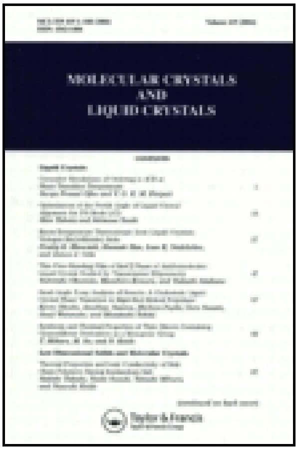

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Dialkylamines—Molybdenum Disulfide. Intercalates. Synthesis, Characterization, and Electrical Properties

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Dialkylamines – Molybdenum Disulfide. Intercalates. Synthesis, Characterization, and Electrical Properties

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The synthesis and characterization of secondary amine-molybdenum disulfide intercalation compounds are described. Products which are layered organic-inorganic nanocomposites behave as mixed ionic electronic conductors with electrical conductivities depending on the nature ofthe amine of about 10^{-2} S cm^{-1}

Keywords: Dialkylamines; molybdenum disulfide; nanocomposites; intercalation compounds; mixed conductors

INTRODUCTION

Intercalation of organic guest into layered materials like transition metal dichalcogenides has been considered to be an area specially interesting for the production of new materials potentially useful for electronic devices[1,2]. The intercalation of donors species specially in titanium or tantalum dichalcogenides has been extensively studied during of the 70's[3]. However, intercalation of donors into MoS_2 is relatively new[4,5].

Indeed, appropriate route for intercalating chemical species in MoS_2 was reported only in 1986[6]. The intercalation of organic polymers[7,8], metallocenium cations[9], cobalt clusters[10], transition metals[11], substituted ferrocenes[12], and lately naphthalene[13] and 1,10-phenantroline[14] are known. This phenantroline was the unique example of the intercalation of amines into MoS_2 published before[15]. In this paper is described the preparation and characterization of the new series of compounds with relatively high conductivity arising from the intercalation of dialkylamines into MoS_2.

EXPERIMENTAL

The compounds were prepared by two different methods, starting both from exfoliated MoS_2 [16]: i) After treating the amine with the aqueous single layer suspension of MoS_2 under stirring for about 24 hrs, the mixture is decanted and the black solid washed three times with distilled water, centrifuged and dried under vacuum at room temperature for 8 h.. ii) The amine is treated with a suspension in n-hexane of dry exfoliated MoS_2 under stirring for 12 h. The mixture is washed with n-hexane, centrifuged, and dried under vacuum for 4 h. According to elementary analysis, thermal analysis and diffraction patterns the products are in both cases the same.

RESULTS AND DISCUSSION

Secondary amines, diethyl-, dibutyl-, dipentyl-, dihexyl-,N-isopropyl cyclohexil-and dicyclohexyl-amine react with exfoliated MoS_2 leading to layered solids $Li_{0.1}MoS_2(HNR_2)_y$. The products always retain about 0.1 mol Li per mol of MoS_2. The organic to inorganic ratio, *y*, depends on molecular volume of the amine. X-Ray powder diffraction patterns displaying clear *00l* reflections show that the product are pure phases (Fig 1) with characteristic MoS2 interlaminar distances (table).

The stability as well as the composition of the products was determined by simultaneous DTA/ TGA. Such analysis show that an important mass

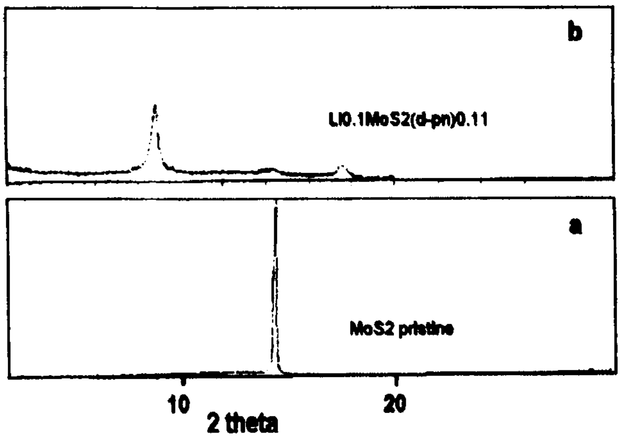

FIGURE 1. Powder x-ray Diffraction patterns of (a) MoS_2 pristine and (b) $Li_{0.1}MoS_2$ (*d*-pn)$_{0.11}$. (Cu-Kα radiation).

loss occurs just at the temperature corresponding to the boiling point of the amine. FTIR spectra are relatively poor. However, absorptions in the range 3500-3300 cm^{-1}, assignable to the N-H stretching, as well as the absence of the NH^+ bending modes in the range 1635-1380 cm^{-1}, assignable to alkyl ammonium compounds[17,18], agree more with the presence of free amine than with the corresponding ammonium ions.

The electrical conductivity of the products was obtained by a.c. complex impedance analysis using pellets with ion blocking gold electrodes. Results are summarized in the Table. Galvanostatic polarization analysis of a specimen with electron-blocked electrodes shows that the nanocomposites are mixed electronic-ionic conductors.

The polarization curves follow typical relationships deduced for mixed conductor[19,20]. Ionic conductivity obtained for the compound $Li_{0.1}MoS_2(di\text{-}but)_{0.19}$ is about $5 \cdot 10^{-5}$ S cm^{-1}. The electronic to ionic ratio $(\sigma e / \sigma i)$ results to be approximately $4 \cdot 10^4$. It is known that the intercalation of lithium or organic guests enhance the electron transport in MoS_2. Features observed after intercalation of amines are comparatively high and, therefore, of interest for the development of MoS_2-based conducting materials

TABLE. Composition, Lattice Expansion and Electronic Conductivity in MoS_2-Dialkylamines Nanocomposites.

Amine	Guest/Host	Lattice	Conductivity
Diethylamine (*d*-eth)	0.42	3.74	0.251
Dibutylamine (*d*-but)	0.19	3.90	0.197
Dipentylamine (*d*-pn)	0.11	4.04	---
Dihexylamine (*d*-hex)	0.07	4.30	0.159
N-isopropylcyclo-	0.21	4.26	---
Dicyclohexylamine	0.21	4.45	0.038
MoS_2	---	---	$2.09 \cdot 10^{-6}$

The comparison of the interlaminar distance with the molecular geometry of the guest has been widely used[13]. The amine molecular dimensions in the gas phase may be estimated from models considering optimized molecular configuration and the van der Waals radii of the atoms. The matrix effects on the amine dimension may be analyzed assuming that the amine in the intercalated state: (i) it has a configuration near to that in gas phase; (ii) it is arranged with its long axes parallel to the host layers; and (iii) that it can rotate freely around its molecular axis. In Fig 2, experimental interlaminar distances are compared with those expected from calculated molecular diameters. The comparatively smaller values of the experimental interlaminar distances indicate that the amine is consistently contracted in the intercalated state. The area occupied by the contracted amines and the available interlayer distance, of *ca.* 8.6Å per molybdenum atom in MoS_2, agree with the stochiometry observed for the products.

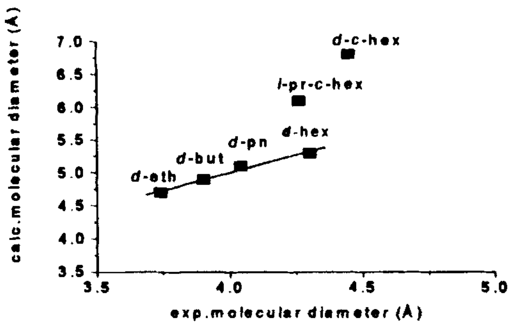

FIGURE 2. Comparison of the experimental and calculated diameter of the amines.

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