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Notes

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Convenient Synthesis of the Chevrel Phases $M_xMo_6S_8$ (M = Cu, Pb, La, or Gd)[†]

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Ternary molybdenum chalcogenides of the general formula $M_xMo_6X_8$ (X = S, Se), known as Chevrel phases, have attracted much attention in view of their unique structure and electronic properties.[1] A serious limitation in investigating these solids arises from the difficulties in preparing stoichiometric, monophasic materials.[2-4] Sulfide Chevrel phases are generally prepared by heating a mixture of the ternary metal, molybdenum, and sulfur at 1100-1200 °C in evacuated ampules. For the synthesis of rare-earth Chevrel phases, an intimate mixture of the rare-earth sesquisulfide, MoS_2, and Mo metal is heated in the sealed ampule. Such ceramic preparations do not yield single-phase compounds and in addition give rise to nonstoichiometry in the products. Impurities in ceramic preparations are usually Mo_2S_3, Mo, and MS_x. Attempts have therefore been made by several workers[2,4-6] to develop new methods for the synthesis of Chevrel phases. In this report, we describe a simple synthesis of Chevrel phase sulfides starting from appropriate sulfide precursors.

The precursor method is known to provide an easy, energy-saving route for preparing complex metal oxides,[7,8] some of which are metastable or cannot be prepared otherwise by a direct solid-state reaction of the components. It was our expectation that a similar approach might be possible for preparing Chevrel phases. For this purpose, we have employed polythiomolybdates as convenient precursors. Salts of MoS_4^{2-} are precluded as precursors because of unfavorable M/Mo ratios in such compounds. Polythiomolybdate species such as $Mo_2S_8^{2-}$, $Mo_2S_{10}^{2-}$, $Mo_2S_{12}^{2-}$, $Mo_3S_9^{2-}$, and $Mo_3S_{13}^{2-}$ have been prepared by the redox reaction of $(NH_4)_2MoS_4$ in aqueous or nonaqueous media.[9] Among these, salts of the $Mo_3S_9^{2-}$ ion[9d] with appropriate ternary metals constitute ideal precursor compounds for the synthesis of Chevrel phases. We have synthesized a new series of compounds of the general formula $M_p(NH_4)_qMo_3S_9$ (M = Cu, Pb, La, or Gd); these sulfides, on being heated in a hydrogen atmosphere around 1000 °C, directly yield the Chevrel phase sulfides $M_xMo_6S_8$.

Experimental Section

$(NH_4)_2MoS_4$ was prepared[9d] by passing H_2S through an ammonium hydroxide solution of $(NH_4)_6Mo_7O_{24}$ at ~50 °C. Preparation of $M_p(NH_4)_qMo_3S_9$ (M = Cu, Pb, La, or Gd) was achieved by a procedure similar to that employed by Pan et al.[9d] To a solution of $(NH_4)_2MoS_4$ (4 g, 15.37 mmol) in DMF (130 mL) was added a DMF solution of the metal chloride (M = Cu, Pb, La, or Gd) (Cu, 0.6890 g, 5.12 mmol; Pb, 0.7125 g, 2.56 mmol); La, 0.6280 g, 2.56 mmol; Gd, 0.6750 g, 2.56 mmol) was added. The resulting mixture was heated over a water bath (~90 °C) for 5-6 h while N_2 was bubbling. The reaction mixture was filtered and the filtrate diluted with ether (1:5 ratio by volume). The black solid that separated out overnight was collected, washed with small amounts of methanol, and air-dried. The solid products were identified to be $M_p(NH_4)_qMo_3S_9$ by chemical analysis and infrared spectroscopy (Table I). The results of chemical analysis are good to ±1%.

Chemical analyses of M, Mo, and S were carried out by standard methods.[10] Molybdenum was separated out by digestion with Na_2S and NaOH and estimated as MoO_3 gravimetrically. For La and Gd compounds, the rare-earth metal was separated as hydroxides by treating the solid with hot aqueous ammonia and estimated gravimetrically as sesquioxides. Sulfur was determined gravimetrically as $BaSO_4$ after oxidizing the samples with Br_2 in CCl_4 followed by a treatment with concentrated HNO_3.

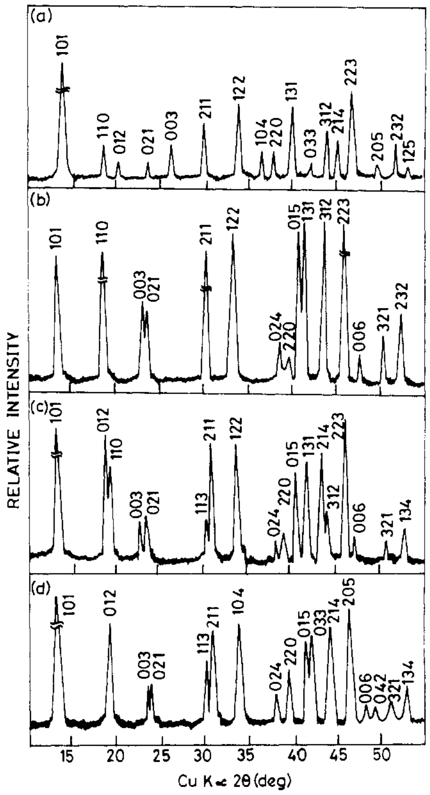

Figure 1. X-ray powder diffraction patterns of Chevrel phase sulfides prepared by the precursor method: (a) $Cu_2Mo_6S_8$; (b) $PbMo_6S_8$; (c) $LaMo_6S_8$; (d) $GdMo_6S_8$.

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Table I. Characterization of $M_p(NH_4)_qMo_3S_9$ Precursors and the Chevrel Phases Obtained from Them

$M_p(NH_4)_qMo_3S_9$	anal. found,[a] % M	Mo	S	IR abs bands	Chevrel phase[b]	hexagonal lattice params, Å
$Cu(NH_4)Mo_3S_9$	9.70	42.75	42.16	1380 (m), 510 (m)	$Cu_2Mo_6S_8$	a_h = 9.610 (4)
	(9.65)	(43.75)	(43.86)	485 (s)		c_h = 10.240 (3)
$Pb_{0.5}(NH_4)Mo_3S_9$	14.45	41.50	40.70	1380 (m), 510 (s)	$PbMo_6S_8$	a_h = 9.207 (3)
	(14.84)	(41.23)	(41.34)	465 (m)		c_h = 11.470 (2)
$La_{0.5}(NH_4)_{0.5}Mo_3S_9$	10.35	44.65	44.00	1400 (m), 540 (sh)	$LaMo_6S_8$	a_h = 9.122 (2)
	(10.60)	(43.95)	(44.06)	510 (s), 470 (m)		c_h = 11.552 (3)
$Gd_{0.5}(NH_4)_{0.5}Mo_3S_9$	11.55	42.25	42.20		$GdMo_6S_8$	a_h = 9.076 (4)
	(11.84)	(43.34)	(43.45)			c_h = 11.350 (3)

[a] Calculated percentages are given in parentheses. [b] Chevrel phases are obtained by heating the $M_p(NH_4)_qMo_3S_9$ at 1000 °C in hydrogen for 4–5 h.

Infrared spectra in KBr pellets were recorded by using a Perkin-Elmer Model 580 spectrometer. X-ray powder diffraction patterns were recorded with a JEOL JDX-8P powder diffractometer using nickel-filtered Cu Kα radiation. ^{1}H NMR spectra were recorded on a Bruker MSL-300 instrument. Electrical resistivity measurements were made on pressed, sintered pellets by a four-probe ac method.

Results and Discussion

Synthesis of salts of $Mo_3S_9^{2-}$ with a number of cations is readily achieved in DMF medium. Accordingly, we first attempted synthesis of a copper salt of composition $CuMo_3S_9$ as a potential precursor to prepare $Cu_2Mo_6S_8$. We found that the copper compound obtained by the procedure described in the Experimental Section had the composition $Cu(NH_4)Mo_3S_9$, copper being present in the monovalent state. This compound on heating in hydrogen at 1000 °C for 4 h converts neatly to $Cu_2Mo_6S_8$ (Figure 1).

Encouraged by this result, we proceeded to synthesize complex salts of $Mo_3S_9^{2-}$ ion with a variety of M cations known to form Chevrel phases. The compositions of the precursor sulfides of the general formula $M_p(NH_4)_qMo_3S_9$ with M = Cu, Pb, La, and Gd are listed in Table I. Infrared spectra show characteristic bands of the $Mo_3S_9^{2-}$ ion between 400 and 600 cm^{-1}; a band seen around 1400 cm^{-1} is due to the bending mode (ν_4) of the NH_4^+ ion. All the precursor sulfides are converted to single-phase $M_xMo_6S_8$ ($x = 2p$) compounds on heating them at 1000 °C for 4–5 h, according to

$$2M_p(NH_4)_qMo_3S_9 + 10H_2 \rightarrow M_{2p}Mo_6S_8 + 10H_2S + 2qNH_3 + qH_2 \quad (1)$$

What is significant is not only that the method yields single-phase products but also that the products are nearly stoichiometric as revealed by chemical analysis of the Mo/S ratio (e.g. this ratio in $LaMo_6S_8$ is found to be 0.753). We feel that the method is useful for the synthesis of stoichiometric Chevrel phase sulfides of several metals. The method is particularly important for the synthesis of rare-earth Chevrel phases where synthesis of the conventional ceramic method is plagued by the presence of a number of impurity phases referred to earlier.

In the precursor $M_p(NH_4)_qMo_3S_9$, the value of p is fixed by the ratio of the reactants, $(NH_4)_2MoS_4$ and the metal chloride, and there is no excess of $(NH_4)_2MoS_4$. It is to be noted that the MoS_4^{2-} is readily converted to $Mo_3S_9^{2-}$ in DMF medium around 90 °C. Choice of DMF as the solvent is therefore crucial because of its relatively high boiling point.

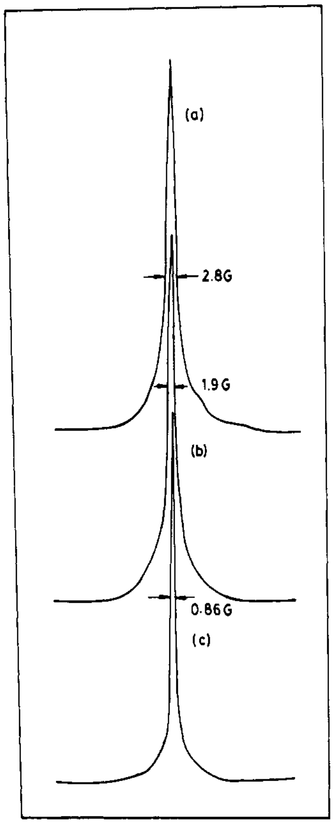

Figure 2. Integrated hydrogen line in the NMR spectrum: (a) $Cu_2Mo_6S_8$; (b) $PbMo_6S_8$; (c) $LaMo_6S_8$, prepared by the precursor method.

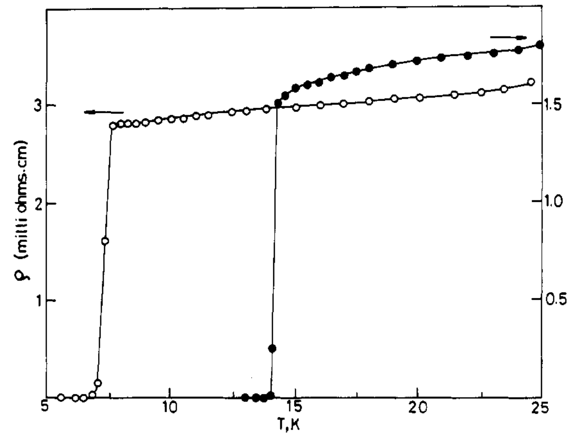

Figure 3. Temperature variation of electrical resistivity of $LaMo_6S_8$ (open circles) and $PbMo_6S_8$ (solid circles) prepared by the precursor method.

In the method of preparation adopted by us, we avoid the incorporation of oxygen since we employ pure, dry hydrogen in the reduction reaction. Absence of oxygen in the final Chevrel phases is also indirectly shown by the c_h/a_h ratio of $PbMo_6S_8$ (1.246), which corresponds with that in the literature.[11] We would however expect some hydrogen to be present in the Chevrel phases by virtue of reaction 1. We have carried out NMR studies in the Chevrel phases prepared by us and the spectra (Figure 2) indeed show evidence for the presence of hydrogen. The presence of hydrogen in Chevrel phases has been reported earlier by Alekseevskii et al.,[12] Schramm et al.,[13] and Gocke et al.[14] In order to find out the nature of hydrogen, we carried out infrared

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spectroscopic studies and find no evidence for water,[15] the characteristic stretching and bending frequencies being absent. The nature of hydrogen in these solids needs to be further investigated.

We have carried out electrical resistivity measurements of $LaMo_6S_8$ and $PbMo_6S_8$ in order to see whether the method of preparation reported here has any effect on the superconducting critical transition temperature (T_c). In Figure 3, we show the variation of resistivity with temperature of these two compounds. We see that zero resistance is attained at 6.79 and 14.05 K for $LaMo_6S_8$ and $PbMo_6S_8$, respectively. The literature values of transition tempertures for these two solids[16,17] prepared by the ceramic method are 4.74–6.76 and 9.5–15.2 K, respectively, depending on the stoichiometry and homogenity of the samples. The T_c values of the present sample suggest that they are nearly stoichiometric. It is clear that the method reported by us has no adverse effect on the T_c. It is particulary noteworthy that single-phase $LaMo_6S_8$ was prepared by us at 1000 °C, while the method reported recently by Tsunekawa et al.[16] requires temperatures as high as 1500 °C.

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Synthesis of a Novel Tetrameric Palladium(II) Complex Having Bridging Chlorides and Corner-Spanning Methylenebis(phosphinic acidate) Ligands

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The tetrakis(μ-pyrophosphito)platinate(II) complex $Pt_2(pop)_4^{4-}$ (pop = μ-$P_2O_5H_2^{2-}$) continues to attract interest because of its unique photophysical properties and photochemical reactivity.[2,3] More recently an analogue diplatinate(II) complex $Pt_2(pcp)_4^{4-}$ (pcp = μ-$P_2CO_4H_4^{2-}$) has been prepared, and its preliminary photophysical and structural properties have been described.[4,5] All previous attempts to prepare the palladium analogue complexes with the pop ligands have failed because the synthetic routes from phosphorous acid cause rapid reduction of the added palladium salts to the free palladium metal. Aqueous solutions of Na_2PdCl_4 and $CH_2(PH(O)OH)_2$ ($pcpH_2$) under all pH conditions also give palladium metal as the final product, but in methanol solvent this reduction does not occur, and we have isolated the first pcp palladium complex.

Table I. Crystal, Data Collection, and Refinement Parameters for **1**

formula	$Pd_4Cl_4P_8Na_2C_4H_{34}O_{24}$
cryst system	monoclinic
space group	$P2_1/n$
a, Å	8.5390 (10)
b, Å	15.713 (2)
c, Å	13.857 (2)
β, deg	106.60 (1)
V, Å^3	1781.7 (8)
D(calcd), g cm^{-3}	2.474
Z	2
temp, °C	26
cryst dimens, mm	0.06 × 0.24 × 0.40
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)
diffractometer	Enraf-Nonius CAD4
transmission (max/min)	99.66/76.56
θ limits, deg	1–25
decay, %	0
no. of unique data	3127
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2660
GOF	2.205
R, %	2.8
R_w, %	3.9

Experimental Section

Sodium tetrachloropalladate was purchased from Mathey Bishop Inc. Methylenebis(phosphinic acid) was prepared by the literature procedure.[5] Infrared spectra were measured as Nujol mulls on a Perkin-Elmer Model 683 spectrometer. Far-infrared spectra were measured as Vaseline mulls on a Mattson Cygnus 100 FTIR spectrometer.

Sodium Tetrakis(μ-chloro)bis(μ-methylenebis(phosphinic acidato)(2–))bis(μ-methylenebis(phosphinic acidato)(1–))tetrapalladate(II), $Na_2[Pd_4(\mu\text{-}Cl)_4(pcp)_2(pcpH)_2]$. To a 10-mL round-bottom flask was added sodium tetrachloropalladate trihydrate (50 mg, 0.14 mmol), methylenebis(phosphinic acid) (41 mg, 0.28 mmol), and methyl alcohol (1 mL). The solution was heated in an oil bath at 53 °C for 1 h. A precipitate of sodium chloride formed as the brown solution changed color through yellow to almost colorless. The solvent was removed either on a rotary evaporator or by passage of a stream of nitrogen gas. The residue was dissolved in 3–5 mL of aqueous sodium chloride (1 M), and the flask was stoppered. After several hours a pale yellow compound began to precipitate. After 7–10 days the supernatant liquid was removed by pipette, and the residual solid was washed with water (2 × 5 mL). The solid product was dried in vacuo to give the complex as the octahydrate. Yield: 20 mg (10%). Extended heating of the reaction mixture gave a different unidentified compound that shows a red emission at 77 K.

Crystals of $Na_2[Pd_4Cl_4(CH_2PO_4H_2)_2(CH_2PO_4H_3)_2]\cdot 8H_2O$ suitable for x-ray diffraction were obtained directly from the synthetic procedure. A crystal was placed in a capillary tube for data collection. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator by $\omega/2\theta$ scans of variable rate designed to yield $\sigma(I) = 0.02I$ for all observable data. A maximum of 120 s was used for the scan time of weak reflections. The data were corrected for Lp, background, and absorption effects. The absorption correction was based on ψ scans of reflections near $\chi = 90°$. Data having $I > 3\sigma(I)$ were used in the refinement. Crystal details are collected in Table I. The structure was initially solved by heavy-atom techniques. The tetramer lies on a center of symmetry in $P2_1/n$, and the crystals contain eight molecules of water per tetramer. The charge balance was accommodated by a model where both oxygen atoms on P(1) are protonated. All H atoms were located, but they did not successfully refine; in the final model only the hydrogens on CH_2 were refined. The oxygens O(1)–O(5) are linked by a hydrogen bond; O(2) donates a hydrogen bond to a neighboring tetramer (O(2)–O(3)′ = 2.651 (3) Å).

The crystal has a slight disorder where the entire anion is rotated by 90° without greatly affecting the P and Cl atom positions. This happens for approximately 4% of the molecules. Refinement was by full-matrix least squares with weights $w = \sigma^{-2}(F_o)$. Final residuals are given in Table I. Non-hydrogen atomic positions are given in Table II, and selected bond distances and angles are collected in Table III.

Results and Discussion

The colorless residue from the reaction of $PdCl_4^{2-}$ and $CH_2(PH(O)OH)_2$ in methanol gives, on heating in aqueous sodium chloride solution and allowing the mixture to stand for a few days, yellow crystals of a new complex. This insoluble complex shows

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