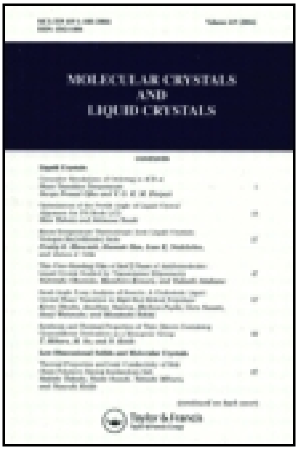

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Anthony V. Powell [a] , Laura Kosidowski [a] & Andrew McDowall [a]

[a] Department of Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK

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Novel Intercalation Compounds of MoS_2

ANTHONY V POWELL, LAURA KOSIDOWSKI
and ANDREW MCDOWALL

Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK

Intercalation of naphthalene and its substituted derivatives into MoS_2 has been achieved by exfoliation-reflocculation. Intercalation results in an expansion of the lattice in a direction perpendicular to the dichalcogenide layers and, in the case of naphthalene, modifies the electrical properties of the host.

Keywords: intercalation; dichalcogenides; organic guests; transport properties

INTRODUCTION

Layered transition metal dichalcogenides are versatile intercalation hosts which are able to accommodate guest species by expansion of the interlayer space.[1] The electron transfer from guest to host, which accompanies the reaction, imposes electronic constraints on the host. Materials containing group 4 and 5 cations 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. By contrast, the presence of a filled low-lying dz^2 band in the group 6 materials results in a more limited intercalation chemistry, mainly restricted to alkali metal guest species.

An alternative synthetic procedure involving the formation of a colloidal dispersion of the layered dichalcogenide has been described.[2] Reflocculation in the presence of a solution of a guest species, leads to encapsulation of the guest in the interlayer space. This method, which permits the intercalation of sterically disfavoured molecules[3] and poor electron donors,[4] offers the potential to extend the intercalation chemistry of the group 6 dichalcogenides. Recent reports,[5],[6] have described the incorporation of conducting polymers in the van der Waals gap of MoS_2, yielding materials with unusual electronic properties. Our investigations[7] have focused on the introduction of small, electron-rich organic molecules into MoS_2. The intercalation of naphthalene and substituted derivatives is described here.

EXPERIMENTAL

Sufficient deionised water was added to $LiMoS_2$ to produce a suspension of 0.08 g ml^{-1} exfoliated MoS_2 (denoted $\{MoS_2\}_{exf}$). This was sonicated for 30 min prior to the addition of a saturated solution of the guest species in dichloromethane (acetonitrile in the case of 1,5-dihydroxynaphthalene) to give a 5:1 molar ratio of guest:$\{MoS_2\}_{exf}$. After stirring for 24h, reflocculation of the suspension was achieved by reducing the pH to 2 with HCl. After stirring for periods of up to 21 days, the solid was separated, washed with water and solvent and dried under vacuum. Reflocculation in the absence of a guest molecule provided a control sample. Products were examined by powder X-ray diffraction and compositions determined by a combination of combustion analysis and thermogravimetry. Electrical conductivity was investigated by the four-probe DC technique on cold-pressed ingots. Magnetic susceptibility data in a field of 1kG were collected with a SQUID magnetometer.

RESULTS AND DISCUSSION

Powder X-ray diffraction data (Figure 1) suggest that in the absence of a guest molecule, exfoliation-reflocculation produces poorly crystalline restacked MoS_2 with an interlayer distance (6.2Å) similar to that in pristine 2H-MoS_2. The pattern exhibits a characteristic saw-tooth shape as a result of asymmetric Warren broadening of reflections. Powder diffraction data for the products from reactions in which a guest molecule was introduced, are similar in appearance, consisting of one or more moderately intense 00λ reflections and a sequence of Warren broadened lines. However, the 00λ reflections are shifted to lower angles, indicating an expansion of the lattice in a direction perpendicular to the MoS_2 layers. This is consistent with the incorporation of the organic species in the interlayer space. Carbon and hydrogen are present in all product materials. Hydrogen contents are slightly in excess of those expected from guest molecule stoichiometries. Thermogravimetry indicates that this is due to residual water: approximately 0.05-0.25 per mole of MoS_2. However, repeated preparations identified no correlation between the interlayer expansion and the water content, suggesting that the water is present on the surface of the sample. For this reason, water contents are not included in the product compositions which are presented in Table 1, together with the increases in interlayer spacings, Δc.

The in-plane dimensions of naphthalene, determined by molecular modelling, are *ca.* 6.8 × 5.1 Å, whilst the p_π orbitals give the aromatic rings an effective thickness of *ca.* 3.7Å. Hence, the observed Δc suggests that molecules are oriented with the molecular plane parallel to the MoS_2 layers. A recent inelastic neutron scattering study[8] supports this view. Almost all of the intense features arising from out-of-plane motions are suppressed on intercalation, only that at 959cm^{-1}, assigned as π(CH), having any appreciable intensity.

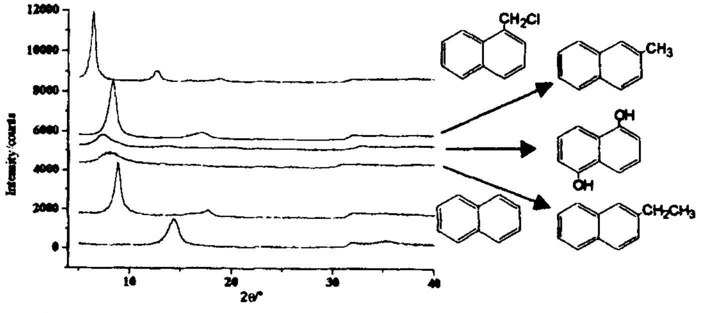
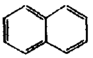
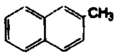
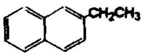
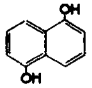
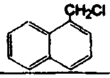


FIGURE 1 Powder X-ray diffraction data for restacked MoS_2 (lowest trace) and intercalated materials.

TABLE 1 Compositions and interlayer expansions of intercalated materials.

Guest	x in (Guest)$_x$MoS$_2$	Interlayer spacing/Å	Δc/Å
	0.13	10.0	3.8
	0.19	10.5	4.3
	0.09	9.7	3.5
	0.40	11.9	5.7
	0.36	13.8	7.6

Geometric considerations suggest a limiting composition for naphthalene in this orientation of *ca.* 0.25 per mole of MoS$_2$, although steric repulsions between neighbouring molecules are likely to prevent this being attained. At the longest reaction times, a maximum uptake of 0.20 was observed. The methyl derivative shows a similar degree of insertion and a slightly larger lattice expansion. Despite the extra bulk of the substituent group, the ethyl derivative causes a smaller increase in interlayer spacing, although this may be due to staging associated with the lower uptake. We conclude therefore, that naphthalene and its alkylated derivatives are incorporated with the molecular plane parallel to the inorganic layers. Much larger increases in interlayer spacing are observed for the 1,5-dihydroxy- and 1-chloromethyl-derivatives and the extent of insertion of both molecules is greater than the geometrically limiting value. The presence of two hydroxyl groups is unlikely to alter the effective ring thickness significantly. Therefore, a lattice expansion of 5.7Å appears inconsistent with a parallel orientation of guest molecules. In-plane dimensions of *ca.* 6.7 × 6.2Å, together with the large degree of insertion, suggest that the molecular plane is perpendicular to the MoS$_2$ layers. Although the -CH$_2$Cl side-chain in 1-chloromethylnaphthalene increases the effective ring thickness to *ca.* 5.4Å, the large Δc of 7.6Å and the high degree of insertion, appear to rule out a monolayer of molecules oriented with the molecule plane parallel to the dichalcogenide layers. In-plane dimensions of 6.7 × 6.0Å indicate a perpendicular orientation of the guest molecule, similar to that suggested for the 1,5-dihydroxy derivative. It is possible that this orientation of the guest species is stabilised by an interaction between the polar substituents and the dichalcogenide layers.

MoS_2 is a semiconductor with an activation energy of 0.235eV below 790K.[9] Semiconducting behaviour persists on exfoliation and restacking (Figure 2), although it is no longer of the Arrhenius type. The naphthalene intercalate is semiconducting down to 100K, where there is a sharp discontinuity in ρ(T) and d(lnρ)/dT) changes sign. Data for the other materials indicate semiconducting behaviour over the temperature range 80≤T/K≤300. Although these data suggest that $(C_{10}H_8)_{0.13}MoS_2$ undergoes a semiconductor to metal transition on cooling, the resistivity below 100K is considerably higher than that expected for a metal. Polymer intercalates of MoS_2 have much lower resistivities down to low temperatures, where a sharp increase in measured resistance is observed.[5],[6] It was suggested that the high conductivity at room temperature indicates a metallic state, arising from stabilisation of an

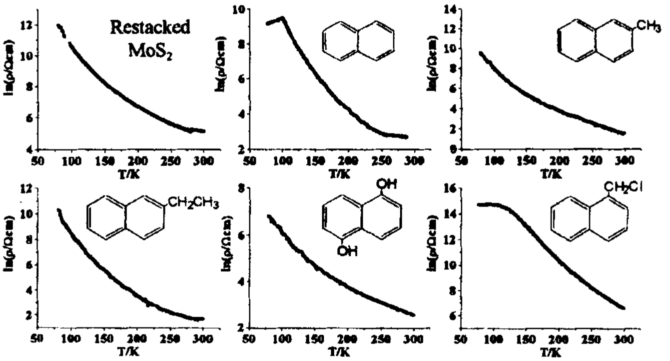


FIGURE 2 Resistivity data for restacked MoS_2 and intercalated phases.

octahedral coordination for molybdenum, which in metastable 1T-MoS_2, gives rise to Pauli paramagnetism.[10] Despite the high resistance of the materials prepared here, weak paramagnetism is observed (Figure 3). However, it is not clear that the molybdenum coordination is octahedral as the Mo-S bond length determined by EXAFS[8] (2.41Å), is identical with that in 2H-MoS_2. Significantly, EXAFS does indicate distortion of the MoS_2 layers, producing a range of Mo-Mo distances (2.8-3.8Å), rather than the single distance of 3.16Å of the crystalline phase. These distortions are likely to have an important influence on the transport and magnetic properties.

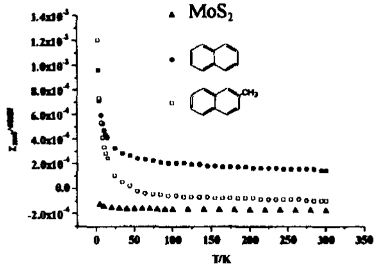


FIGURE 3 Magnetic susceptibility data for MoS_2 and intercalates.

Acknowledgements
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