$^{249}_{98}Cf^{3+}$, that is $^{249}_{98}Cf^{4+} + {}^{0}_{-1}e^{-} \rightarrow {}^{249}_{98}Cf^{3+}$. The necessity to maintain overall electroneutrality in the trichloride sample favors the maintenance of metal ion oxidation state. The retention of both local and long-range structures by the daughter $CfCl_3$ is expected in these $BkCl_3$ samples owing to the very small energies ($\leq$0.3 eV) imparted to the daughter Cf nuclei at the moment of β-particle emission ($E_{\beta^-} \leq 126$ keV) from the parent ^{249}Bk nucleus. These recoil energies are insufficient to remove the daughter Cf nucleus from the lattice site of its parent Bk nucleus, and thus the structure of the parent Bk compound is retained by the daughter Cf compound. These observations are in agreement with our earlier findings on dimorphic $BkBr_3$, where o-$CfBr_3$ resulted from the β decay of o-$BkBr_3$.[11]

Acknowledgment. We gratefully acknowledge the U.S. Department of Energy's Transplutonium Program Committee for making available the ^{249}Bk and ^{249}Cf used in this work as part of its national program of transplutonium element production and research.

Registry No. ^{249}Bk, 14900-25-5; ^{249}Cf, 15237-97-5; $^{249}BkCl_3$, 20063-16-5; $^{249}CfCl_3$, 89759-77-3.

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Hydrothermal Synthesis of Copper Molybdates

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Several copper molybdate phases were prepared either hydrothermally or by reflux reactions at ambient pressures. $Cu_4Mo_6O_{20}$ was obtained by the hydrothermal reaction of CuO and MoO_3 in H_2O. It is triclinic, space group $P\bar{1}$, with $a = 10.071$ (4) Å, $b = 9.796$ (6) Å, $c = 8.052$ (4) Å, $\alpha = 104.98$ (4)°, $\beta = 100.63$ (4)°, $\gamma = 82.91$ (4)°, and $Z = 2$. The structure consists of chains of edge-sharing MoO_6 octahedra with the copper ions residing between the chains. $Cu_3(MoO_4)_2(OH)_2$ was prepared through precipitation from the reaction of $CuSO_4{\cdot}5H_2O$ and $Na_2MoO_4{\cdot}2H_2O$. The same product formed hydrothermally when CuO and MoO_3 were treated in aqueous sodium molybdate. The use of NaOH in hydrothermal reaction led to the formation of $NaCu(OH)(MoO_4)$, which is isomorphous with the zinc phase previously reported. Hydrothermal treatment of $Cu_3(MoO_4)_2(OH)_2$ in sodium molybdate also resulted in the formation of the latter phase.

Introduction

The preparation and structure of a number of copper molybdate phases have been reported in the literature. Most of these phases were prepared by solid-state reactions of the oxides of copper and molybdenum. The first crystal structure determined was that of $CuMoO_4$ prepared at ambient pressures.[1,2] This triclinic phase and its isostructural analogue $ZnMoO_4$, were recognized as having more distorted structures compared to the similar phases formed with other 3d transition metals. The high-pressure form of $CuMoO_4$ has a triclinic (distorted wolframite) structure,[3] while some of the other high-pressure molybdates, e.g. $MnMoO_4$, are monoclinic.[4] One of the main structural features of both $CuMoO_4$ phases is the irregular coordination around copper, and in the low-pressure polymorph there is also the presence of different coordination numbers for individual copper atoms. This latter feature is also observed in the structure of $Cu_3Mo_2O_9$, which contains CuO_5 tetragonal pyramids in addition to distorted CuO_6 octahedra.[5] A partially reduced form of this compound[6] has a structure with the formula $Cu_{3.85}Mo_3O_{12}$ instead of $Cu_3Mo_2O_8$ as originally proposed.[7]

Studies on the phase relationships in the Cu_2O-CuO-MoO_3 system reveal the existence of two cuprous molybdates, $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$.[8-11] Recently, the latter phase was described as $Cu_6Mo_5O_{18}$ rather than $Cu_6Mo_4O_{15}$.[12] The structure determination of this phase revealed a three-dimensional arrangement consisting of MoO_6 octahedra and CuO_4 tetrahedra. In addition to direct synthesis, these phases also form as the intermediate or final products in the reduction of cupric molybdates depending on the reaction temperatures. The temperature of preparation is a very important factor since each of the cupric or cuprous molybdates form only in a limited temperature range.

In addition to the interest that exists in the structural characteristics of transition-metal molybdates, their catalytic properties are also significant. $CuMoO_4$ has specifically been applied to the oxidation of propene.[13]

We report here the results of several reactions in aqueous media. The possibilities for forming new phases and growing crystals large enough for single-crystal X-ray studies were examined with use of both reflux and hydrothermal techniques. In this report we describe three such phases, namely $Cu_4Mo_6O_{20}$, $Cu_3(MoO_4)_2(OH)_2$, and $NaCu(OH)(MoO_4)$.

Experimental Section

All of the chemicals used were ACS reagent grade, and distilled, deionized water was used throughout.

Reflux Reactions. Several reactions were carried out with use of aqueous solutions of $Na_2MoO_4{\cdot}2H_2O$ and $CuSO_4{\cdot}5H_2O$ in the concentration range 0.5-1 M. One of the solutions was brought to boiling in a round-bottom flask. The second solution was added dropwise with stirring. The order of addition did not affect the nature of the final product. The mixture was refluxed for ca. 24 h. Similar procedures have been reported earlier.[14]

Hydrothermal Reactions. These reactions were performed in a small (15 mL) Parr bomb fitted with a Teflon liner. A typical reaction involved placing equimolar quantities of the solid starting materials, e.g. CuO and

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Table I. Crystallographic Data for Copper Molybdate Phases

	NaCu(OH)(MoO$_4$)	Cu$_4$Mo$_6$O$_{20}$
fw	263.48	1149.82
cryst dimens, mm	0.14 × 0.07 × 0.04	0.25 × 0.22 × 0.20
cryst color, form	green, needles	dark blue, prisms
space group	*Pnma*	$P\bar{1}$
syst absences	$0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$	none
cell params		
a, Å	7.726 (2)	10.071 (4)
b, Å	5.968 (2)	9.796 (6)
c, Å	9.495 (3)	8.052 (4)
α, deg	90.0	104.98 (4)
β, deg	90.0	100.63 (4)
γ, deg	90.0	82.91 (4)
V, Å^3	437.8 (1)	751.8 (13)
Z	4	2
d_{calcd}, g/cm^3	3.997	5.073
transmission factor range	86.30–99.52	81.40–99.76
μ, cm^{-1}	78.55	133.04
temp, °C	23	23
no. of reflcns		
total	783	4379
unique, $I > 3\sigma$	530	3932
standards	1,1,3; 1,2,1; 2,1,2	$0,3,\bar{1}$; $1,\bar{2},2$; $2,\bar{1},2$
R^a	0.034	0.045
$R_w{}^b$	0.042	0.064

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = (1/\sigma)|F_o|^2$.

Table II. Positional and Thermal Parameters for Cu$_4$Mo$_6$O$_{20}$

atom	x	y	z	B_{eqv}, Å^2	occupancy
Mo1	0.79930 (5)	0.79927 (5)	0.03380 (6)	0.703 (9)	
Mo2	1.08763 (5)	0.79079 (6)	−0.13225 (6)	0.718 (9)	
Mo3	0.51538 (5)	0.80411 (5)	−0.24815 (7)	0.680 (9)	
Mo4	0.63142 (5)	0.46538 (5)	−0.34954 (6)	0.671 (9)	
Mo5	0.23437 (5)	0.98518 (5)	0.24617 (6)	0.676 (9)	
Mo6	0.82174 (5)	0.67941 (5)	0.57696 (6)	0.627 (8)	
Cu1	1.0295 (1)	0.6232 (1)	0.2558 (1)	1.82 (2)	
Cu2	0.5813 (1)	0.8505 (1)	0.3335 (1)	1.96 (2)	
Cu3	0.8375 (2)	1.0973 (1)	0.4009 (2)	2.41 (3)	0.76 (1)
Cu3′	0.8897 (7)	0.0930 (5)	0.4127 (6)	4.0 (1)	0.24 (1)
Cu4	0.6369 (1)	0.5323 (2)	0.1391 (2)	4.19 (3)	0.89 (1)
Cu4′	0.6054 (8)	0.4640 (10)	0.0877 (12)	2.1 (2)	0.11 (3)
O1	1.1476 (5)	0.7557 (5)	−0.2959 (6)	1.10 (8)	
O2	0.3256 (4)	0.1653 (4)	0.4200 (5)	0.68 (7)	
O3	0.2739 (5)	0.4652 (5)	0.5433 (5)	0.91 (8)	
O4	0.3461 (4)	0.0824 (5)	0.0922 (5)	0.78 (8)	
O5	0.3836 (5)	0.8818 (5)	0.2863 (6)	1.19 (9)	
O6	0.4626 (5)	0.5572 (5)	0.1962 (6)	1.22 (9)	
O7	0.0374 (5)	0.4257 (5)	0.3069 (6)	0.83 (8)	
O8	0.6901 (5)	0.7368 (5)	0.1435 (6)	1.10 (8)	
O9	0.2263 (5)	0.6497 (5)	0.3250 (6)	1.32 (9)	
O10	0.8592 (5)	0.1279 (5)	0.9522 (6)	1.08 (9)	
O11	0.1377 (5)	0.9717 (5)	0.3994 (6)	1.24 (9)	
O12	0.8616 (5)	0.9438 (5)	0.1827 (6)	1.26 (9)	
O13	0.0456 (5)	0.3248 (5)	0.9684 (6)	0.95 (8)	
O14	0.5970 (5)	0.0708 (5)	0.3277 (7)	1.5 (1)	
O15	0.7939 (5)	0.4203 (5)	0.0742 (6)	1.32 (9)	
O16	0.4777 (5)	0.6326 (5)	0.5610 (6)	1.02 (8)	
O17	0.1148 (5)	0.1699 (4)	0.1895 (6)	0.77 (8)	
O18	0.3035 (4)	0.3526 (5)	0.2207 (6)	0.84 (8)	
O19	0.5618 (5)	0.2394 (6)	0.1012 (6)	1.53 (9)	
O20	0.9087 (5)	0.7209 (5)	0.4339 (6)	1.19 (9)	

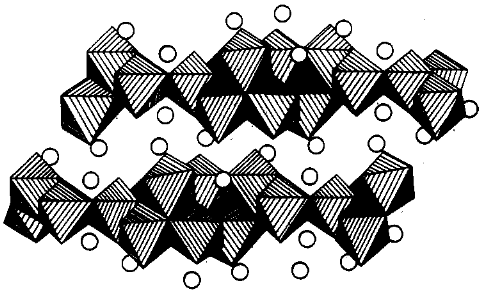

Figure 1. Arrangement of the MoO$_6$ octahedra in the structure of Cu$_4$Mo$_6$O$_{20}$. The infinite chains of octahedra are parallel to the *ab* plane, and the copper atoms are shown as circles.

MoO$_3$, into the bomb with water. The amount of water added corresponded to 50–60% of the total volume of the liner. The bomb was then sealed and placed in a furnace at temperatures ranging from 200 to 300 °C. Reaction times were approximately 24 h.

X-ray powder patterns were obtained with Cu Kα filtered radiation on a Seifert-Scintag PAD-II automated powder diffractometer. ESR spectra were taken at 77 K with a Varian E-6S spectrometer. The spin concentrations were determined relative to a phosphorus-doped silicon standard with $g = 1.9987$. Thermogravimetric analyses were performed with a Cahn RG unit at a heating rate of 4°/min under a nitrogen atmosphere.

X-ray Data Collection and Refinement. X-ray intensity data for Cu$_4$Mo$_6$O$_{20}$ and NaCu(OH)(MoO$_4$) were collected on a CAD-4 automated κ-axis single-crystal diffractometer (Enraf-Nonius) at ambient temperatures. The instrument was equipped with an incident beam graphite crystal monochromator, and Mo radiation was used ($\lambda = 0.71073$ Å). Data were collected by the ω–2θ method to 80.0° in 2θ. Scan speeds varied from 20°/min for the reflections with the highest intensities to approximately 2°/min for the weakest reflections. The angular scan width was $A + 0.347(\tan \theta_{\lambda\alpha_2})$, where $\theta_{\lambda\alpha_2}$ is determined from the formula

$$\theta_{\lambda\alpha_2} = \theta_{\lambda\alpha_1} + \frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha}\,\frac{360}{2\pi} \tan \theta_{\lambda\alpha_1}$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for these structures was 0.70. The scan was extended on each side of the peaks by 25% for background determination. Accurate unit cell parameters were determined from 25 reflections collected at high 2θ angles ($2\theta > 30°$).

Three standard reflections were measured approximately every 150 reflections as a check of crystal and electronic stability; only statistical variations of these intensity standards were observed. Data were corrected for Lorentz and polarization effects. A series of ψ scans was used to empirically correct for absorption (SDP series of programs).[15] The important crystallographic informaion for the structures is listed in Table I.

The structure of NaCu(OH)(MoO$_4$) was solved by three-dimensional Patterson methods, which yielded the positions of the molybdenum and copper atoms. Successive difference Fourier syntheses yielded the remaining atoms. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods; the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o{}^2/\sigma(F_o{}^2)$ and only data having $I > 3\sigma(I)$ were included in the refinement. The standard deviation of intensities, $\sigma(I)$, is defined as $\sigma(I) = [S^2(C + R^2B) + (PI)^2]^{1/2}/Lp$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and P is an instrumental factor that in this case was 0.05.

The structure of Cu$_4$Mo$_6$O$_{20}$ was solved with use of direct methods (MITHRIL)[16] which located all of the molybdenum and two of the copper atoms. Successive difference Fourier syntheses were then used to locate the rest of the atoms. After all of the oxygens had been located, rather high residual peaks (~20 e/Å^3) were present around both Cu3 and Cu4. This feature, in addition to the relatively high temperature factors (~6 Å^2) for Cu3 and Cu4, indicated that a disorder model was needed. Removal of Cu3 and Cu4 followed by a difference Fourier yielded partially occupied sites Cu3/Cu3′ and Cu4/Cu4′. Population refinement of this model proved successful; the refined populations for Cu3/Cu3′ and Cu4/Cu4′ added up to 1 within experimental error. The populations were then adjusted and fixed so the total would be exactly 1.0. This clearly shows a distorted arrangement with partial occupancies for each pair of positions. All of the atoms were refined anisotropically.

Results

Cu$_4$Mo$_6$O$_{20}$. Hydrothermal reactions involving MoO$_3$ and CuO (in ratios ranging from 1:1 to 2:1) in H$_2$O resulted in the formation of large (1.4 × 0.4 × 0.4 mm) dark blue crystals. All of the final products contained some unreacted starting materials. The X-ray

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[15] "Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1981 (revised).

[16] "TEXAN Crystallographic System"; Molecular Structure Corp.: College Station, TX, 1985.

Table III. Bond Distances (Å) for $Cu_4Mo_6O_{20}$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo1	O4	2.039 (3)	Mo4	O9	1.725 (4)	Cu2	O2	2.069 (3)
Mo1	O8	1.780 (4)	Mo4	O16	2.274 (4)	Cu2	O5	1.958 (4)
Mo1	O12	1.703 (4)	Mo4	O16′	1.937 (3)	Cu2	O8	2.053 (4)
Mo1	O13	1.857 (3)	Mo4	O18	1.941 (3)	Cu2	O14	2.196 (4)
Mo1	O17	2.234 (3)	Mo5	O2	2.137 (3)	Cu3	O1	1.882 (5)
Mo1	O18	2.347 (3)	Mo5	O4	2.259 (3)	Cu3	O11	1.865 (5)
Mo2	O1	1.724 (3)	Mo5	O5	1.733 (4)	Cu3	O12	2.027 (5)
Mo2	O7	2.029 (3)	Mo5	O10	1.859 (3)	Cu3	O14	2.415 (10)
Mo2	O13	2.157 (3)	Mo5	O11	1.745 (3)	Cu3′	O1	1.917 (10)
Mo2	O17	2.259 (3)	Mo5	O17	2.149 (3)	Cu3′	O11	1.860 (12)
Mo2	O10	1.910 (3)	Mo6	O2	1.988 (3)	Cu3′	O11′	2.639 (10)
Mo2	O15	1.729 (4)	Mo6	O3	1.777 (3)	Cu3′	O12	2.039 (13)
Mo3	O2	2.391 (3)	Mo6	O7	1.896 (3)	Cu4	O3	2.544 (10)
Mo3	O4	1.943 (3)	Mo6	O17	2.116 (3)	Cu4	O6	1.868 (4)
Mo3	O14	1.729 (4)	Mo6	O18	2.338 (3)	Cu4	O6′	2.656 (10)
Mo3	O16	1.984 (3)	Mo6	O20	1.721 (3)	Cu4	O8	2.126 (4)
Mo3	O18	2.251 (3)	Cu1	O7	2.068 (3)	Cu4	O15	1.886 (4)
Mo3	O19	1.694 (4)	Cu1	O9	1.988 (4)	Cu4′	O6	1.842 (8)
Mo4	O3	2.250 (3)	Cu1	O13	1.991 (3)	Cu4′	O6′	2.225 (10)
Mo4	O6	1.759 (3)	Cu1	O20	2.025 (3)	Cu4′	O15	1.911 (8)
						Cu4′	O19	2.329 (10)

Table IV. O–Cu–O Bond Angles (deg) for $Cu_4Mo_6O_{20}$

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O7	Cu1	O9	96.9 (2)	O1	Cu3	O14	101.1 (2)	O3	Cu4	O15	89.8 (2)
O7	Cu1	O13	127.0 (1)	O11	Cu3	O12	113.2 (2)	O6	Cu4	O6′	90.6 (2)
O7	Cu1	O20	95.1 (1)	O11	Cu3	O14	95.5 (2)	O6	Cu4	O8	106.5 (2)
O9	Cu1	O13	112.1 (2)	O12	Cu3	O14	87.9 (2)	O6	Cu4	O15	153.0 (2)
O9	Cu1	O20	116.6 (2)	O1	Cu3′	O11	112.2 (4)	O6′	Cu4	O8	100.3 (3)
O13	Cu1	O20	108.7 (2)	O1	Cu3′	O11′	146.0 (3)	O6′	Cu4	O15	83.6 (3)
O2	Cu2	O5	119.1 (2)	O1	Cu3′	O12	91.8 (3)	O8	Cu4	O15	100.5 (2)
O2	Cu2	O8	112.3 (1)	O11	Cu3′	O11′	95.9 (4)	O6	Cu4′	O6′	106.3 (4)
O2	Cu2	O14	105.2 (1)	O11	Cu3′	O12	78.6 (4)	O6	Cu4′	O15	153.1 (6)
O5	Cu2	O8	121.5 (2)	O11′	Cu3′	O12	112.8 (6)	O6	Cu4′	O19	95.0 (3)
O5	Cu2	O14	89.3 (2)	O3	Cu4	O6	87.4 (2)	O6′	Cu4′	O15	96.0 (3)
O8	Cu2	O14	102.8 (2)	O3	Cu4	O6′	161.5 (1)	O6′	Cu4′	O19	98.4 (4)
O1	Cu3	O11	149.2 (4)	O3	Cu4	O8	97.8 (2)	O15	Cu4′	O19	96.3 (4)
O1	Cu3	O12	93.2 (4)								

single-crystal structure determination confirmed the formation of a new phase. Its space group was unambiguously found to be $P\bar{1}$. The positional and thermal parameters are listed in Table II, and the bond distacnces are given in Table III. The structure consists of chains made up of distorted MoO_6 octahedra that are edge-shared. The copper atoms are situated between these chains bonding to the terminal oxygens of the molybdate units. This structural arrangement is shown in Figure 1.

Cu1 and Cu2 are tetrahedrally coordinated. The Cu–O bond distances in each tetrahedron are close to each other with an average of 2.018 (10) Å for Cu1 and 2.069 (19) Å for Cu2. There is some distortion in the angles; for Cu1 they range from 95.1 (1) to 127.0 (1)° whereas for Cu2 the range is from 89.3 (2) to 121.5 (2)°.

Each of the remaining two coppers are statistically distributed in two different positions. The coordinations of these sites are shown in Figure 2. The bonding arrangement of the sites occupied by Cu3 are very similar. They consist of three normal Cu–O bonds and one significantly longer (2.415 (10) Å for Cu3; 2.639 (10) Å for Cu3′) to result in a very distorted tetrahedral arrangement. The two sites, Cu3 and Cu3′, are 0.515 (9) Å apart. Cu4 presents a different situation. Its two sites are 0.762 (9) Å apart, and these two positions have different coordinations. The Cu4 site, which has the majority of the population (0.89), has a tetragonal pyramid arrangement with two of the basal oxygens, at opposite ends, having a considerably longer distance than the others. The Cu4′ site, however, is four-coordinate and similar to Cu3 in its distorted coordination. Although there is variation in its four Cu–O bond distances (1.842 (8) – 2.329 (10) Å), the range is smaller and it does not have one unusually longer bond as was observed in Cu3 and Cu3′.

The ESR measurements show a signal at $g = 2.112$ which is due to the presence of Cu(II). However, a quantitative study indicated that the signal from Cu(II) corresponded to only 0.2% of the total amount of Cu present in the sample. Considering the presence of starting materials in the final product, it is expected that some copper(II) oxide was mixed with the crystals picked for the ESR study especially on the crystal surfaces. It is therefore apparent that all of the copper atoms in $Cu_4Mo_6O_{20}$ are monovalent. No signal for lower valence molybdenum was observed, confirming the hexavalent nature of all the molybdenum atoms.

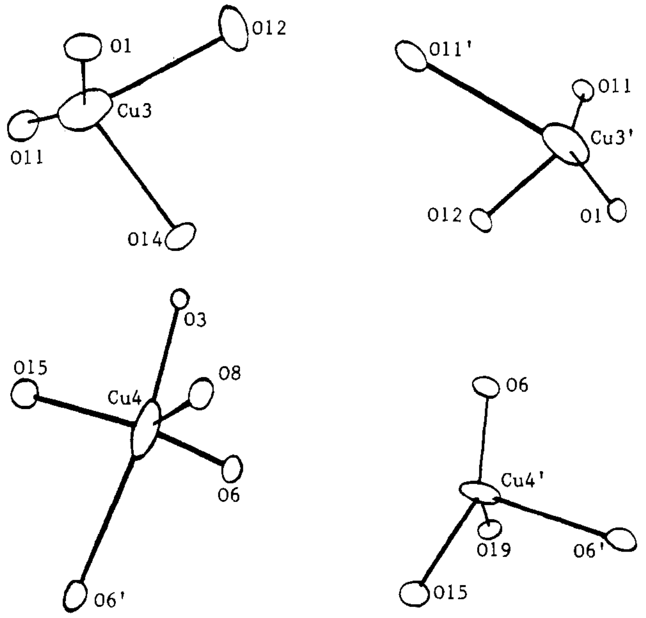

Figure 2. coordination of the copper atoms in $Cu_4Mo_6O_{20}$.

Table V. Positional and Thermal Parameters for $NaCu(OH)(MoO_4)$

atom	x	y	z	B_{eqv}, Å^2
Mo	0.1314 (9)	−0.2500 (0)	0.16289 (7)	0.72 (1)
Cu	0.5000 (0)	0.0000 (0)	0.0000 (0)	0.75 (2)
Na	0.3697 (5)	0.2500 (0)	0.3056 (4)	1.60 (7)
O1	0.3259 (9)	−0.2500 (0)	0.0546 (7)	1.3 (1)
O2	0.1201 (7)	−0.4895 (8)	0.2686 (5)	1.47 (8)
O3	−0.0445 (11)	−0.2500 (0)	0.0469 (9)	2.7 (2)
O4	0.3681 (8)	0.2500 (0)	0.0612 (6)	0.9 (1)

Table VI. Bond Distances (Å) for $NaCu(OH)(MoO_4)$

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	O1	1.820 (6)	Cu	O4	1.898 (3)[a]
Mo	O2	1.749 (4)[a]	Na	O2	2.502 (5)[a]
Mo	O3	1.750 (7)	Na	O2′	2.580 (5)[a]
Cu	O1	2.075 (4)[a]	Na	O3	2.659 (8)
Cu	O2	2.385 (4)[a]	Na	O4	2.321 (6)

[a] Twice.

$Cu_3(MoO_4)_2(OH)_2$. This phase, which is known as lindgrenite,[17] was obtained from a reflux reaction involving 100 mL of 0.5 M $CuSO_4{\cdot}5H_2O$ and 100 mL of 0.5 M $Na_2MoO_4{\cdot}2H_2O$. The variations of this reaction included other concentrations but the same molar ratio, and lower pH brought about by adding sulfuric acid to the solutions. The pH of the attempted reactions ranged from 3 to 6. In all these cases, the X-ray powder pattern was identified as that of $Cu_3(MoO_4)_2(OH)_2$ (JCPDS PDF No. 10–395). This rather dominant phase in the aqueous reactions was also obtained when MoO_3 and CuO were treated hydrothermally in an aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (~0.7 M) at 200 °C. The addition of sodium molybdate results in a more basic solution, which aids in the formation of this product. Although no sodium is incorporated into the formula, a significant difference is observed compared to the hydrothermal reactions which were conducted in pure water.

Thermogravimetric studies on this phase revealed a weight loss of approximately 3.3%, which is equivalent to 1 mol of H_2O. This loss takes place between 310 and 365 °C. The X-ray powder pattern of the heated product was identified as $Cu_3Mo_2O_9$ (JCPDS PDF No. 24–55).

$NaCu(OH)(MoO_4)$. The hydrothermal treatment of $Cu_3(MoO_4)_2(OH)_2$ in a $Na_2MoO_4{\cdot}2H_2O$ solution (1–2 M) resulted in the formation of this new phase. The products of these reactions were always microcrystalline, but attempts to grow larger single crystals were never successful. However, hydrothermal reactions involving MoO_3 and CuO (in ratios ranging from 1:1 to 2:1) in 0.5 M NaOH yielded green single crystals of $NaCu(OH)(MoO_4)$ along with the starting materials.

This phase is isostructural with $NaZn(OH)(MoO_4)$.[18] The space group is orthorhombic *Pnma* as was found for the zinc phase[19] rather than the originally reported *Pna*2$_1$. The structural features are as described previously.[18,19] Table V lists the positional and thermal parameters; the bond distances are given in Table VI. The position of the proton could not be determined by difference Fourier techniques. However, on the basis of the explanation offered for the zinc phase, it can be placed on O4.

Certain variations of the hydrothermal reaction have shown that the high-pressure phases that could be obtained are not limited to those presented here. The use of more acidic conditions or higher CuO to MoO_3 ratios have also been found fruitful. The synthetic and structural details of those phases will be reported later.

Discussion

The reflux reactions that were reported here along with many other variations have shown that formation of copper molybdates from solution at ambient pressures is rather limited: $Cu_3(MoO_4)_2(OH)_2$ and $NaCu(OH)(MoO_4)$ were the only phases obtained.

Table VII. Sodium-Containing Molybdate Phases Obtained from Solution[a]

M	$NaM_2(OH)(H_2O)(MoO_4)_2$ (**1**)	$NaM(OH)(MoO_4)$ (**2**)
Mn	H[a]	
Ni	R	
Cu		H and R
Zn	H and R	H

[a] Abbreviations: H = hydrothermal; R = reflux.

The relation of the latter to the isomorphous phase obtained from zinc demonstrates a unique connection that exists between the sodium-containing molybdates of several transition metals. Previous studies involving zinc,[18,20–22] manganese,[14] and nickel[23] had revealed the existence of two types of sodium-containing phases: $NaM_2(OH)(H_2O)(MoO_4)_2$ (**1**) and $NaM(OH)(MoO_4)$ (**2**) where M is the transition metal. Table VII shows the phases that were obtained for each transition metal and the method of synthesis. It is clear that these two phases show selectivity toward different metals. Perhaps the most surprising aspect of the results is the formation of **2** from both reflux and hydrothermal reactions for copper.

The hydrothermal technique as described here presents an aspect of this method that has not been investigated in detail in the past. We find it very significant to be able to use oxides of very low solubility such as CuO and MoO_3 in water or aqueous solutions to form a variety of phases. The reaction conditions seem to provide the ideal pressure for these phases to form. Another favorable feature of this technique is the ease with which relatively large single crystals can be grown. Any of the variables such as pH of the solution, ratio of the oxides, temperature, and time can be carefully adjusted to alter the outcome of these reactions. Recently, the hydrothermal synthesis of $Cu_6Mo_5O_{18}$ appeared in the literature.[12] There is similarity in the method of synthesis, but it should be noted that the pressures and temperatures are considerably lower in the reactions that are reported here.

The reduction of Cu(II) to Cu(I) in the preparation of $Cu_4Mo_6O_{20}$ is a feature that we have also observed in some other hydrothermal reactions involving copper. It is possible that water behaves as the reducing agent at the drastic conditions created by the hydrothermal reaction. The crystal structure of $Cu_4Mo_6O_{20}$ represents another copper molybdate phase which is of low symmetry and is highly distorted. An interesting structural arrangement is created by the buildup of molybdate octahedra in one dimension through edge sharing. It is significant that these continuous chains are made up of molybdate units only and that the copper atoms fall between these chains. This is somewhat similar to the structure of $Cu_6Mo_5O_{18}$.[12] The coordinations of the copper atoms show similarity to previous structures in terms of different coordination numbers and distortions in bond distances and angles.[2,3,5]

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Registry No. **2** (M = Cu), 104051-32-3; $Cu_4Mo_6O_{20}$, 73257-02-0; $Cu_3(MoO_4)_2(OH)_2$, 27739-50-0; Na_2MoO_4, 7631-95-0; $CuSO_4$, 7758-98-7; CuO, 1317-38-0; MoO_3, 1313-27-5; $Cu_3Mo_2O_9$, 11133-51-0.

Supplementary Material Available: Tables of anisotropic temperature factors and bond angles for each structure (5 pages); tables of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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