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Intercalation of a pendant-arm tetraazamacrocycle into molybdenum disulfide

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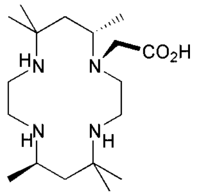
A novel macrocycle-MoS$_2$ nanocomposite has been synthesized and characterized using the exfoliation/restacking properties of LiMoS$_2$, providing the first of a new family of intercalation compounds.

There is significant interest in the properties of polyazamacrocycles bearing pendant-arms, particularly those having arms attached at the nitrogen atoms of the macrocycles. Interest in these complexes has focussed on applications to catalysis, ion-selectivity[1] and their use as radioimmunotherapy agents.[2] Transition metal macrocycles find utility as electrocatalysts in fuel cells,[3] or as catalysts for decomposition of environmentally important small molecules (NO$_x$, SO$_x$ and CO$_2$).[4] Cobalt macrocycles will bond sulfur directly to the metal[5] and these complexes, which are also extremely stable in aggressive environments, provide excellent candidates for both fundamental and applied studies of hydrodesulfurization (HDS) of fossil fuels. Thus macrocycles may provide a portal to a completely unique class of intercalation compounds, that may prove to be robust, efficient HDS catalysts.

While the synthesis of nanocomposite materials is an important area of research and there have been a number of reports of intercalation of, for example, crown ethers into phyllosilicates[6] and inorganic hosts,[7] there have been no reports to date of intercalation of tetraazamacrocyclic compounds, particularly of the pendant-arm variety. This class of compound is particularly interesting, given its ability to form extremely stable redox active transition metal complexes. Molybdenum disulfide is a very attractive host material for nanocomposites and has already been shown in its own right to be an effective catalyst in the hydrodesulfurization (HDS) process.[8] It also finds application as a solid lubricant[9] and as a cathode material in high energy density lithium batteries.[10] Despite the importance of MoS$_2$ in industrial applications, formation of its intercalation compounds using redox techniques is usually limited to those of alkali and alkaline earth metals dissolved in liquid ammonia,[11] or to organolithium reagents such as *n*-butyllithium.[12] However, intercalation compounds of MoS$_2$ may be produced by utilizing the exfoliation and restacking properties of LiMoS$_2$. Complete exfoliation of LiMoS$_2$ occurs upon reaction with water. Addition of guest species such as organic molecules and polymers to the de-laminated layers can afford a wide range of intercalation compounds of MoS$_2$.[13] These include the intercalation of crown ethers and polyethylene oxides.[14] In this case, however, washing the intercalation compounds containing alkali metal complexes of the guest ethers caused progressive elimination of the intercalated compounds, giving solids of variable stoichiometry. We have chosen to exploit the LiMoS$_2$ exfoliation technique to attempt to prepare a series of intercalation compounds containing tetraazamacrocycles that should provide new, stable intercalation compounds with novel, useful properties.

We report here the formation and characterization of the first MoS$_2$ intercalation compound containing a pendant-arm tetraazamacrocycle, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetic acid, (L).



The macrocycle L was prepared by following the literature procedure.[15] LiMoS$_2$ was prepared by reacting MoS$_2$ with 3 equivalents of Bu^{n}Li[12] and was exfoliated by reaction with water. Addition of an ethanol solution of L to the delaminated layers resulted in its encapsulation in between the disulfide sheets.

Evidence for the intercalation of L into MoS$_2$ was obtained by powder X-ray diffraction (XRD)† which clearly shows the first eight (00*l*) reflections, indicative of a lamellar structure (Fig. 1). The observed *d*-spacing of the intercalated compound is 11.48 Å, showing an interlayer expansion of 5.3 Å with respect to pristine MoS$_2$, which has a *d*-spacing value of 6.15 Å. This expansion is consistent with a monolayer of L lying virtually co-planar with the MoS$_2$ sheets.

The stoichiometry of the sandwiched compound was determined by thermogravimetric analysis under air. This method has been shown previously[13] to give reliable results that agree closely with elemental analysis data. Examination of the thermogram showed that the inclusion compound is stable up to 308 °C. Thereafter, a major weight loss was observed up to 450 °C, followed by the formation of MoO$_3$, which was stable up to 650 °C. The identity of the MoO$_3$ phase was confirmed by XRD. From the thermogram, the composition of the intercalated material was found to be L$_{0.11}$MoS$_2$. It was also found that 0.11 is the maximum loading of L into MoS$_2$. Increasing the molar ratio of L : MoS$_2$ from 0.11 to 1.0 during the intercalation process had no effect. The average particle size of L$_{0.11}$MoS$_2$ was calculated from its powder pattern by using the Scherrer formula[16] and was found to be 80 Å, which may be compared

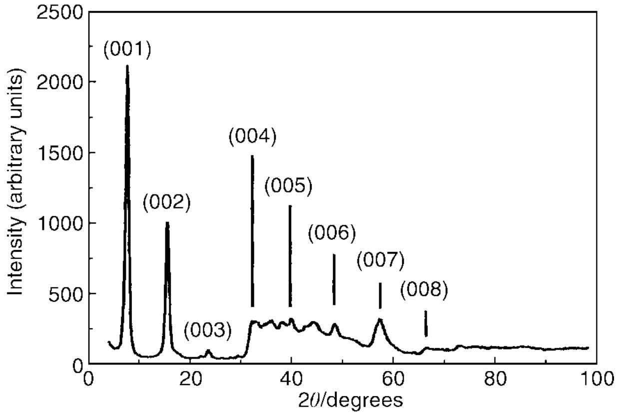


Fig. 1 Powder X-ray diffraction pattern for L$_{0.11}$MoS$_2$.

with an average particle size of 129 Å for the pristine MoS_2 used in this study. The decrease in particle size of MoS_2 upon intercalation corresponds to a significant loss in crystallinity of the material since upon exfoliation it does not restack quite as well as in its initial state.

The room temperature electronic conductivity of $L_{0.11}MoS_2$ was assessed by the two-probe technique on a pressed pellet of the sample. The measured conductivity value is 2.5×10^{-3} S cm^{-1}, which shows a 250-fold increase with respect to pristine MoS_2. The latter, which is in the 2H form, is a semiconductor with a room temperature electrical conductivity of 10^{-5} S cm^{-1}. This increase in electrical conductivity is explained by a structural transformation of the MoS_2 which takes place during the intercalation process. In 2H-MoS_2, the molybdenum atoms are bonded to the sulfur atoms in a trigonal prismatic arrangement. Upon treatment of 2H-MoS_2 with Bu^nLi, reduction of the layers takes place forming $LiMoS_2$ that contains molybdenum atoms octahedrally coordinated to six sulfurs. The reaction of $LiMoS_2$ with water is fast, where oxidation of the layers results in the formation of single layers trapped in the octahedral geometry. When the single layers restack with L sandwiched in between, the octahedral geometry of the MoS_2 is retained. Band structure calculations by Matthesis showed that MoS_2 in the octahedral (O_h) form is metallic.[17] However, this form is metastable and reverts to the thermodynamically more stable 2H state. This is consistent with the observed continuous decrease in conductivity of our samples over a period of time. This effect is currently being examined as well as the effect of temperature and pressure on the conductivity of $L_{0.11}MoS_2$, and will be the subject of a future paper. The structural conversion of MoS_2 in $L_{0.11}MoS_2$ has also been probed by differential scanning calorimetry which shows a broad exothermic peak with a peak maximum at 200 °C. This is consistent with the structural transformation of MoS_2 from the O_h to the 2H form. The observed transition was found to be irreversible. restacked MoS_2 (d-spacing 6.15 Å) has been reported to show a similar transition at 100 °C.[18] It seems that an increase in d-spacing leads to an increase in the transition temperature and we are currently exploring this effect by using macrocycles of different sizes and with differing number and bulk of substituents. A detailed study of the steric effects of pendant-arm macrocycles on the properties of their MoS_2 intercalation compounds is currently underway. This work provides the first evidence that pendant-arm macrocycles are viable guests in intercalation compounds hosted by MoS_2, which may lead to materials with unique and useful properties.

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Notes and references

† A diffractometer equipped with a graphite monochromator and an analyzer crystal was used, along with a scintillation detector. Cu-Kα radiation (λ = 1.542 Å) was utilized and the data collection was carried out at 22 °C. Samples were run under vacuum with a scan range of 4–100°.

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