JOURNAL OF SOLID STATE CHEMISTRY **58**, 290–300 (1985)

First Example of Monodispersed $(Mo_3Se_3)^1_\infty$ Clusters

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Received August 23, 1984; in revised form November 30, 1984

The close relationship of the structure of ternary molybdenum chalcogenides to molecular cluster compounds suggests that these chalcogenides might be synthesized from such clusters or be solubilized as clusters. However, in contrast to molybdenum *halide* clusters which can be obtained in solution from the solid phase, many attempts to solubilize these chalcogenide clusters were unsuccessful. This is the first report that some of the pseudo-one-dimensional compounds ($M_2Mo_6X_6$, X = Se, Te; M = Li, Na) can be dissolved when exposed to highly polar solvents such as dimethylsulfoxide or N-methylformamide. We show using optical microscopy, TEM, and light scattering that some of these solutions contain individual $(Mo_3X_3)^1_\infty$ chains. This is also the first example of a purely inorganic transition-metal polymer solution. The behavior with respect to flocculation is consistent with the double layer theory. We show that the $(Mo_3X_3)^1_\infty$ chains can be oriented in solution.

Introduction

Molybdenum cluster compounds Mo_6X_8 containing either chalcogens (X = S, Se, Te) (*1*) or halogens (X = Cl, Br, I) (*2*) have been intensively investigated. These clusters are bound together either by intercluster molybdenum chalcogen bonds such as in the Chevrel phases or by bridging halogens such as in Mo_6Cl_{12} (*3*). The physical properties of these compounds are determined by the extent of intercluster wave function overlap. This overlap is to a large extent determined by the hybridization of the cation and anion orbitals. Such hybridization is larger for the chalcogenide phases than for the halides. At the same time the direct metal–metal intercluster interaction is generally larger in the chalcogenides, where intercluster metal–metal distances as short as 3 Å are found (*1*). For example, in Mo_6Cl_{12} and $Mo_6Cl_{10}Se$ (*3, 4*) the *d* electrons are localized within the individual clusters leading to semiconducting behavior or even magnetic moments as in Nb_6I_{11} (*5*), while for the Chevrel phases metallic conductivity and quite often superconductivity is observed. The different balance between the ionic and covalent components of the bonding (i.e. the extent of hybridiza-

0022-4596/85 $3.00

tion) is also responsible for the difference in chemical behavior of these compounds. Indeed the solution-phase chemistry of the halide clusters $\mathrm{Mo_6}X_8^{4+}$ is well known (*6*), while so far no similar chemistry has been reported for chalcogenide clusters such as $\mathrm{Mo_6Se_8^{4-}}$, $\mathrm{Mo_9S_{11}^{4-}}$, $\mathrm{Mo_{12}S_{14}^{6-}}$, or $(\mathrm{Mo_3S_3^-})^1_\infty$ (*7*, *8*). The quasi-one-dimensional $M_2\mathrm{Mo_6}X_6$ compounds, which can be thought of as infinite linear chains of $(\mathrm{Mo_3}X_3)^1_\infty$ clusters separated by the ternary element, have a large intercluster (e.g., interchain) distance (6.40 Å) in contrast to the distance of about 3.40 Å commonly observed for the other Chevrel phases (*9*). This considerably reduced intercluster interaction leads one to expect the solution chemistry of molybdenum chalcogenides to be easiest for this linear chain species. Recently we have reported the synthesis of new 1-D compounds by an ion-exchange reaction of M^+ for $\mathrm{In^+}$ in $\mathrm{In_2Mo_6}X_6$ (X = Se, Te) at low temperature, yielding new metastable phases such as $\mathrm{Li_2Mo_6Se_6}$ (*10*). In this paper, we report that some of the one-dimensional compounds ($\mathrm{Li_2Mo_6Se_6}$, $\mathrm{Na_2Mo_6Se_6}$) dissolve into solution or form colloidal suspensions when exposed to strong (e.g., highly polar) solvents. Using transmission electron microscopy (TEM), electron paramagnetic resonance (EPR), and light scattering, we show that some of these solutions contain individual $(\mathrm{Mo_3}X_3)^1_\infty$ chains. This is the first example of a purely inorganic transition-metal polymer solution.

Experimental

The polycrystalline lithium and sodium compounds were prepared as previously described (*10*), according to the reaction

$$\mathrm{In_2Mo_6}X_6 + x\mathrm{Li(Na)I} \xrightarrow{600^\circ\mathrm{C}} \mathrm{In}_{2-x}\mathrm{Li(Na)}_x\mathrm{Mo_6}X_6 + \mathrm{InI} \qquad 0 \le x \le 2.$$

The resulting powders (with a grain size of about 80 ± 20 μm) were entirely "dissolved" in solvents (distilled prior to use) at concentrations of about 0.01 mole (moles of $M_2\mathrm{Mo_6}X_6$ per mole of solvent). In the case of $\mathrm{In}_{2-x}\mathrm{Li}_x\mathrm{Mo_6}X_6$, when $x > 1$, thick gel-like masses were observed to spontaneously form without stirring in times varying from several hours to as short as a few minutes. The shorter times were obtained with the most polar solvents such as *N*-methyl formamide (NMF). These gels can be greatly diluted leaving behind *no* solid materials to produce macroscopically homogeneous, free flowing liquids that look reddish or purple for the selenides and tellurides, respectively.

We have examined these liquids by a variety of techniques in order to determine the nature and form of solvation of the solids. The very dilute liquids were characterized by light scattering and by their optical spectra. Some of these liquids contained small colloidal particles which were studied by optical microscopy. We concentrated the gels by gently warming them in vacuum to show by X-ray diffraction and X-ray fluorescence that the original starting compound was recovered. Also we examined by TEM the morphology of the solid resulting from evaporation of a solution on a copper mesh grid. Magnetic susceptibility as well as electron paramagnetic resonance data were collected on both solid and liquid samples.

Results

The conditions for swelling as shown in Table I are strongly affected by the nature of the ternary element, its concentration in the starting material, and by the physical properties of the solvent. Both the dipolar moment and the dielectric constant of the solvent are highly correlated with its ability to dissolve the solid. For instance, $\mathrm{Li_2Mo_6Se_6}$ powder does not swell with solvents such as hexane, toluene, hexamethylphosphoramide (HMPP), or tetrahydrofurane

TABLE I

SOLUBILITY OF $M_2Mo_6X_6$ COMPOUNDS WITH RESPECT TO VARIOUS SOLVENTS

	Product							
	$In_{2-x}Li_xMo_6Se_6$						Dipole moment, M (debyes)	Dielectric constant, E
Solvent	$x = 1$	$x = 1.5$	$x = 1.8$	$x = 2$	$Na_2Mo_6Se_6$	$LiInMo_6Te_6$		
Tetrahydrofurane (THF)	—[a]	—	—	—	—	—	1.63	7.32
Hexane	—	—	—	—	—	—	1.89	13.9
Hexamethyl phosphoramide	—	—	—	—	—	—	2.86	9.18
Methanol	—	—	—	—	—	—	1.66	32.6
Glycerol	—	—	—	—	—	—	2.56	42.83
Acetonitrile	—	—	—	*	—	—	3.37	37.45
Propylene carbonate (PC)	—	*	+	+	—	—	4.0	64.4
Dimethylsulfoxide (DMSO)	+	+	+	+	*	*	3.90	46.7
N-Methyl formamide (NMF)	+	+	+	+	*	*	3.82	182

[a] —, No solubility; *, partially soluble; +, completely soluble.

(THF), while it does swell (Fig. 1a) in solvents such as propylenecarbonate, dimethylsulfoxide (DMSO), or NMF leading to a large volume expansion. Acetonitrile is a "borderline" solvent. Furthermore, Table I indicates that with the same solvent, the swelling is easier for materials with high lithium content. Finally among the several solvents investigated, DMSO and NMF at room temperature, as well as water when heated, are the only ones to induce swelling of $Na_2Mo_6Se_6$. No swelling occurs when M = K, Rb, or Cs.

When $Li_2Mo_6Se_6$ and $Na_2Mo_6Se_6$ are dissolved and then dried out in vacuum, X-ray fluorescence analysis reveals the same Mo/Se ratio for both the bulk and the dried sample. The X-ray powder diffraction patterns present some differences, namely the presence of primarily ($hk0$) reflections in the dried material which indicates a strong preference for the chains (the c axis) to orient parallel to the surface of the substrate. In addition, the dried samples sometimes show extra X-ray diffraction peaks at low angle ($2\theta = 7.20$ and $10.20°$) most likely associated with the presence of intercalated solvent species, since these peaks vanish by heating the sample above 200°C. The swelling reappears when these dried samples are exposed again to a polar solvent. Also it is important to mention that, when M = Li, the dried films are moisture sensitive (as are the bulk materials) (*10*) and when exposed to air they decompose to form Mo_6Se_6 + LiOH. Once oxidized, the material no longer swells upon exposure to the solvent. We conclude that negatively charged chains and highly polarizing positive cations are necessary for solvation.

The gels can be diluted, leading to dispersions for which the homogeneity is strongly dependent on both solvent and initial material. The diluted liquids fall into two broad categories: true polymeric solutions and colloidal suspensions. For example, when

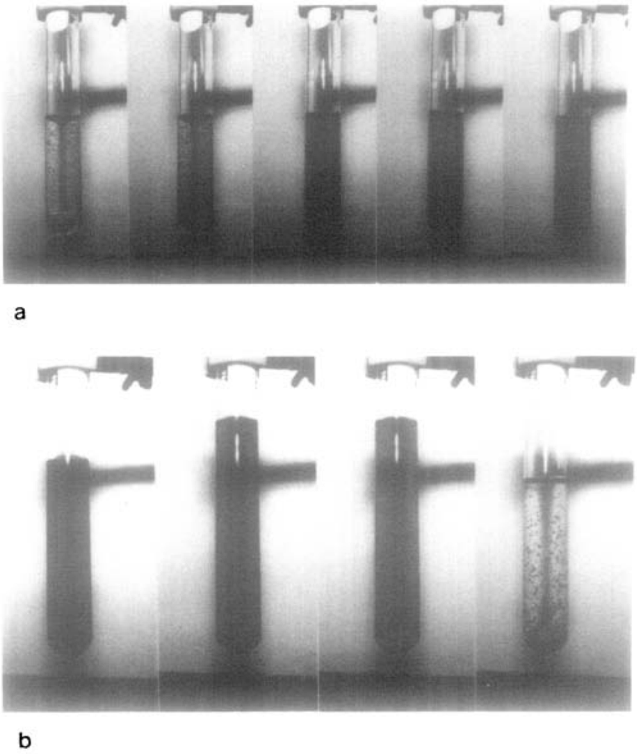

FIG. 1. Instantaneous dissolution of $Li_2Mo_6Se_6$ when exposed to NMF (a); decoloration and floculation of the colloid by adding salts (b).

$Na_2Mo_6Se_6$ in NMF is examined with an optical microscope, the presence of rod-like particles having a diameter of about 1 μm and a wide range of lengths, 20 μm being the upper limit (Fig. 2), is revealed. Attempts to reduce the diameter of these rods to a value where they could not be detected by optical microscopy were unsuccessful. Even in very diluted liquids that had been agitated by an ultrasonic source these rods are always visible. Consequently the solutions of $Na_2Mo_6Se_6$ are always colloidal, in contrast to those of $Li_2Mo_6Se_6$. For the fully lithiated phase, the separation of the chains $(Mo_3X_3)^1_\infty$ In NMF or PC appears to be complete, as we detail later.

After the gels are formed with the highly polar solvents, more dilute liquids can be prepared by adding the same solvent or by adding somewhat less polar solvents that do not themselves cause swelling of the solid. The latter solvents include acetonitrile, glycerol, and methanol but not hexane or THF. However, *none* of the liquids appear to be stable for more than 3 or 4 weeks under ambient conditions. With NMF, PC, or acetonitrile the solutions become darker and small particles form. With methanol after only 1 week, a dark flocculant mass irreversibly forms, which can not be redissolved by adding more solvent or by ultrasonic agitation. Adding glycerol to the liquid results in a slower flocculation process than even in the single component solvents. We suspect decomposition of the solvent, probably involving the lithium cations, as the source of these irreversible reactions. (As we mentioned previously, the

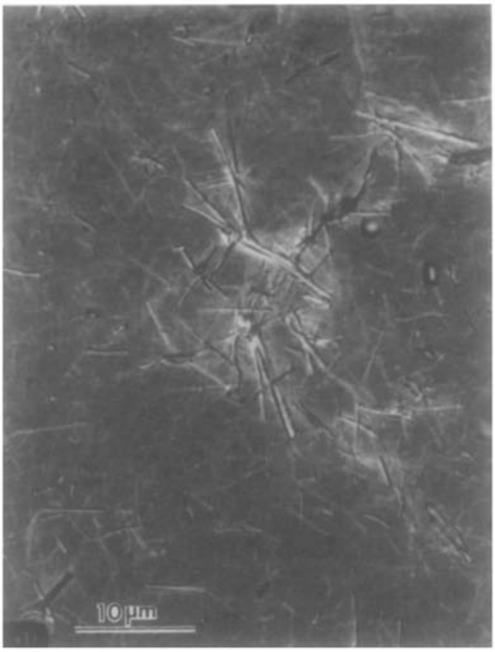

FIG. 2. $Na_2Mo_6Se_6$ colloidal was observed by optical microscopy. Due to the Brownian motion of the rod-like particles the image has been collected after complete evaporation of solvent.

lithium activity in the bulk compound is high enough to reduce water.) Glycerol may help protect from or decrease hydrolysis after the dispersion is formed.

The dissolved solid can also be precipitated from the solvent by adding salts or acids, leaving a clear solution behind (Fig. 1b). The precipitation rate increases as the concentration and charge of the ionic species in solution increase and decrease with increasing cation size. This behavior is similar to that observed for colloidial suspensions of very small charged particles (*11*) or clays (*12*).

Materials precipitated by adding one of the alkali iodide salts (LiI, NaI, KI, RbI, or CsI) were investigated by X-ray fluorescence analysis and X-ray diffraction. The diffraction patterns of the precipitated products were independent of added salt and were the same as that of the starting $Li_2Mo_6Se_6$ or $Na_2Mo_6Se_6$ with preferential orientation, as seen in the intentionally dried material (Fig. 3). Thus, there is no evidence of ion exchange in "salting out" the chains.

Following the experiments of Murphy *et al.* (*13*) on individually solvated *layers* of TaS_2, we looked for adsorption of cationic dyes such as methylene blue on the solvated chains. The spectra of methylene blue measured both in pure PC and in a solution formed from $Li_2Mo_6Se_6$ gel diluted with PC are similar and reveal no shift in the position of the dye-absorption peak within the accuracy of the experiment (Fig. 4). This suggests that this dye does not adsorb on

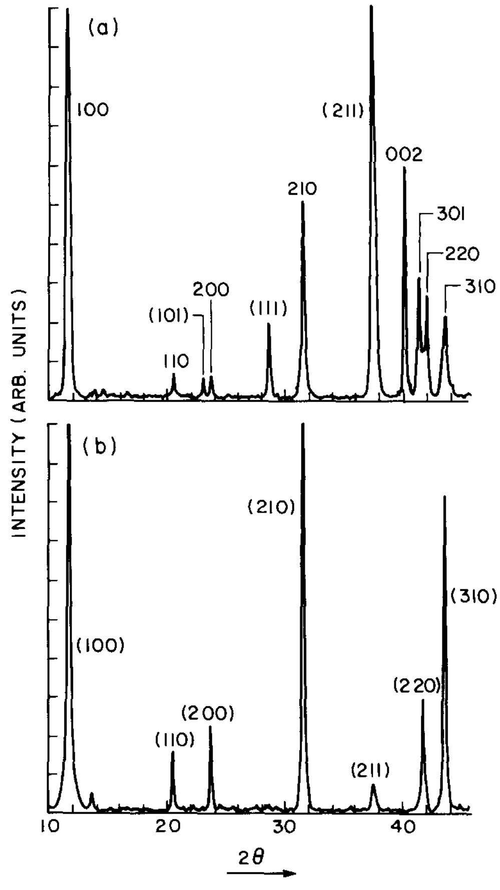

FIG. 3. X-Ray diffraction patterns of $Na_2Mo_6Se_6$: (a) prior to dissolution; (b) after precipitation (see text).

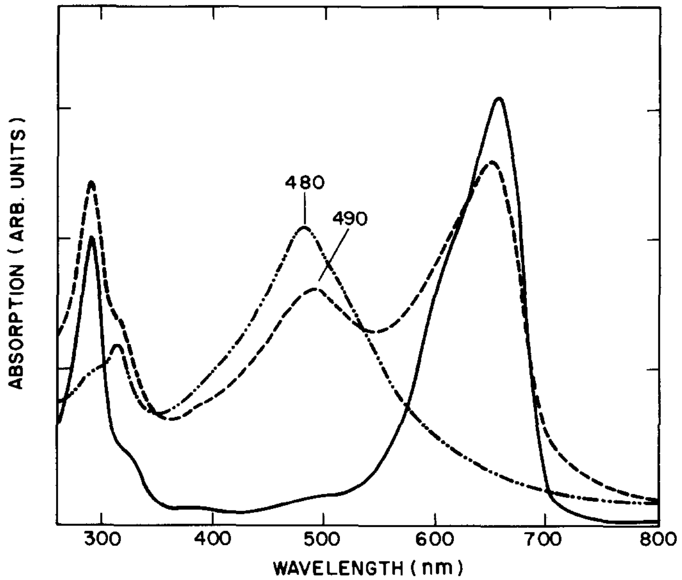

FIG. 4. Absorption spectra of $Li_2Mo_6Se_6$ solution (—··); methylene blue alone (solid curve), and in the presence of $Li_2Mo_6Se_6$ solution (dashed curve).

the negatively charged chains $(Mo_3Se_3)^1_\infty$, assuming that the adsorption of molecules on charged rods and on surfaces should affect the absorption spectra of the dye in a similar way.

In order to better understand the nature of the liquids obtained from the solid lithium molybdenum chalcognides, a number of physical measurements were undertaken. In the gel-like state (concentration ~0.01 *M*) X-ray absorption fine structure (EXAFS) measurements at the Se and Mo edges are now in progress. When more dilute liquids (10^{-3} to 10^{-4} *M*) are dried out, the solid material left behind consists of long fibers (≈10 μm) whose average diameter decreases as the concentration of the starting liquid decreases. This is clearly shown by the TEM micrographs in Fig. 5. The uniformity of chain width increases with increasing dilution, so that in Fig. 5b the diameters are on the order of 20 Å (e.g., of about three times the interchain $(Mo_3Se_3)^1_\infty$ distance or twice the hexagonal unit cell parameter a_h). These fiber diameters represent *an upper limit* on the diameter of the fibers in solution, since the charged chains and lithium cations will tend to pull together or "crystallize" as the solvent is dried out. Note that even in the concentrated solution, some rather fine chains are also present (Figs. 3a, b). The finer chains appear to be much more flexible than the larger ones. The bending of the chains appears to be quite smooth although occasionally sharp kinks alongs chains are observed. Electron diffraction patterns obtained from some larger chains (≳ a few hundred angstroms in diameter) indicate that the chains are single crystals (Fig. 6) with structural and lattice parameters identical to those of the bulk material. These data strongly suggest that, in the dilute solutions at least, individual $(Mo_3Se_3)^1_\infty$ chains are completely solvated into solution along with the lithium counter ions.

Finally, light scattering was used to characterize the species present in very dilute solutions of $Li_2Mo_6Se_6$. The solutions were centrifuged a number of times until no mac-

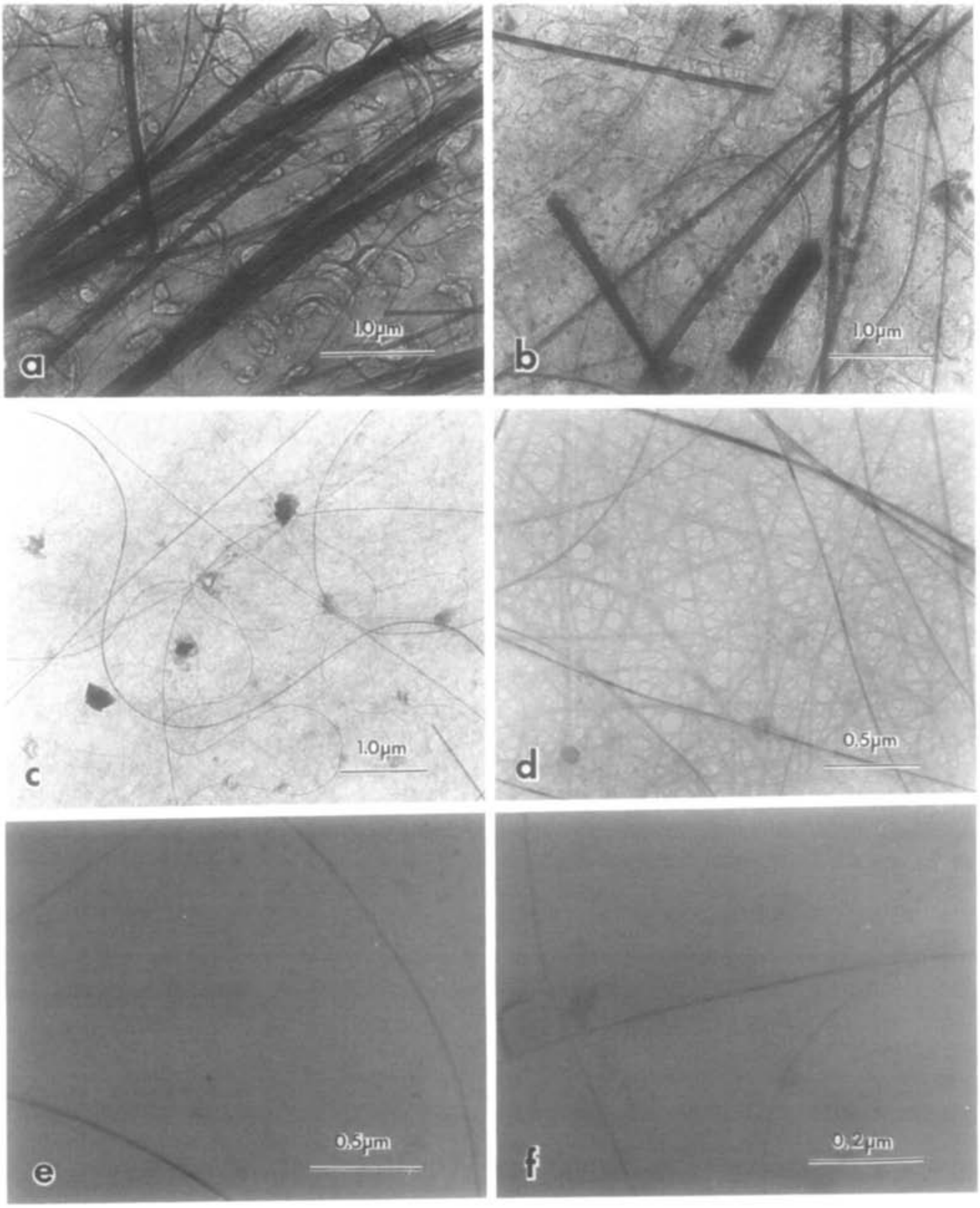

FIG. 5. Transmission electronic microscopy pictures collected for a solution of $Li_2Mo_6Se_6$ with increasing dilution. The dilution increases by alphabetical order.

roscopic particles could be seen at the bottom of the centrifuge tube. Since these solutions degrade in air, cylindrical scattering cells were filled in a helium atmosphere dry box. The intensity of the depolarized scattering was very strong and demonstrated a great deal of angular dependence, strongly suggesting very large anisotropic particles. A minimum in the angular dependence of the depolarized intensity at ~40° is consis-

FIG. 6. Electron diffraction pattern of 100-Å-diameter chains which result from evaporated $Li_2Mo_6Se_6$ solution.

tent with a model of rigid rod-like particles of length ~2 μm. The values of the translational and rotational diffusion constants of the particles in solution were obtained from the depolarized intensity–intensity autocorrelation function which was measured as a function of angle from 10 to 90°. Using these values and the Perrin equations (*14*, *15*), which models the particle as ellipsoids, particle length of ~2 μm and an axial ratio of ~0.04 was determined. This length is consistent with that found from the static intensity measurements and from TEM. However, due to the uncertainty in determining the rotational diffusion constants, we should emphasize that the axial ratio could range from 0 to 0.15. The axial ratio is small enough to indicate very rod-like particles. These light scattering measurements are described in more detail elsewhere (*16*).

Optical absorption spectra were measured in the region from 200 to 800 nm for $Li_2Mo_6Se_6$ and $Li_1In_1Mo_6Te_6$ solutions. Each spectrum reveals two strong adsorption peaks. The longer wavelength peak is broader due to a shoulder at low energy (Fig. 7). The position of these peaks is independent of the solvent. However, the broad peak and its shoulder near 480 and 540 nm in the selenide shift about 40 and 80 nm, respectively, to longer wavelengths in the telluride, while the first one at 320 nm is essentially unchanged (Fig. 7).

Finally, low temperature EPR measurements performed on both bulk and liquid samples reveal the existence of an anisotropic signal ($g_\parallel$ and $g_\perp$) for the liquid only (Fig. 8), details of which will be published elsewhere (*17*). The signal appears in the concentrated gel-like state and persists as the solution is diluted. It is probably related to the creation of "localized electrons" on the chain at defect sites, such as chain ends. The low temperature static magnetic susceptibility of the gel has a larger Curie component than the bulk material consistent with this defect explanation. The anisotropic EPR signal is strongly influenced by the orientation of the chains. We note that the chains may be oriented by shearing the solution (drawing or painting). For instance we found that solutions flowing either through a flat thin tube (0.5 mm) or a small capillary strongly polarized transmit-

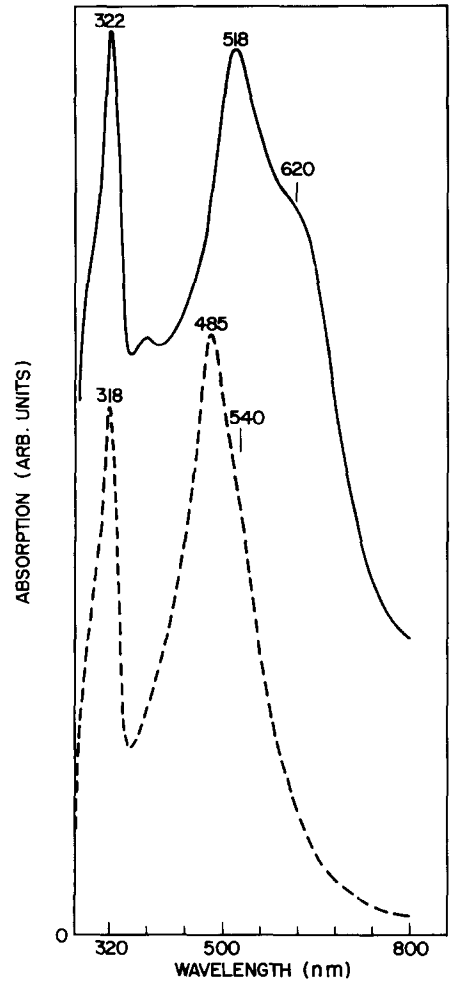

FIG. 7. Optical absorption spectrum of both $Li_2Mo_6Se_6$ solution (dashed curve), and $LiInMo_6Te_6$ solution (solid curve), are shown.

ted light (Fig. 9). This means that the solutions contain rod like particles oriented parallel to the wall surface by the flow. This orientation can be produced and maintained in larger diameter tubes by mixing these solutions with viscous solvents such as glycerol. The latter helps prevent the chains from misaligning after only a short period of time. Finally, we also note that these these chains may be aligned by brushing a thin layer of solution in one direction on a substrate. For instance films of about 2 ± 1 μm prepared by quickly drying out these "painted on" solutions show a longitudinal conductivity (in the direction of the paint) five times greater than the transverse one.

Discussion

The above observations on the swelling of the one-dimensional compounds are similar to the behavior of clays and other layered compounds, polyelectrolytes, or even silver iodide sols. In fact such sols have been intensively used for testing double layer and colloidal stability theories. Polar solvents such as DMSO, PC, and NMF are obviously strong enough to solvate the small cations and perhaps even the chains leading to the swelling of $Li_2Mo_6Se_6$ and $Na_2Mo_6Se_6$ as reported above. Indeed previous studies (*10*) indicated that in the case

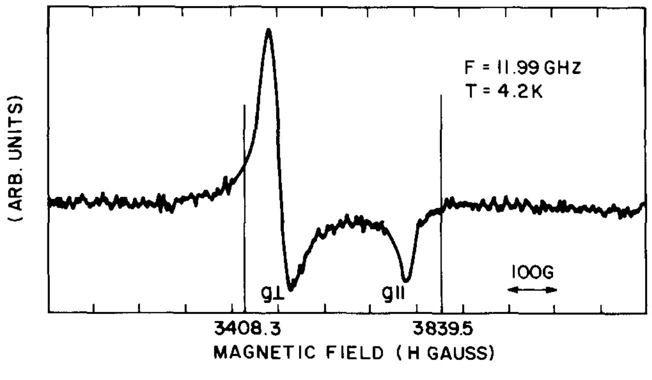

FIG. 8. Observed ESR spectrum of $Li_2Mo_6Se_6$ colloid.

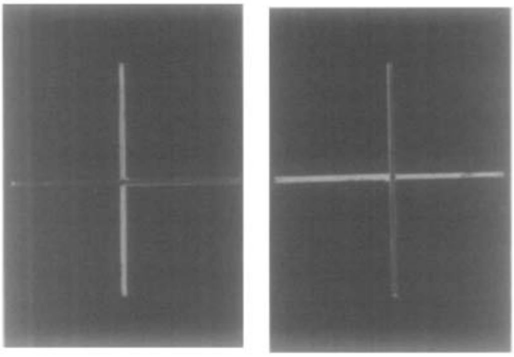

FIG. 9. The ability of the solution to polarize light is shown. Between a and b the polarizer has been rotated by 90°.

of the Li-salt, the interchain repulsion is large enough to hold the chains further apart than would be expected by extrapolating from the interchain distances of the other alkali metal compounds $M_2Mo_6Se_6$. Such repulsion enhances the stability of the solvated state over the solid state. In dilute solutions the negatively charged chains would be surrounded by a "cloud" of solvated Li ions. This establishes a difference in potential between the compound and the solvent in which it is immersed, similar to an electrical double layer that forms at a macroscopic electrode. Stability against aggregation is a consequence of both the strong repulsive interactions between similarly charged electric double layers around each chain and cation-solvent affinity. By adding excess salt the electrical double layer diameter is decreased, which, below a critical diameter, leads to a net attraction between the chains via their mutual attraction to the cations (which in the solid compares to the Madelung energy). The absence of swelling for the $M_2Mo_6X_6$ compounds (M = K, Rb, Cs; X = Se, Te) as well as the presence of macroscopic rod-like particles with $Na_2Mo_6Se_6$ in contrast to $Li_2Mo_6Se_6$ is quite remarkable. Such behavior is the result of a competition between lattice energy and solvation energy. $Na_2Mo_6Se_6$ is certainly the borderline where the lattice energy just about balances the solvation energy leading to an enthalpy of solution close to zero. Further work to understand the particle size effect in $Na_2Mo_6Se_6$ is not in progress.

Conclusion

We report the solubility of some of the one-dimensional compounds $M_2Mo_6X_6$ (M = Li, Na) in strongly dissociating solvents (high polarity) such as NMF and DMSO. We show evidence for the presence of these chains in solution with the help of optical microscopy, transmission electron microscopy and light scattering. We also described their strong ability to be oriented by shear flow. Polarized light as well as EPR and resistivity measurements was used to determine the orientation of these chains.

Acknowledgments

Valuable discussions with D. W. Murphy and G. D. Patterson are gratefully acknowledged.

References

1. M. B. MAPLE AND F. FISCHER, "Superconductivity in Ternary Compounds I, II," Springer-Verlag, Berlin (1982).
2. F. A. COTTON, *Quart Rev. (London)*, **20,** 389 (1966); "McGraw-Hill Yearbook of Science and Technology," McGraw-Hill, New York (1966).
3. J. C. SHELDON, *J. Chem. Soc.*, 1007, 3106 (1960); 750 (1961); 410 (1962); 4183 (1963); 1287 (1964).
4. H. SCHAFER, H. G. VON SCHNERING, J. TILLACH, F. KUHNEN, H. WÖHRLE, AND H. BAUMAN, *Z. Anorg. Allgem. Chem.* **353,** 287 (1967).
5. A. SIMON, *Z. Anorg. Algem. Chem.* **355,** 295 (1967).
6. C. PERRIN, M. SERGENT, F. LETRAON, AND A. LETRAON, *J. Solid State Chem.* **25,** 197 (1978).
7. T. HUGHBANKS AND R. HOFFMAN, *J. Amer. Chem. Soc.* **105,** (1983).
8. M. POTEL, R. CHEVREL, M. SERGENT, M. DECROUX, AND O. FISHER, *C.R. Acad. Sci. Paris Ser. C* **288,** 429 (1979).
9. M. POTEL, R. CHEVREL, AND M. SERGENT, *Acta Crystallogr. B* **36,** 1545 (1980).
10. J. M. TARASCON, G. W. HULL, AND F. J. DISALVO, *Mater. Res. Bull.* **19,** 915 (1984).

11. E. Matijevic, *Prog. Colloid Polym. Sci.* **61,** 24 (1976).

12. H. Van Olphen, "An Introduction to Clay Colloid Chemistry," 2nd ed., Wiley, New York (1977).

13. D. W. Murphy and G. W. Hull, *J. Chem. Phys.* **62,** (1975).

14. F. Perrin, *J. Phys. Radium* **5,** 497 (1934).

15. F. Perrin, *J. Phys. Radium* **7,** 1 (1936).

16. P. J. Carroll, G. D. Patterson, and J. M. Tarascon, *Phys. Rev. Lett.*, to be published.

17. M. Walsh, L. Rupp, J. M. Tarascon, and F. J. DiSalvo, *Macromolecules,* to be published.