$$\underset{0.818}{nC_4H_8(NH)_2} + \underset{\begin{array}{r}1.620\\ -0.017\\ \hline 1.603\end{array}}{2n(CH_3)_2NB_2H_5} \longrightarrow \underset{1.651}{2nH_2} + \underset{1.600}{2n(CH_3)_2NBH_2} + \underset{0.818\ (89.7\ \mathrm{mg})}{(H_2BNC_4H_8NBH_2)_n}$$

The infrared spectrum of this polymer, in the form of a white film deposited from the gas phase upon the gas-cell windows, was recorded (in cm^{-1}) by the Beckman IR7 instrument. The hydrocarbon and C–N modes could be correlated with the 70° vapor-phase spectrum of pure piperazine; however, its complex patterns in the ranges 700–850 and 2700–2840 cm^{-1} were absent, presumably because their intensity was suppressed by the high polarity of the $N{-}BH_2$ groups. The B–H stretching modes were found at 2433 s, 2408 s, and 2350 m cm^{-1} (not CO_2!), correlating with 2446 vs, 2370 s, and 2230 m cm^{-1} for $(CH_3)_2NBH_2$ vapor. The B–N stretching mode showed at 1218 mw and 1184 s cm^{-1}; *cf.* 1209 s and 1192 s cm^{-1} for $(CH_3)_2NBH_2$ vapor. A characteristic BH_2 motion at 950 vs cm^{-1} compares with a 965–960 vs cm^{-1} doublet for $(CH_3)_2NBH_2$. A strong peak at 878 cm^{-1} is not understood. All of these frequencies are quite distinct from the piperazine spectrum.

Rapid scanning of a quickly heated sample by the Perkin-Elmer 337 instrument showed new peaks at 2550 vs and 2480 s cm^{-1}, evidently representing the monomer vapor. All other peaks correlated closely with those for the film.

The aqueous–HCl hydrolysis of $(H_2BNC_4H_8NBH_2)_n$ gave 100% of the expected hydrogen, but the methanol–HCl solvolysis gave only 70% of the expected piperazine hydrochloride and boric acid. A milky suspension indicated retention of a polymeric condition. Apparently the replacement of B–H by $B{-}OCH_3$ bonds made it sterically more difficult for the acid to break down the B–N bonds in the new polymeric mass.

Other Polymers.—Various other approaches led to more complex mixed-polymer products, usually more refractory than the pure sublimable $(H_2BNC_4H_8NBH_2)_n$. One experiment began with a demonstration of adduct formation at 25°

$$\underset{0.526}{C_4H_8(NH)_2} + \underset{\begin{array}{r}1.075\\ -0.553\\ \hline 0.522\end{array}}{(CH_3)_2NB_2H_5} \longrightarrow \underset{0.524}{HNC_4H_8NH\cdot(CH_3)_2NB_2H_5}$$

Then the pure adduct during 1 hr at 100° yielded 0.425 mmol of $(CH_3)_2NH$ and 0.626 mmol of H_2, leaving a white solid which neither melted nor volatilized *in vacuo* at 250°. Apparently this was stabilized by N–(BH)–N bonding but also included $(CH_3)_2N{-}B{-}H$ material.

Another approach aimed at the process

$$nC_4H_8(NB_2H_5)_2 + 2n(CH_3)_3N \longrightarrow 2n(CH_3)_3NBH_3 + (H_2BNC_4H_8NBH_2)_n$$

running 16 hr at 150° in a sealed tube with toluene as a possible solvent. However, the process was only partially quantitative: although the calculated amount of $(CH_3)_3N$ was absorbed, the recoverable yield of $(CH_3)_3NBH_3$ was only 84% and that of the sublimable polymer was 79%.

Direct dissociation also was tried: a 0.42-mmol sample of $C_4H_8(NB_2H_5)_2$, in a sealed tube immersed in an oil bath, was heated during 20 min from 170 to 210°, yielding $1.40H_2$, $0.06B_2H_6$, and $0.08B_5H_9$ per mole; then the white powdery product was inert to 12 *M* HCl and to various organic solvents. Its infrared spectrum (in a KBr pellet) showed the expected piperazine modes, along with B–H at 2515 cm^{-1} and BH_2 at 945 cm^{-1}. It probably was an intimate combination of $(H_2BNC_4H_8NBH_2)_n$ with boron–hydride units coming from loss of hydrogen from BH_3.

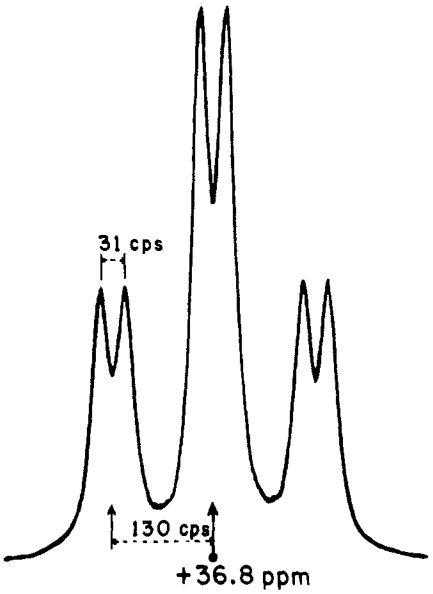

Figure 1.—Boron nmr spectrum of hexane solution of $C_4H_8(NB_2H_5)_2$ at 32.1 Mc. The chemical-shift reference is $B(OCH_3)_3$.

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Transition Metal Molybdates of the Type $AMoO_4$

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Considerable confusion has existed regarding structural relationships for molybdates of the type $AMoO_4$ where A is Mg, Mn, Fe, Co, Ni, or Zn. Young and Schwartz[1] have reported that high-pressure modifications of these molybdates are all isotypic with the analogous tungstates ($NiWO_4$ structure[2]). However, none of the structures of the normal (STP) molybdates has been known until recently. Smith and Ibers[3] have now reported the structure of α-$CoMoO_4$, and it

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(1) A. P. Young and C. M. Schwartz, *Science*, **141**, 348 (1963).

(2) R. O. Keeling, *Acta Cryst.*, **10**, 209 (1957).

(3) G. W. Smith and J. A. Ibers, *ibid.*, **19**, 269 (1965).

is known that α-$NiMoO_4$ is isotypic.[1,4] Although Kozmanov[5] has stated that α-$FeMoO_4$ is also isotypic with α-$CoMoO_4$, this has been disputed by others.[1,4,6]

Abrahams and Reddy[6] recently described the structure of α-$MnMoO_4$, and, although it has been suggested[1,6] that α-$MgMoO_4$ is isotypic with α-$MnMoO_4$, cell dimensions for α-$MgMoO_4$ have apparently never been given. Gleiser, *et al.*,[7] have suggested that there are high-temperature modifications of $NiMoO_4$ and $CoMoO_4$ which are isotypic with α-$MnMoO_4$.

Experimental Section

All reactants were of at least reagent grade quality. Four different preparative techniques were used. By the first method, appropriate amounts of reactants were intimately mixed, sealed in evacuated silica or platinum tubes, and then heated at about 1000° for 1–2 days. One reactant was always MoO_3; others were MgO; MnO_2 and Mn; Fe_2O_3 and Fe or Mo; Co_3O_4 and Co; NiO; or ZnO for the respective molybdates.

In the second method, a solution containing the appropriate divalent metal chloride was mixed stoichiometrically with an Na_2MoO_4 solution. After heating to 100°, the precipitate was filtered, washed, and dried at 400° under vacuum ($\sim 10^{-3}$ mm).

Hydrothermal experiments, method 3, were carried out as for method 1 except that the reactants were sealed in thin-walled gold tubes with water. These sealed collapsible tubes were heated at 700° for 8 hr or longer with 3000 atm of supporting pressure. Experiments in either platinum or gold containers at 65 kbars and 900°, method 4, used the same reactants as in method 1 or the products of method 1. The tetrahedral anvil used for these high-pressure experiments has been described elsewhere.[8]

X-Ray powder patterns were obtained on all samples at 25° using a Hägg–Guinier camera. The radiation was strictly monochromatic Cu $K\alpha_1$, and an internal standard of high-purity KCl (a = 6.2931 Å) was used. High-temperature powder patterns were obtained for $FeMoO_4$, $CoMoO_4$, and $NiMoO_4$ with an MRC high-temperature camera using an evacuated chamber. All cell dimensions were refined by least squares. Indexed powder patterns for α-$MgMoO_4$, $MgMoO_4$-II, α-$MnMoO_4$, $MnMoO_4$-II, α-$FeMoO_4$, β-$FeMoO_4$, $FeMoO_4$-II, β-$CoMoO_4$, $CoMoO_4$-II, α-$NiMoO_4$, β-$NiMoO_4$, $NiMoO_4$-II, and $ZnMoO_4$-II have been sent to ASTM.

Dta experiments were performed with a Du Pont 900 differential thermal analyzer. The heating rate was 15°/min, and a protective argon atmosphere was used.

Nomenclature

Letters of the Greek alphabet used as prefixes to compounds will designate the various polymorphs of a given composition occurring with increasing temperature. For polymorphs occurring with increasing pressure, Roman numerals are used as suffixes. The polymorph apparently stable under normal (STP) conditions is arbitrarily designated as the α form. These designations have no direct implications concerning the structures of the various polymorphs. Thus, while all the $AMoO_4$-II phases discussed in this paper happen to be isotypic, α-$MgMoO_4$ and α-$MnMoO_4$ are isotypic with β-$FeMoO_4$, β-$CoMoO_4$, and β-$NiMoO_4$.

Results

The results of the various preparations are summarized in Table I, and the unit cell dimensions are given in Table II. All samples prepared at 65 kbars had an $NiWO_4$-related structure as has been reported by Young and Schwartz.[1] All such high-pressure products exhibited endotherms on heating in argon, and the temperatures of the peaks are also given in Table II. The peak temperatures were reproducible to within 20°. Since the transformation temperature might be a function of time, three samples, $MgMoO_4$-II, $NiMoO_4$-II, and $ZnMoO_4$-II, were heated at 500° in air for 24 hr. Only $MgMoO_4$-II transformed under these conditions. High-temperature X-ray and dta experiments indicate that these transformations are irreversible, and X-ray powder patterns of the transformed products show the normal (STP) forms.

TABLE I

STRUCTURE TYPES OBTAINED BY VARIOUS PREPARATIVE METHODS[a]

	Method			
Compound	Solid state	Precipitation	Hydrothermal	High pressure
$MgMoO_4$	M	M	U	N
$MnMoO_4$	M	M	N	N
$FeMoO_4$	$\mathrm{M} \overset{400°}{\rightleftarrows} \mathrm{C}$	C	N	N
$CoMoO_4$	$\mathrm{M} \overset{500°}{\rightleftarrows} \mathrm{C}$	C	C	N
$NiMoO_4$	$\mathrm{M} \overset{690°}{\rightleftarrows} \mathrm{C}$	C	N	N
$ZnMoO_4$	Z	U	U	N

[a] Structure types: M, α-$MnMoO_4$; C, α-$CoMoO_4$; N, $NiWO_4$; Z, α-$ZnMoO_4$; U, undetermined.

Several of the high-pressure molybdates ($MnMoO_4$-II, $FeMoO_4$-II, and $NiWO_4$-II) could be prepared at 3 kbars and 700° hydrothermally. Although no attempt was made to determine the P–T diagrams for any of the molybdates, it is obvious that, for at least some of them, very little pressure is required for them to become isotypic with their analogous tungstates.

Under normal pressure $FeMoO_4$, $CoMoO_4$, and $NiMoO_4$ were found to undergo structural transformations at the temperatures indicated in Table I. These transformations were determined both by dta and high-temperature X-ray diffraction. In every case the high-temperature, β, form was found to be isotypic with α-$MnMoO_4$ while the low-temperature, α, form was found to be isotypic with α-$CoMoO_4$. It was possible to obtain β-$FeMoO_4$ and β-$CoMoO_4$ at STP, nearly free of the α form, by quenching from above the α–β transformation temperature. Attempts to obtain β-$NiMoO_4$ at room temperature by quenching were unsuccessful; consequently, the unit cell dimensions for β-$NiMoO_4$ (α-$MnMoO_4$ type) in Table II are based on X-ray powder data collected at 975°. A mixture of α- and β-$FeMoO_4$ was easily obtained at room temperature. Such a mixture may be completely converted to α-$FeMoO_4$ by grinding or by cooling to 78°K.

α-$ZnMoO_4$ has a unique structure which has been

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(4) G. W. Smith, *Acta Cryst.*, **15**, 1054 (1962).

(5) Yu. D. Kozmanov, *Zh. Fiz. Khim.*, **31**, 1861 (1957).

(6) S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2533 (1965).

(7) M. Gleiser, W. L. Larsen, R. Speiser, and J. W. Spretnals, Special Technical Publication No. 171, American Society for Testing Materials, Philadelphia, Pa., 1955.

(8) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).

TABLE II

CRYSTALLOGRAPHIC AND DTA DATA FOR SOME $AMoO_4$ MOLYBDATES[a]

	α-$MnMoO_4$ type					α-$CoMoO_4$ type					$NiWO_4$ type					
Compound	a	b	c	β	V	a	b	c	β	V	a	b	c	β	$4V$	Dta peak temp, °C
$NiMoO_4$	10.13[b]	9.28	7.02	107.2	630	9.592[c]	8.755	7.665	114.24	586.8	4.587	5.679	4.887	90.44	509.2	750
$CoMoO_4$	10.21[d]	9.31	7.01	106.4	639	9.712[e]	8.865	7.666	114.03	602.9	4.657	5.682	4.917	90.45	520.4	660
$MgMoO_4$	10.278	9.291	7.027	106.90	642.1						4.694	5.689	4.900	90.35	523.4	495
$ZnMoO_4$											4.695	5.729	4.894	90.32	526.5	580
$FeMoO_4$	10.290	9.394	7.072	106.31	656.1	9.805	8.950	7.660	114.05	613.9	4.708	5.701	4.944	90.27[f]	528.4	620
$MnMoO_4$	10.498[g]	9.532	7.156	106.17	687.7						4.822	5.753	4.963	90.85	550.6	630

[a] Errors are estimated to be about ±2 in the last figure given although the standard deviations from the least-squares calculations were generally several times smaller than this. Temperatures are 25° unless otherwise indicated, and the units are: ångströms for a, b, and c; degrees for β; and cubic ångströms for V. [b] The cell dimensions for β-$NiMoO_4$ are based on data collected at 975°. [c] Smith[4] has given $a = 9.555$, $b = 8.745$, $c = 7.693$ Å, and $\beta = 113.65°$ for α-$NiMoO_4$. [d] The cell dimensions for β-$CoMoO_4$ are based on diffractometer data obtained at 10°. [e] Smith[4] has given $a = 9.666$, $b = 8.854$, $c = 7.755$ Å, and $\beta = 113.75°$ for α-$CoMoO_4$. [f] $FeMoO_4$-II is actually triclinic with α and γ equal to 90.67 and 87.68°, respectively. The conventional reduced cell has $a = 4.944$, $b = 5.701$, $c = 4.708$ Å, $\alpha = 92.32°$, $\beta = 90.27°$, and $\gamma = 89.33°$. [g] Abrahams and Reddy[6] have given $a = 10.469$, $b = 9.516$, $c = 7.143$ Å, and $\beta = 106.28°$.

reported by Abrahams.[9] There are apparently no phase changes for this compound on heating to its melting point.[9]

Discussion

We have found that α-$NiMoO_4$ and α-$FeMoO_4$ are isotypic with α-$CoMoO_4$ and that α-$MgMoO_4$, β-$FeMoO_4$, β-$CoMoO_4$, and β-$NiMoO_4$ are isotypic with α-$MnMoO_4$. Although α-$MnMoO_4$ and α-$CoMoO_4$ have the same space group (C2/m) and similar cell dimensions, they are not isotypic. A β angle of about 114° is characteristic of the α-$CoMoO_4$ isotypes, while this angle is always about 106° for the α-$MnMoO_4$ isotypes. That these two structures are definitely different is shown by the abrupt transition[10] from the α-$CoMoO_4$ type to the α-$MnMoO_4$ type found for $FeMoO_4$, $NiMoO_4$, and $CoMoO_4$. High-temperature X-ray diffraction shows that during the α–β transition, the peaks of the α form become weaker as the peaks of β appear and become stronger; the peaks do not merely change intensity and position gradually. Furthermore, α and β forms of $FeMoO_4$ and $CoMoO_4$ may coexist at room temperature giving two distinct X-ray powder patterns. Patterns of mixtures of α- and β-$FeMoO_4$ are readily obtained, and such complex patterns have apparently led others[6] to believe that normal (STP) $FeMoO_4$ is triclinic.

The high-pressure modifications were found to be structurally related to $NiWO_4$ as has been reported by Young and Schwartz.[1] However, more accurate cell dimensions are given in Table II, and the β angle has now been determined in every case. It is interesting that while $FeMoO_4$-II is really triclinic, all of the other high-pressure molybdates are apparently monoclinic as has been reported for the corresponding tungstates, including $FeWO_4$. Details on the $FeMoO_4$ modifications are reported elsewhere.[11]

All of the high-pressure molybdates were found to give endothermic peaks on transforming to the corresponding low-pressure modification. An irreversible transformation of a metastable to a stable form is usually exothermic but may be exothermic or endothermic on heating, whereas a reversible-equilibrium transformation must be endothermic on heating. Thus, possibly the high-pressure forms are the stable modifications at STP. This seems unlikely, however, because preparations at temperatures below the endothermic peaks (Table I) do not yield the high-pressure forms at low pressures.

A comparison of cell volumes (Table II and Figure 1) shows that the high-pressure modifications are consistently 13–14% more dense than the corresponding α-$CoMoO_4$ isotypes and about 19% more dense than the α-$MnMoO_4$ isotypes. The α-$CoMoO_4$ isotypes are about 6% denser than the corresponding α-$MnMoO_4$ isotypes. The basic difference between the α-$CoMoO_4$

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(9) S. C. Abrahams, *J. Chem. Phys.*, **46**, 2052 (1967).

(10) The α–β transitions are abrupt only on a microscopic level. The α and β forms coexist for extended lengths of time during the transformation, and in this sense the transformations are sluggish.

(11) A. W. Sleight, B. L. Chamberland, and J. F. Weiher, *Inorg. Chem.*, **7**, 1093 (1968).

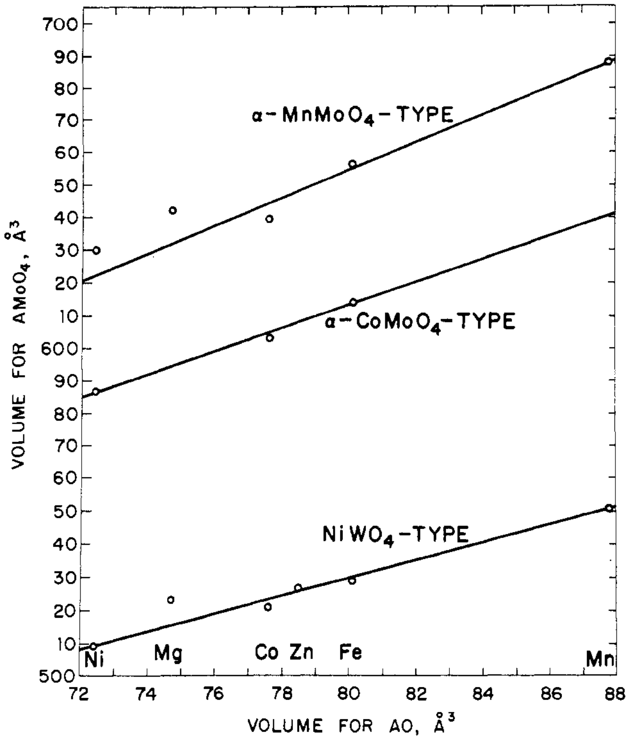

Figure 1.—Plot of the volumes of $AMoO_4$ molybdates *vs.* the volumes of corresponding AO oxides with the rock salt structure.

and the α-$MnMoO_4$ structure is the coordination of Mo which is tetrahedral in α-$MnMoO_4$ and essentially octahedral in α-$CoMoO_4$. Tetrahedral Mo also occurs in $AMoO_4$ molybdates where A is Ca, Sr, Ba, Cd, or Pb (scheelite structure). The occurrence of tetrahedral or octahedral Mo in $AMoO_4$ molybdates would thus appear to depend on the size and electronegativity of the A cation. The two most electropositive cations in the series, Mg, Mn, Zn, Fe, Co, and Ni are Mg and Mn, and of this series it is only Mg and Mn that form normal (STP) molybdates with tetrahedral molybdenum. While Mn is the largest of the above series, Mg is not the second largest.

In Figure 1 the cell volumes of the $AMoO_4$ molybdates are plotted against the cell volumes of the rock salt AO compounds.[12] The trends are relatively consistent although magnesium appears to be larger in the molybdates than in MgO. The figure dramatically shows the large density difference between the α-$CoMoO_4$ isotypes and the $NiWO_4$ isotypes. This is interesting because in both of these structure types the A and Mo atoms are in octahedral coordination. However, the oxygen atoms are nearly closed-packed in the $NiWO_4$ structure type whereas this is not the case in the α-$CoMoO_4$ structure. Smith and Ibers[3] describe the oxygen packing in α-$CoMoO_4$ as cubic-close-packed *except* that one out of nine oxygen sites is vacant. Thus, during the transformation from the α-$CoMoO_4$ structure to the $NiWO_4$ structure the oxygen atoms become nearly close-packed whereas the coordination numbers of the atoms remain unchanged.

Acknowledgment.—The 65-kbar experiments were supervised by C. L. Hoover, the X-ray data were obtained by K. R. Babcock, M. S. Licis, and J. F. Whitney, and the dta experiments were performed by H. W. Williams.

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[12] Data for the rock salt cell volumes were taken from R. W. G. Wyckoff, "Crystal Structures," Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 86–91, except the value for ZnO which was obtained from C. H. Bates, W. B. White, and R. Roy, *Science*, **137**, 993 (1962).

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Complexes of Titanium Tetrafluoride with Substituted Pyridines

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Most of the titanium tetrafluoride complexes described in the literature have been with monofunctional oxygen donors. Usually the complexes are *cis* adducts of the type $TiF_4 \cdot 2$(donor), thus reflecting the tendency of titanium to achieve sixfold coordination. In contrast to the large number of oxygen-containing diadducts, very few complexes have been reported with other donor atoms. Reactions of various amines with TiF_4 have been investigated.[1-4] Reactions with secondary amines have resulted in aminolysis reactions with the formation of dialkylamidotitanium(IV) trifluorides and dialkylammonium hexafluorotitanates.[1,2] With tertiary amines and pyridine, addition compounds are formed.[2] Depending upon reaction conditions, it is possible to obtain both the 1:1 complex and 2:1 complex, $TiF_4 \cdot 2$py, with pyridine[2-4] (py = pyridine). The 2:1 complex slowly loses pyridine on standing in a dry atmosphere. The addition compound appeared to be polymeric and the titanium was postulated to be octahedrally coordinated through fluorine bridging.[4] No F^{19} nmr data were reported for the pyridine complexes. As a result, we felt it of interest to prepare complexes of several substituted pyridines in an attempt to clarify their structure(s) by nuclear magnetic resonance spectroscopy.

Experimental Section

Materials.—Dimethoxyethane obtained from Matheson Coleman and Bell was dried by distillation from sodium metal. Titanium tetrafluoride obtained from Allied Chemical Co. was used without further purification. 2-Chloropyridine, 2-bromopyridine, 3-bromopyridine, and 3-chloropyridine obtained from Aldrich Chemical Co., pyridine, 2-methylpyridine (Practical grade), 4-methylpyridine, and 2,6-dimethylpyridine (Practical grade) obtained from Eastman Organic Chemicals, and 2,4-dimethylpyridine (Practical grade) obtained from Matheson Coleman and Bell were dried by distillation from calcium oxide.

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[1] J. A. Chandler, J. E. Wuller, and R. S. Drago, *Inorg. Chem.*, **1**, 65 (1962).

[2] J. A. Chandler and R. S. Drago, *ibid.*, **1**, 356 (1962).

[3] H. J. Emeléus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).

[4] E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).