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New Intercalation Compounds of Molybdenum Disulfide with Transition Metals, $A_z(H_2O)_yMoS_2$ (A = Fe, Co, Ni, Y, La, Er, Th)

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Ion-exchange interaction of a single-layer dispersion, prepared by hydration of $LiMoS_2$, with transition metal salts leads to new intercalation compounds of molybdenum disulfide with these metal cations.

The insertion of metallic atoms into the interlayer space of MoS_2 crystals is of much interest as a potential method for modifying the properties of this material, which is used in catalytic petroleum systems,[1] in lubricants[2] and in battery cathodes.[3] However, the peculiarity of the electronic structure of this layer matrix (its semiconductor character and wide forbidden zone) hampers the delocalization of electrons over its layers, which is responsible for matrix activation during the solid-phase intercalation reaction.[4] Up to now this has constrained the possibilities of obtaining intercalation compounds of MoS_2 with metals, and it was only possible to insert alkali metals into interlayer spaces of MoS_2.[5] In this connection the possibility of using a single-layer dispersion of MoS_2, formed on hydration of the intercalation compounds $LiMoS_2$ under ultrasound,[6] is very interesting. As shown recently,[7] ion-exchange interaction of a single-layer dispersion with alkali metal salts or alkylammonium halogenides results in the formation of intercalation compounds $A_x(H_2O)_yMoS_2$ (A = Li, Na, K) or $(R_4N)_xMoS_2$, respectively. In this paper we present the results of an investigation into the interaction between single-layer dispersions of MoS_2 and transition (3d) or rare earth metal salts, along with the composition and structures of the intercalation compounds obtained.

The addition of soluble salts of metals AB (10 mol mol^{-1} MoS_2; for salts La and Er, 20 mol mol^{-1}) to a single-layer dispersion of MoS_2 (1 g l^{-1}), which was obtained by the hydration of $LiMoS_2$ under ultrasound treatment (60 kHz, 160 W), causes rapid (after 5–15 min) production of a flake-like precipitate. X-Ray fluorescence analysis[†] of the compounds obtained (after washing with water to remove excess salt) shows that they contain metals, and the metal content depends on the nature of the salt cation (Table 1). When metal chlorides were used, only traces of chlorine were found in the intercalation compounds by the above-mentioned method.

According to diffractometric data,[‡] the obtained substances are one-phase crystalline compounds with a layered structure. The essential increase of parameter *c* of the lattice in comparison with MoS_2 indicates that the intercalation of hydrated metal cations into the interlayer space of MoS_2 takes place as previously described for the interaction of this dispersion with alkali metal salts.[7]

It is evident that the formation of intercalation compounds in single-layer solutions must proceed without diffusion limits, which occur in the process of penetration of atoms or molecules into the interlayer space of the crystal during the solid phase intercalation reaction. It is the absence of these limitations that seems to cause an unusually high metal content in the layer solvates obtained $A_z(H_2O)_yMoS_2$ ($0.17 < z < 0.56$, see Table 1) in comparison with the compounds $M_x(H_2O)_yMoS_2$ (M = alkali metal, $x \leqslant 0.1$), which were prepared[8] by hydration of crystalline M_xMoS_2.

From Table 1, the content of intercalated cations decreases with increase in their charge. In addition, the contents of cations with equal charges are closely related to each other. Thus, the ratio A/Mo (*z*) for A^{2+} cations is 0.5–0.56, for A^{3+} cations it is 0.31–0.36 and for Th^{4+} it is 0.17. This also agrees with the ion-exchange mechanism of the reaction and indicates that the cations compensate for the negative charge of the macroions $(MoS_2)^{z-}$ during precipitation of intercalation compounds. It should be mentioned that the value of the negative charge, which was nominally calculated from the content of intercalation cations A^{n+} ($z{\cdot}n$), is in the range 0.68–1.12 electrons per Mo atom, which is close to the maximum (1 electron per Mo), derived from the stoichiometry of the initial species $Li_1^+(MoS_2)^-$. This value is markedly higher than the similarly calculated quantity of electrons on the layers when intercalation compounds of MoS_2 were formed with alkylammonium and potassium cations.[7] In the latter case this value did not exceed 0.3. It should be noted that the real value of the negative charge on the layers S-Mo-S in the case of intercalation of transition metal cations may be less than the calculated one; this may be due to, for example, stabilization of intercalated hydroxocomplexes $A^{n+}(OH^-)_m$, when $n > m$, between the layers of MoS_2.

A comparison of interlayer distances in obtained MoS_2 intercalation compounds (with Fe, Co and Ni) with the Van-der-Waals diameter H_2O (3 Å) shows a bilayer (along the *c* axis) arrangement of water molecules in the hydration shell of the intercalated cations. This is in agreement with the packing of interlayer space with hydrated metal cations which are arranged in a tetrahedral (coordination number 4) or octahedral (coordination number 6) surrounding of water molecules. A bilayer arrangement of water molecules was observed in the case of solvates based on TiS_2, TaS_2 and NbS_2 with these cations when the compounds were obtained by exchange of K^+ in the corresponding crystalline layer solvate.[9] According to diffractometric data, the phase composition is the same for the compounds obtained with Fe, Co and Ni ions both after vacuum pumping (1 day) and after exposure to air for at least 2.5 months.

It can be seen from Table 1, that significantly higher Δc values are found in the case of cations La^{3+}, Y^{3+}, Er^{3+} and Th^{4+}. In addition, Δc increases with increase in the charge/radius ratio for a cation (e_0/r), which is proportional to the energy of hydration. But this increase does not take place in steps of 3 Å as was

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[†] VRA–30, Cr-anode, 40 kV, 20 mA, crystal analyser LiF, PE, counter SD, FD, analytical lines for Cl, Fe, Co, Ni, Y – K_α, for La, Er, Th – L_α.

[‡] DRON–3, CuK_α-radiation, Ni-filter.

Table 1 Conditions of synthesis, interlayer distance (c), lattice expansion (Δc) and content of intercalated cations (z) in the compounds $A_z(H_2O)_yMoS_2$

Cation	Anion	Ionic radius of a cation[a]	Charge/radius ratio for a cation	c/Å	Δc/Å	z
Fe^{2+}	SO_4^{2-}	0.78	2.56	11.1	4.9	0.50
Co^{2+}	Cl^-	0.74	2.70	11.2	5.0	
Co^{2+}	NO_3^-	0.74	2.70	11.2	5.0	0.55
Ni^{2+}	Cl^-	0.69	2.89	11.6	5.4	0.56
Y^{3+}	NO_3^-	0.90	3.33	16.9	10.7	0.36
La^{3+}	NO_3^-	1.03	2.91	13.2	7.0	0.31
La^{3+}	Cl^-	1.03	2.91	13.3	7.1	
Er^{3+}	Cl^-	0.89	3.37	16.0	9.8	0.35
Th^{4+}	NO_3^-	0.94	4.25	17.7	11.5	0.17

[a] After Shannon.

observed in refs. 8 and 9, when water molecules change their packing in the interlayer space from mono- to bilayer (for $e_0/r < 1$ and $e_0/r > 1$, respectively). We think that the interlayer distances, which are observed during intercalation of La, Y, Er and Th ions, are determined by their tendency to form aqua complexes with large coordination numbers (8 and 9).[10] Such a filling of the coordination sphere of intercalated ions causes the loose packing of water molecules in the interlayer space and more than two water layers in projection on the c axis. It should be mentioned that these compounds are not stable. According to diffractometric data, one can see after 1 h a decrease in the interlayer distance and a broadening of reflections. Then, after vacuum pumping or exposure to air during 1–2 days the compounds become amorphous.

In conclusion, the results obtained show that interaction of a single-layer dispersion of MoS_2 with transition metal salts proceeds according to the ion-exchange mechanism:

$$[x\mathrm{Li}^+_{\mathrm{aq}} + (\mathrm{MoS_2})^{x-}_{\mathrm{aq}}] \xrightarrow{\mathrm{A}^{n+}\mathrm{B}^{n-}} \mathrm{A}_z(\mathrm{H_2O})_y\mathrm{MoS_2} + x\mathrm{Li}^+ + x/n\mathrm{B}^{n-}$$

It can also be concluded that new intercalation compounds of MoS_2 with metal cations are formed in this way.

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