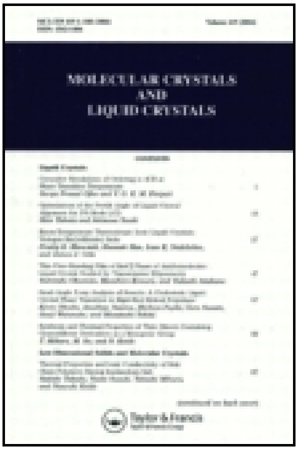

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Nanocomposites Built from MoS_2 and Various Metal-Containing Layers

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Nanocomposites built from MoS_2 and various metal-containing layers

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Restacking of exfoliated MoS_2 in the presence of cationic metal complexes (M = Fe, Co, Ni, Ru) or metallic cations (M = Mn, Fe Co, Ni) leads to nanocomposite materials consisting of alternating layers of molybdenum disulfide and metal complex compounds or metal hydroxide clusters respectively.

Keywords : molybdenum disulfide; exfoliation; nanocomposite materials

A soft chemistry route to MoS_2-containing nanocomposites can be based on the use of single-layer dispersions of molybdenum disulfide, in which MoS_2 slabs are separated by water molecules. These dispersions are formed upon hydration of the $LiMoS_2$ intercalate, as previously shown by R. Frindt et al.[1] The exfoliation process was suggested to include hydration of Li^+ cations and redox reaction between negatively charged $(MoS_2)^-$ layers and water molecules, giving a metastable system consisting of $(MoS_2)^{x-}$ macroanions, hydroxide anions, and lithium cations[2] :

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

Ion-exchange interaction of the dispersion with various cations (e.g. alkylammonium, phenanthrolinium) was already found to result in precipitation of MoS_2 intercalation compounds with the corresponding cations[3,4]. Some examples of layered materials obtained in a similar way, starting from MoS_2 single-layers and metal-containing cationic species, will be reported hereafter : those obtained using cationic complex solutions $M(phen)_3Cl_2$, $M(bpy)_3Cl_2$ (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridyl, M = Fe, Co, Ni) and (arene)Ru(H_2O)$_3$$SO_4$, and those obtained using 3d metal M(II) chloride (or sulfate) solutions (M = Mn, Fe, Co, Ni).

INTERCALATION OF CATIONIC COMPLEXES

As it could be expected considering the ionic nature of the dispersions, their interactions with cationic complex solutions proceed in ion-exchange way giving intercalation compounds of MoS_2 with the corresponding complexes :

$$[Li^+ + (MoS_2)^{x-} + (1-x)\ OH^-]_{aq} \xrightarrow{[M(phen)_3]Cl_2/HCl} [M(phen)_3{}^{2+}]_yMoS_2$$

In the case of $M(phen)_3{}^{2+}$ complexes, addition of a complex chloride solution (0.03 mol/mol MoS_2) to the dispersed $LiMoS_2$ (1 g/l) followed by stirring during 2 h and acidification of the reaction mixture to pH = 4 allows the complex to be completely trapped from the solution into interlayer space of MoS_2.

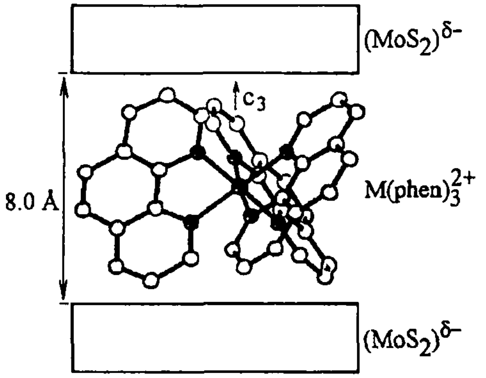


FIGURE 1. Orientation of the $M(phen)_3{}^{2+}$ complexes in the interlayer space of MoS_2.

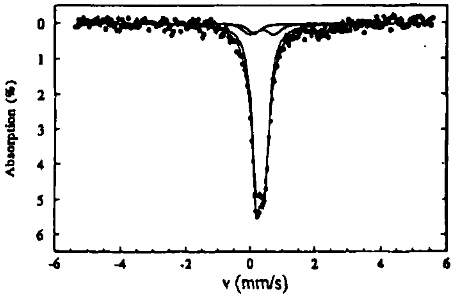


FIGURE 2 ^{57}Fe Mössbauer spectrum (300 K) of $Fe(phen)_3{}^{2+}$ intercalated into MoS_2. The contributions found in the spectrum are:
δ_1 = 0.31 mm/s, Δ_1 = 0.24 mm/s, 80% Fe(II) LS;
δ_2 = 0.35 mm/s, Δ_2 = 0.75 mm/s, 10% Fe(III) HS;
δ_3 = 1.17 mm/s, Δ_3 = 2.10 mm/s, 10% Fe(II) HS.
δ values refer to α-Fe (300 K).

The *c*-periodicity expansion, Δc, is *ca.* 8 Å, independently of the nature of M. The *c* value indicates that the complexes are oriented so as to give minimal layer separation, which is reached when the C3 axis of the octahedral complex is perpendicular to the MoS_2 layer plane (Fig. 1).

Mössbauer study of the iron derivative shows that intercalation of the complex is accompanied by the formation of some amount of iron oxides (hydroxides) whose contributions can be seen in the spectra as doublets of high-spin Fe(II) and Fe(III). These high-spin iron-containing species can further be almost completely removed by washing of the material with HCl. The final compound so obtained mainly contains intercalated low-spin tris(phenanthroline) iron(II) complex as shown by the parameters of the (300 K) ^{57}Fe Mössbauer spectrum (contribution 1, Fig. 2). Considering the quadrupole splitting value ($\Delta = 0.24$ mm/s), which is somewhat larger than that of crystalline $Fe(phen)_3^{2+}$ complexes ($\delta = 0.31$ mm/s, $\Delta = 0.15$ mm/s at 300 K), it can be thought that, probably due to structural strain, distortion of iron surrounding from octahedral symmetry is increased in the intercalated complex with respect to the crystalline ones.

Similar intercalation compounds are formed also with tris(2,2'-bipyridyl)iron(II) complex $Fe(bpy)_3^{2+}$, which causes interlayer spacing expansion of *ca* 8.5 Å. Low-spin configuration of the pristine octahedral complex is also retained in the interlayer space as evidenced by ^{57}Fe Mössbauer spectroscopy study ($\delta = 0.32$ mm/s, $\Delta = 0.35$ mm/s at 300 K).

TABLE 1 Composition, interlayer spacing (c) and interlayer spacing expansion (Δc) of intercalation compounds $[(arene)Ru(\mu\text{-}OH)_3Ru(arene)]_xMoS_2$. (The compounds were obtained at pH = 8.5 using an excess of $(arene)Ru(H_2O)_3SO_4$.)

arene	x	c / Å	Δc / Å
C_6H_6	0.12	12.2	6.0
$1,2,4,5\text{-}(Me)_4C_6H_2$	0.11	16.8	10.6
$1,4\text{-}Me(i\text{-}Pr)C_6H_4$	0.06	12.0	5.8

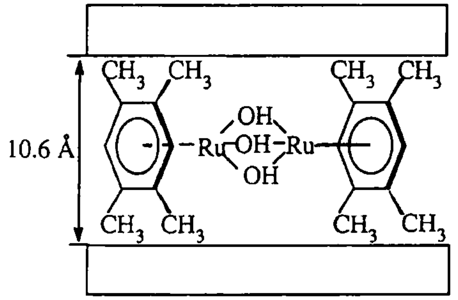


FIGURE 3 Structural model of the $[(arene)Ru(\mu\text{-}OH)_3Ru(arene)]_xMoS_2$ intercalates (case of 1,2,4,5-tetramethyl benzene ligands)

The filling of the MoS_2 interlayer space with ruthenium arene cationic complexes $(arene)Ru(H_2O)_3^{2+}$ was found to proceed in two ways depending on the reaction conditions. In acidic medium, complexes can be intercalated as monomeric cations. In basic medium, where condensation of the complexes is known to occur, they fill the interlayer space as dimeric OH-bridged cationic species $[(arene)Ru(\mu\text{-}OH)_3Ru(arene)]^+$ as it was confirmed recently by the EXAFS technique[5]. Considering the Δc values (Table 1) induced by intercalation of the complexes with different arene ligands in basic medium and van der Waals dimensions of these complexes, the only possibility is that aromatic rings are roughly perpendicular to the MoS_2 slabs (Fig. 3). In this case two substituents in para-positions (1,4-Me(i-Pr)) can be directed towards neighboring cations without increasing the layer separation observed with unsubstituted benzene, when four substituents have to increase Δc (case of 1,2,4,5-tetramethylbenzene). The content of each type of complex in the intercalates is very close to the maximal amount allowed by the above mentioned orientation, thus indicating rather dense packing of the organic cations in the interlayer space. On heating, the arene ligands can be removed ; the resulting layered material presumably contains RuO_x clusters between the MoS_2 slabs.

INTERCALATION OF METAL HYDROXIDE CLUSTERS

Upon interaction of single-layer dispersions with 3d-metal (M) salt solutions, hydroxide anions also participate in the formation of the intercalates. The precipitates result from reaction mixtures containing an excess of the salt (10 mol/mol MoS_2), they have layered structures and show interlayer spacing expansions listed in Table 2. M/Mo atomic ratio in these substances was found to be always *ca* 0.5. The composition (M/O atomic ratio determined by EELS) and the structure (M-O, M···M distances refined from EXAFS data for M = Co, Ni[6]) of the species formed in the interlayer space of MoS_2 are close to those of the corresponding metal hydroxides $M(OH)_2$. These hydroxides are known to have layered structures, with every metal layer situated between two OH^- layers. It is also important that the structural *a* parameters of their hexagonal lattices are close to that of pristine MoS_2 (a = 3.16 Å). This similarity of the two different lattices is evidently favorable to the formation, in solution, of unusual structures consisting of alternating layers of molybdenum disulfide and metal hydroxide, which can then precipitate (Fig. 4).

TABLE 2 Structural parameters of the nanocomposites materials $[M(OH)_2]_{1/2}MoS_2$. (The parameters of $M(OH)_2$ are given for comparison.)

M	Nanocomposite		$M(OH)_2$	
	c / Å	Δc / Å	c / Å	a' / Å
Mn	11.3	5.1	4.68	3.33
Fe	11.1	4.9	4.47	3.24
Co	11.3	5.1	4.64	3.18
Ni	11.5	5.3	4.60	3.14

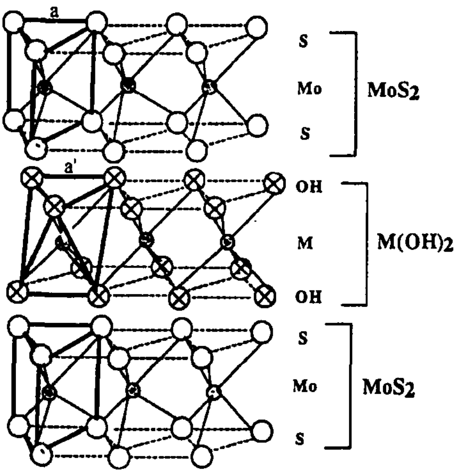
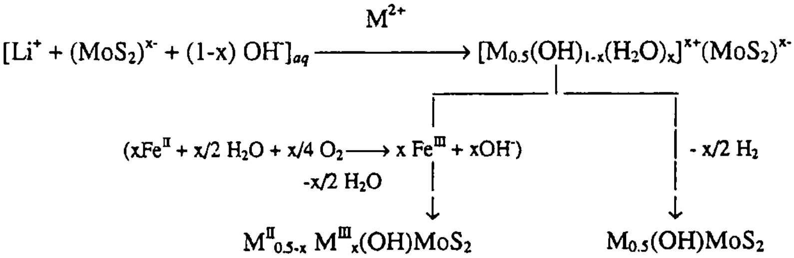


FIGURE 4 Alternation of the MoS_2 and $M(OH)_2$ layers in the nanocomposite materials.

At the first step of this process, extended two-dimensional clusters, containing in their oxygen sublattices not only hydroxide anions but also water molecules, are formed on the surface of dispersed MoS_2 (see scheme below). The positive charge of these clusters balances the remaining negative charge of the MoS_2 layers. Upon ageing, further transformation of these clusters into OH^- bilayer, thermodynamically more stable, can be expected.

There are two ways for such transformation. One of them is oxidation of M(II) by dissolved O_2 with participation of H_2O and formation of M(III) and required amount of OH^-. The ability of metal cations to increase easily their oxidation state is expected to be favorable to this process and it is probably the reason why it is observed in the case of iron(II).



Effectively, Mössbauer spectroscopy study of the compounds resulting from interaction of single-layer dispersions with ferrous sulfate solutions shows the presence of an important amount of Fe(III) in the materials. The room temperature spectra and those recorded at lower temperatures (down to 20 K) can be reproduced using two doublets whose isomer shifts (ref. α-Fe 300 K) and quadrupole splittings correspond to Fe^{3+} and Fe^{2+}, both surrounded by oxygen-containing species (δ_1 = 0.43 mm/s, Δ_1 = 0.60 mm/s and δ_2 = 1.12 mm/s, Δ_2 = 2.24 mm/s at 300 K). The relative contributions of the two iron oxidation states are nearly equivalent. On further cooling both Fe^{2+} and Fe^{3+} contributions simultaneously split into magnetic patterns (δ_1 = 0.46 mm/s, Δ_1 = -0.64 mm/s, θ =90°, H_1 = 490 kG; δ_2 = 1.45 mm/s, Δ_2 = -2.54 mm/s, θ =90°, H_2 = 115 kG) thus indicating the presence of Fe^{2+} and Fe^{3+} in a unique phase. Similar conclusion can also be drawn considering rather homogeneous distribution of Fe^{2+}, Fe^{3+} in the particles of the material, evidenced by EELS measurements[2]. The transition from paramagnetic Mössbauer spectra to magnetic ones proceeds in the manner expected in the case of small magnetic domains. It occurs within a narrow temperature range, which means that the size distribution of these domains is probably rather homogeneous.

The second possible mechanism for transformation of the intermediate positively charged metal(aqua)hydroxo species can consist in redox-interaction of water with negatively charged $(MoS_2)^{x-}$ macroanions. It can finally give $M(OH)_2$ single-layer structure with the only +II metal oxidation state (see scheme above). This mechanism probably predominates in the case of formation of nanocomposites with Co and Ni, for which the +II oxidation state is evidenced by the following magnetic results.

Effective numbers of Bohr magnetons found in these nanocomposites for Ni (p = 3.2 calculated from Curie-Weiss low, ^3A ground term) and Co (p = 5.2 found from the formula $p = (8\chi T)^{1/2}$, $^4T_1$ ground term) are indeed very similar to those reported for Ni(II) and high-spin Co(II) in the corresponding lamellar hydroxides $M(OH)_2$[7]. As in these bulk $M(OH)_2$, short-range intralayer ferromagnetic interactions also exist in the nanocomposites, as shown for Ni by the Weiss constant value ($\theta = +26$ K) and for Co by the significant increase of the χT product below 40 K. However, down to 5 K, the nanocomposites do not undergo 3-D magnetic ordering transition, contrary to bulk $M(OH)_2$ in which it occurs due to antiferromagnetic interlayer coupling ($T_N = 30$ K for $Ni(OH)_2$ and $T_N = 12$ K for β-$Co(OH)_2$). In the nanocomposites, the absence of 3D magnetic ordering could be due to small particle size or to the weakness of interlayer interactions (the $M(OH)_2$ single-layers are separated by non-magnetic MoS_2 layers ; similar features were observed for instance in the case of MCl_2 layers intercalated in graphite[8]).

The results above reported show that the use of MoS_2 single-layer dispersions allow insertion of various metal-containing compounds (monomeric or dimeric complexes, metal hydroxide clusters) between the slabs of MoS_2. This synthesis approach is expected to give possibility to design other new lamellar nanocomposite materials and to monitor and control their structural arrangement.

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