Naphthalene intercalation into molybdenum disulfide

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Exfoliation of $LiMoS_2$ followed by reflocculation permits the intercalation of naphthalene guest molecules into the van der Waals gap of MoS_2.

Layered transition-metal disulfides are versatile intercalation hosts which can accommodate the steric demands of a wide variety of guest species.[1] Their ability to form intercalation compounds is known to be strongly dependent on the electronic structure of the dichalcogenide.[2] This may be traced to the requirement for the host structure to possess low-lying empty electronic states, as a result of the redox process which accompanies the intercalation reaction. Hence, dichalcogenides of group 4 and group 5 transition metals readily form intercalation compounds with a wide variety of guest species. This may be achieved electrochemically or chemically, either by direct reaction with electron donors such as organic Lewis bases or with chemical reducing agents. In contrast, the presence of a low-lying d_{z^2} band in the group 6 materials results in a more limited intercalation chemistry, mainly restricted to alkali metals as guest species.[3]

An alternative route to intercalation compounds of transition-metal disulfides *via* 'single' molecular layers, involving reaction of a colloidal dispersion of the layered host with a solution containing the guest species, has been described.[4] This has successfully been applied to the insertion of sterically disfavoured molecules[5] and those which are poor electron donors including substituted aromatics,[6] polymers[7] and ferrocene.[8] This route potentially provides access to a wide range of intercalation compounds of layered materials and in particular, affords a means of extending the intercalation chemistry of group 6 dichalcogenides to encompass novel guest species. In this work, by describing the synthesis and initial characterisation of a novel naphthalene intercalation compound of MoS_2, we illustrate that guest molecules which are both poor electron donors and non-polar may be introduced by this method.

$LiMoS_2$ was prepared by adding three equivalents of standardised 1.6 M *n*-butyllithium to a dispersion of 2H-MoS_2 in distilled light petroleum (bp 60–80 °C) and stirring for 48 h under N_2. The product, Li_xMoS_2, was washed with several 20 ml portions of light petroleum and dried under vacuum. Powder X-ray diffraction showed it to be single phase with a hexagonal unit cell; $a = 3.312(45)$, $c = 6.394(18)$ Å. The lithium content, x, was determined to be 1.02(2), by flame emission spectroscopy.

All further stages of the reaction were carried out in air. Sufficient de-ionized water was added to $LiMoS_2$ to produce a suspension of 0.08 g ml^{-1} exfoliated MoS_2 (denoted $\{MoS_2\}_{exf}$). The suspension was sonicated for 30 min, a saturated solution of naphthalene in dichloromethane added (in the molar ratio of $C_{10}H_8 : \{MoS_2\}_{exf} = 5:1$) and the mixture stirred for 24 h. The single layer dispersion reflocculated after acidification to pH = 2 using concentrated HCl. Stirring was then continued for periods between one day and three weeks, after which the solid was separated, washed with water and dichloromethane and vacuum dried. The degree of intercalation was found to vary with the length of stirring time following acidification. It was found that repetition of this method consistently led to intercalation providing the reaction was stirred for 7 days or more following acidification.

Upon exposure of $LiMoS_2$ to water, gas evolution was observed together with the formation of a black opaque suspension. This is consistent with a proposed mechanism for exfoliation.[9] Spontaneous movement of the exfoliated material up the walls of the reaction vessel was also seen to occur.

The powder X-ray diffraction pattern of the intercalated material [Fig. 1(a)] shows two strong lines corresponding to the 001 and 002 reflections, whose shift to lower angle indicates an increase in interlayer spacing. It exhibits a characteristic saw-tooth shape comprising asymmetrically broadened peaks. This is a consequence of the Warren effect[10] which arises from the fact that for a two-dimensional layer, the reciprocal lattice becomes a line perpendicular to the layer and so, for higher diffraction angles, a continuous distribution of diffraction intensity appears. The broadness of the Bragg peaks results from the small particle size, estimated from the degree of broadening to be < 150 Å. Omission of naphthalene from the final preparative step produced a material whose powder X-ray diffraction pattern [Fig. 1(b)] is consistent with the formation of poorly crystalline restacked MoS_2.

The content of the intercalated naphthalene in all product materials was determined by C, H elemental microanalysis and by thermogravimetry. A hydrogen content slightly in excess of that required for a C : H ratio corresponding to naphthalene, was found by C, H analysis. This suggested that some residual water was present. An initial low-temperature mass loss observed in thermogravimetric analysis was consistent with this conclusion, and was used to determine the water content independently. This residual water appears to be on the surface of the product

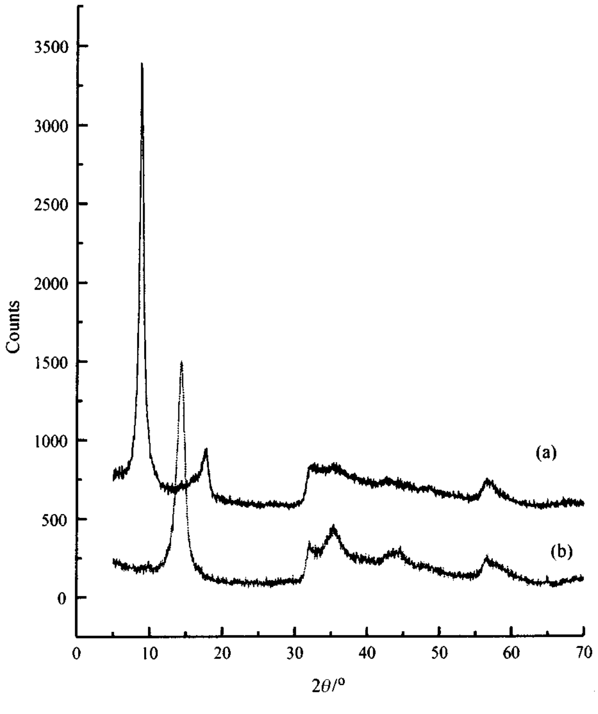

Fig. 1 Powder X-ray diffraction patterns for (a) $(C_{10}H_8)_{0.130}(H_2O)_{0.05}MoS_2$ and (b) restacked MoS_2

Table 1 Characterisation of intercalation compounds

Stirring time/days	Δc/Å	Empirical formula (C, H analysis)	Empirical formula (TG)
1	2.43	$(C_{10}H_8)_{0.07}(H_2O)_{0.11}MoS_2$	$(C_{10}H_8)_{0.07}(H_2O)_{0.06}MoS_2$
7	2.91	$(C_{10}H_8)_{0.08}(H_2O)_{0.33}MoS_2$	$(C_{10}H_8)_{0.08}(H_2O)_{0.28}MoS_2$
9	3.74	$(C_{10}H_8)_{0.11}(H_2O)_{0.26}MoS_2$	$(C_{10}H_8)_{0.11}(H_2O)_{0.20}MoS_2$
13	3.53	$(C_{10}H_8)_{0.13}(H_2O)_{0.19}MoS_2$	$(C_{10}H_8)_{0.13}(H_2O)_{0.14}MoS_2$
14	3.81	$(C_{10}H_8)_{0.13}(H_2O)_{0.05}MoS_2$	$(C_{10}H_8)_{0.13}(H_2O)_{0.05}MoS_2$
14	4.26	$(C_{10}H_8)_{0.20}(H_2O)_{0.19}MoS_2$	$(C_{10}H_8)_{0.20}(H_2O)_{0.12}MoS_2$

material since repeated preparation of samples indicated that there was no relationship between the interlayer expansion and the water content of the sample (Table 1). DSC measurements showed an endothermic transition at 100 °C, again consistent with surface water. It is also unlikely that naphthalene, a hydrophobic molecule, would co-intercalate with water. Atomic absorption analysis of the intercalation product showed it to be free of significant amounts of lithium (< 0.005 moles of Li per mole of MoS_2).

Table 1 shows repeated preparations, only varying in the period of stirring following acidification; their corresponding final interlayer expansion and composition. The length of stirring was found to affect the degree of intercalation observed such that no significant change in the extent of intercalation was observed for stirring times of less than seven days. Beyond this, the extent of intercalation of naphthalene increased with stirring time up to a maximum of 0.20 mole of naphthalene per mole of MoS_2 at 14 days stirring. Longer stirring times did not lead to any increase in the degree of intercalation beyond this value.

The interlayer expansion with respect to MoS_2 is *ca.* 3.8 Å. Molecular modelling calculations[11] indicate the van der Waals size of naphthalene to be *ca.* 6.8×5.1 Å. Hence the observed Δc value would suggest that the plane of the aromatic species is parallel to the MoS_2 layers. The smaller values of Δ_c observed at short reaction times may indicate the occurrence of staging. Further evidence for naphthalene intercalation with this orientation is provided by the fact that the p_z orbitals in naphthalene project above and below the plane of the ring in such a way as to give the ring an effective thickness of *ca.* 3.7 Å[12] which is consistent with the interlayer expansion observed in the product reported here. The area of a naphthalene molecule is *ca.* 35 $Å^2$ which compares with an interlayer area of *ca.* 8.6 $Å^2$ per molybdenum atom in MoS_2. Such a geometric constraint suggests that the maximum uptake of naphthalene is approximately 0.25 per molybdenum atom: the maximum guest content observed is 0.20. Steric repulsion between neighbouring naphthalene molecules is likely to prevent maximum occupancy of the interlayer spacing from being attained.

Insertion of a non-polar species into a group 6 disulfide has been achieved using the synthetic method reported here. An organic/inorganic composite material is obtained with a limiting content of 0.20 moles of naphthalene per molybdenum atom. The interaction of the organic and inorganic fragments of this material would be expected to lead to changes in the physical properties of the host. Studies of the structural, transport and magnetic properties of the material are currently in progress and will be reported in due course.

Notes and References

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