} ions to occur.

Electron microscopic study. Previously published data on the microstructure of the layered $\mathrm{MoS_2}$ compounds obtained by electron microscopy concern only the compounds with cobalt complexes[4] and iron hydroxides[17] and compounds with bipyridine and hexamethylenetetraamine.[18] In the case of cobalt complexes, exposure to the electron beam resulted[4] in the complete loss of phosphine ligands and a sharp decrease in interlayer distances. Therefore, in the present study, special attention was given to the selection of regimes providing stability of structural parameters of the compounds under experimental conditions.

The high-resolution images of the side projections of particles of the starting 2H-$\mathrm{MoS_2}$ and intercalation compounds with phenanthroline $(\mathrm{phen})_{0.3}\mathrm{MoS_2}$ and the copper complex (see Table 1, sample **4**) are shown in Fig. 3. It is seen that all compounds have a pronounced layered structure, which appears as an array of lines with periodical contrast. Unlike crystalline $\mathrm{MoS_2}$ (see Fig. 3, *a*), for the intercalation compounds this structure contains defects of a dislocation type in layer stacking. Comparison with results of the recent study[18] of the $\mathrm{MoS_2}$ compounds with organic molecules shows that this type of defects is characteristic of compounds prepared from the single-layer dispersions of molybdenum disulfide. Moreover, an additional factor of disordering appears in the case of the intercalation compounds, namely, irregularities in filling of the interlayer space with a "guest." For the phenanthroline-containing compound, the average interlayer distance in particles of the sample determined from the Fourier images is 15 Å, which agrees well with X-ray diffactometric results and the earlier[10] proposed model of packing (inclined to the $\mathrm{MoS_2}$ layers) of the planar phen molecules forming an angle of ~60° with the layers. The most part of individual distances between the adjacent layers is 15 Å, although deviations of 1—3 Å toward higher or lower values are also observed, which can be caused by a change in the inclination of the phenanthroline molecules to the layers in particular regions (see Fig. 3, *b*).

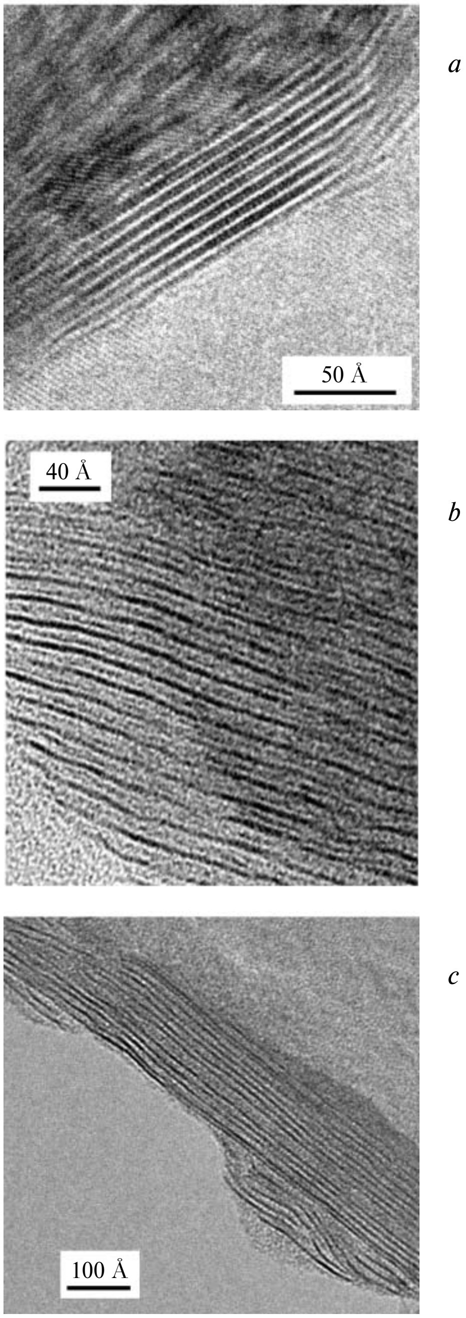

Fig. 3. High-resolution microscopic images of the side projections of particles of crystalline 2H-$\mathrm{MoS_2}$ (*a*), $(\mathrm{phen})_{0.3}\mathrm{MoS_2}$ (*b*), and intercalation compound $\mathrm{Cu_{0.08}(phen)_{0.18}Cl_{0.03}MoS_2}$ (sample **4**, *c*).

Microstructural disordering increases sharply in particles of the compound prepared by intercalation of the copper complex (see Fig. *c*). For example, for an average interlayer distance in a particle by the Fourier images of ~10.5 Å, its different areas contain interlayer distances of 12.3 Å (complex **I** was intercalated) and also distances of ~6 Å (no intercalant or copper ions are intercalated), 9—10 Å (phen molecules parallel to the layers), 11.5 Å (complex **II**), and 14.5 Å (phen molecules inclined to the layers).

Microheterogeneity of this compound and the local parameters of its structure agree with the X-ray diffractometric data and confirm the mechanism proposed for the intercalation of the complex and conjugated with its partial decomposition, although it cannot be excluded that this heterogeneity is additionally enhanced under the electron beam action in a microscope.

The atomic structure of the MoS_2 layers themselves in the compounds prepared by single-layer dispersion was not determined so far. The EXAFS and electron microdiffraction data in some works[16,19—22] suggest that the structure of the initial crystalline 2H-MoS_2 compound (space group $P6_3/mmc$, a = 3.16 Å, c = 2•6.15 Å) is modified when a negative charge is transferred to its layers during preparation of dispersions and intercalation compounds. This results in the appearance of nonequivalent Mo—Mo distances in the *ab* plane of the layer. The distortions caused by charge density waves are manifested as the appearance of superstructural ordering in the layers. It is impossible to determine the exact structural motif of distortions and the area of their propagation by X-ray diffractometry because of the low structural ordering of the compounds. Different models of distortions leading to the appearance of chains in the molybdenum sublattice were proposed on the basis of calculations (for details, see Ref. 23).

To reveal superstructural orderings, we obtained images of the frontal projections of particles of the starting crystalline 2H-MoS_2 and intercalation compounds with the complex oriented perpendicularly to the direction [001] (Fig. 4). As can be seen from Fig. 4, *a*, the Fourier image of a 2H-MoS_2 particle contains only one array of reflections and corresponds to the basal periodicity with the parameter a = 3.16 Å. In the case of the intercalation compound, the Fourier image exhibits both the set of images corresponding to the basal periodicity a {1 0 0}

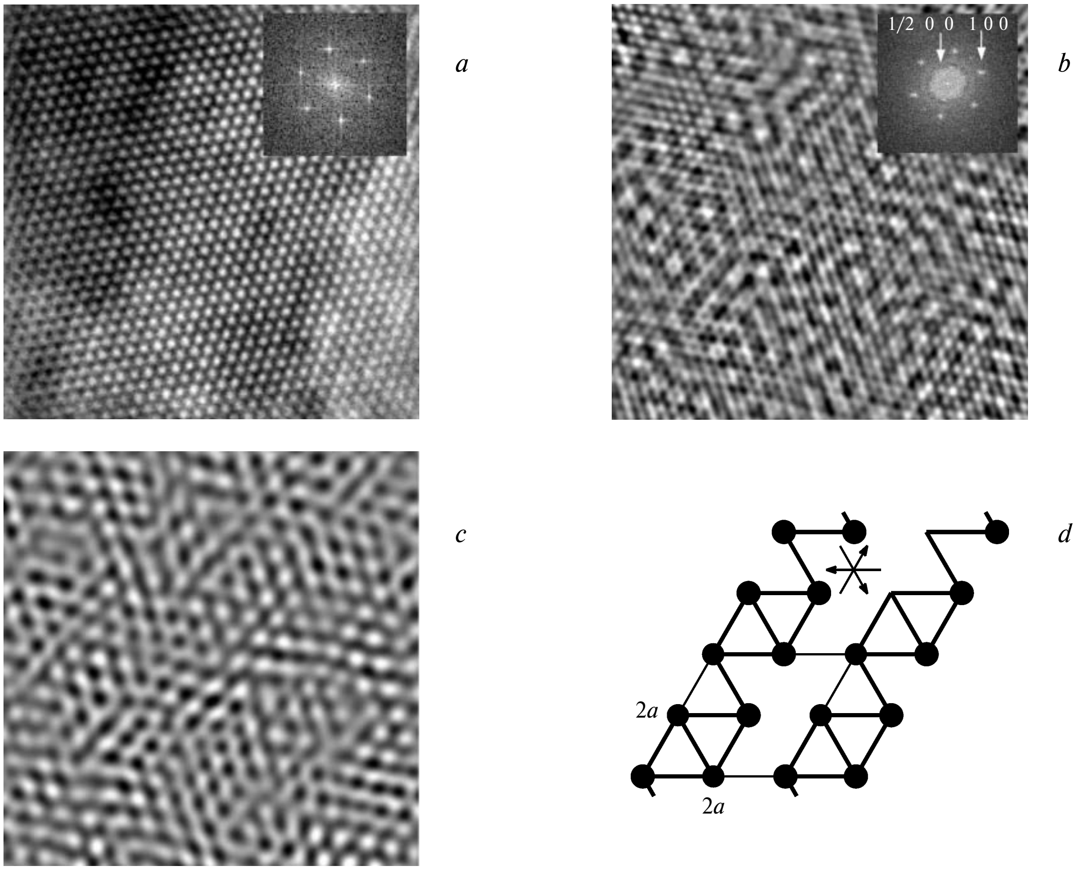

Fig. 4. High-resolution images of the frontal projections of particles of 2H-MoS_2 (*a*) and intercalation compound $Cu_{0.08}(phen)_{0.18}Cl_{0.03}MoS_2$ (sample **4**, *b*, *c*) obtained after Fourier filtration with allowance for all reflections (*a*, *b*) and only superstructure reflections {1/2 0 0} (*c*); the model of formation of rhombus-like chain superstructures $2a\times2a$ by molybdenum atoms in the *ab* plane of the hexagonal cell[24] and possible chain directions in the basal structure (*d*). Fourier images of the initial images are shown in inserts (*a*, *b*).

(d_{100} = 2.75 Å, a = 3.16 Å) and reflections of the superstructure {1/2 0 0}. For analysis of the image, we performed the Fourier filtration that took into account, in one case, the whole set of reflections ({1 0 0}, {1/2 0 0}, *etc.*) on the Fourier image (see Fig. 4, *b*) and, in another case, only superstructural reflections {1/2 0 0} (see Fig. 4, *c*). Comparison of two variants of the Fourier filtration shows that the superstructure appears in the layer plane as a change in the intensity of grouped lattice points with the superstructural period $d_s = 2d_{100}$ = 5.5 Å, which corresponds to the doubled parameter a of the basal hexagonal lattice $a_s = 2a$ = 6.3 Å. The superstructure with the same period has earlier been revealed by electron microdiffraction in the layered MoS_2 compounds with organic molecules[18] and copper ions.[16] Comparison of the images in Figs 4, *b* and 4, *c* also shows that the superlattice points are formed of groups in the form of "elementary rhombi," and the distances between the points differ for different rhombi. Note that analysis of variants of similar two-dimensional networks of Mo showed[24] the energetic preference of the superstructure with periodically approached Mo atoms in the two-dimensional layer to form chains of rhombi. An important feature of this model is that the basal hexagonal lattice contains three nonequivalent directions of propagation of these chains in the plane of the layer, whose symmetry decreases with chain formation (see Fig. 4, *d*)[18].

The image obtained from reflections {1/2 0 0} (see Fig. 4, *c*) indicates that the superstructure propagates over the whole surface area of the frontal projection of a particle of the layered compound. However, the observed nonuniformity in contrast of points {1/2 0 0} in Fig. 4, *c* indicates the mosaic character of the superstructure, and the estimation of sizes of its constituent blocks gives the value about 50 Å. Mosaicity can be caused by both structural defects (for example, dislocations appeared due to the fragmentation of the MoS_2 single layers) and a change in the direction of propagation of superstructural distortions in the basal lattice. Since the typical extension of the fragments composing the MoS_2 single layers in the compounds prepared from dispersions is 100—500 Å,[18] one can conclude that the factor of changing the direction of lattice modulation plays a substantial role in the formation of the mosaic pattern, and the extension of areas modulated in one direction is about 50 Å.

Thus, the layered compounds of molybdenum disulfide with $Cu^{II}(phen)_2Cl^+$ are formed due to assembling of the complex in the interlayer space of the intercalation compound of molybdenum disulfide with phenanthroline upon its treatment with copper(II) chloride and by the interaction of single-layer dispersions of MoS_2 with these complexes. In the last case, the reaction is accompanied by the reduction of some complexes to $Cu^{I}(phen)_2^+$ by the negatively charged layers of molybdenum disulfide followed by their decomposition in the interlayer space to Cu^I ions and phenanthroline.

The data of powder diffractometry and electron microscopy agree with the fact that the interaction of the single-layer dispersions with $Cu^{II}(phen)_2Cl^+$ produces intercalation compounds of MoS_2 with the complex and phenanthroline and copper and show that one particle can contain intercalation domains of different types.

According to electron microscopic data, superstructural orderings of atoms appear in the layers of molybdenum disulfide of the forming intercalation compounds due to their approaching to form rhombi. The superstructure propagates over the whole frontal projection of particles but has a mosaic character with block sizes of ~50 Å.

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